SYNTHESIS AND CHARACTERIZATION OF LANTHANIDE DOPED NANOPHOSPHORS

HUANG HAI

NATIONAL UNIVERSITY OF SINGAPORE

2005
SYNTHESIS AND CHARACTERIZATION OF LANTHANIDE DOPED NANOPHOSPHORS

BY
HUANG HAI
(B.Eng.)

A THESIS SUBMITTED FOR THE DEGREE OF DOCTOR OF PHILOSOPHY
DEPARTMENT OF CHEMISTRY
NATIONAL UNIVERSITY OF SINGAPORE
2005
ACKNOWLEDGEMENTS

I would like to express my deepest gratitude to my respected supervisor, Professor Xu Guo Qin, for his constant encouragement, invaluable guidance and gracious advice throughout this period of my study. I have benefited tremendously from his knowledge and wisdom. I am also profoundly grateful to A/P Chin Wee Shong, Professor Gan Leong Ming and A/P Chew Chwee Har for providing me an excellent research environment, many valuable suggestions, constructive comments and concerns.

My sincere thanks are also extended to the related staff in Department of Chemistry, Department of Biological Science, Department of Physics and Department of Material Science, for their friendly assistance. Special thanks to Madam Leng, Madam Loy, and Dr. Que wen xiu for their efficient help in using TGA, TEM, and PL, respectively.

I wish to express my sincere appreciation to my friends and colleagues for their kind help and encouragement in many ways. They include Miss Quek Chai Hoon, Mr Zhang Zhi Hua, Ms Lu Mei Hua, Dr Jin Zhao Xia, Dr Jiao Hua, Mr Kerk Wai Tat, Dr Ang Tiam Peng, Ms Lim Wen Pei, Dr Wen Ying, Ms Yang Lei, Dr Tao Feng, Mr Chen Zhi Hua, Mr Wang Zhong Hai, Dr Dai Yu Jing, and Mr Huang Hai Gou. Their friendship is a special treasure in my memory.

The National University of Singapore is gratefully acknowledged for awarding me the research scholarship and sponsoring my trip to attend the second International Symposium of Trend of Nanotechnology in Spain in September of 2001.

I am greatly grateful to my parents, my wife and my brother, for their love, consideration and continual and warm support during my academic career.

Finally, I wish to dedicate this thesis to my lovely daughter, Huang Ming Lei, who was born during my Ph.D. study.
## CONTENTS

ACKNOWLEDGEMENTS ................................................................................................................................. i

CONTENTS ................................................................................................................................................... ii

SUMMARY ................................................................................................................................................... vi

### CHAPTER 1 INTRODUCTION .................................................................................................................. 1

1.1 BACKGROUND OF NANOPARTICLES ......................................................................................... 1
1.2 LANTHANIDE-DOPED NANOMATERIALS .............................................................................. 2
1.3 LANTHANIDE-DOPED NANOPARTICLES USED FOR FLAT PANEL EMISSIVE DISPLAYS ......................................................................................................................................................... 9
1.4 LANTHANIDE-DOPED NANOPARTICLES USED FOR UPCONVERTING PHOSPHORS ......................................................................................................................................................... 12
1.5 MICROEMULSION SYSTEMS FOR PREPARING LANTHANIDE-DOPED NANOPARTICLES ......................................................................................................................................................... 18
1.5.1. Microemulsion ........................................................................................................................ 19
1.5.2. Formation of microemulsions ............................................................................................... 22
1.5.3. Reactions in microemulsions ............................................................................................... 25
1.6 SCOPE OF THIS THESIS .............................................................................................................. 28
1.7 REFERENCES ..................................................................................................................................... 31

### CHAPTER 2 EXPERIMENTAL .............................................................................................................. 41

2.1 MATERIALS ........................................................................................................................................ 41
2.2 SYNTHESIS ....................................................................................................................................... 42
2.2.1 Phase behavior of microemulsion systems ............................................................................ 42
2.2.1.1 Systems with cyclohexane-(NP₅+NP₉) and various aqueous solutions of Alkalies ......................................................................................................................................................... 44
2.1.1.2 Systems with petroleum ether-ZnCl₂ solution-NP₅/NP₉ with various weight ratios of NP₅ to NP₉ ......................................................................................................................................................... 47
2.1.1.3 Systems with cyclohexane-(NP₅+NP₉) and various aqueous solutions of salts .................................................................................................. 49

2.1.1.4 The optimal microemulsion system for producing Lanthenide-doped nanoparticles .............................................................................................. 51

2.2.2 Synthesis method .......................................................................................................................... 52

2.3 CHARACTERIZATION TECHNIQUES .......................................................................................... 53

2.3.1 Thermal Analysis ........................................................................................................................ 53

2.3.2 Elemental analysis ....................................................................................................................... 54

2.3.3 XPS measurement ....................................................................................................................... 54

2.3.4 X-ray Diffraction ........................................................................................................................ 55

2.3.5 Scanning Electron Microscope ................................................................................................. 55

2.3.6 Transmission Electron Microscope ............................................................................................ 56

2.3.7 Photoluminescence measurement ............................................................................................ 56

2.4 REFERENCES ............................................................................................................................ 57

CHAPTER 3 RED-EMITTING NANOPHOSPHOR Eu:Y₂O₃.............................................. 58

3.1 RESULTS AND DISSCUSIONS............................................................................................ 60

3.1.1 Elemental analysis of Eu:Y₂O₃ nanoparticles .......................................................... 60

3.1.2 Thermal decomposition of the precursor of Eu:Y₂O₃ nanoparticles ..... 61

3.1.3 Crystallinity and crystalline size of Eu:Y₂O₃ nanoparticles ......................... 63

3.1.4 Morphology of the Eu:Y₂O₃ nanoparticles ....................................................... 66

3.1.5 Transmission electronic microscopy .............................................................................. 68

3.1.6 Photoluminescent properties .................................................................................. 70

3.1.6.1 The emission of Eu:Y₂O₃ ........................................................................... 70

3.1.6.2 The influence of calcination temperature on the emission of Eu:Y₂O₃ ...... 72

3.1.6.3 The influence of Eu³⁺ concentration on the emission of Eu:Y₂O₃ ........... 74

3.1.6.4 The influence of codopants on the emission of Eu:Y₂O₃ ......................... 77

3.1.6.5 Lifetime of Eu:Y₂O₃ nanophosphors .................................................... 81

3.1.6.6 Total decay rates as a function of Eu³⁺ concentration ......................... 85

3.2 SUMMARY ............................................................................................................................ 88
3.3 REFERENCES ........................................................................................................... 89

CHAPTER 4 GREEN-EMITTING NANOPHOSPHOR Tb:Y$_2$O$_3$ ......................... 92

4.1 RESULTS AND DISCUSSIONS ............................................................................. 95

4.1.1 Thermal decomposition of the precursors of Tb:Y$_2$O$_3$ and Tb:La$_2$O$_3$

   nanoparticles ........................................................................................................... 95

4.1.2 Crystallization and crystalline size ................................................................. 98

4.1.2.1 Tb:Y$_2$O$_3$ and Tb, Ce: Y$_2$O$_3$ (calcined at 800$^\circ$C) ......................... 98

4.1.2.2 Tb:Gd$_2$O$_3$ (calcined at 800$^\circ$C) ............................................................ 101

4.1.2.3 Tb:La$_2$O$_3$ ............................................................................................ 102

4.1.3 Morphology ..................................................................................................... 105

4.1.4 Transmission electronic microscopy .............................................................. 105

4.1.5 X-ray photoelectron spectroscopic (XPS) study of Tb,Ce:Y$_2$O$_3$

   nanophosphors ........................................................................................................ 110

4.1.6 Photoluminescence properties ...................................................................... 115

4.1.6.1 Emission of Tb:Y$_2$O$_3$ ........................................................................ 115

4.1.6.2 The influence of codopants on the emission of Tb:Y$_2$O$_3$................... 117

4.1.6.3 Emission of Tb$^{3+}$ in different host materials ...................................... 121

4.2 SUMMARY ......................................................................................................... 124

4.3 REFERENCES .................................................................................................... 125

CHAPTER 5 BLUE-EMITTING NANOPHOSPHOR Tm:Y$_2$O$_3$ ...................... 128

5.1 RESULTS AND DISCUSSIONS ......................................................................... 130

5.1.1 Elemental analysis of Tm:Y$_2$O$_3$ nanoparticles ........................................... 130

5.1.2 Thermal decomposition of the precursor of Tm:Y$_2$O$_3$ nanoparticles ... 130

5.1.3 Crystallization and crystalline size ............................................................... 131

5.1.4 Morphology .................................................................................................... 132

5.1.5 Transmission electronic microscopy ............................................................. 133

5.1.6 X-ray photoelectron spectroscopic (XPS) study of Tm:Y$_2$O$_3$

   nanophosphors ........................................................................................................ 137
SUMMARY

Lanthanide doped nanoparticles play a critical role in many technological applications. Due to the unique electronic structure of lanthanides, they have found a wide variety of optical applications, including lasers, solar-energy converters, optical amplifiers, and photo- or cathodo-excited optical phosphors. Field emission display (FED) and upconverting phosphors are promising applications for lanthanide doped nanoparticles. Research in this area has been very active in the past decade. However, the current theories and experimental databases are inadequate to understand the optical properties of localized lanthanides in nanostructures.

My thesis work starts from two objectives: one is to develop a novel synthesis method for lanthanide doped nanophosphors and the other is to investigate various physical and optical characteristics of lanthanide doped nanophosphors. In this thesis, a series of lanthanide doped nanoparticles were synthesized by microemulsion technique for the first time. They included Eu:Y$_2$O$_3$ (red-emitting), Tb:Y$_2$O$_3$ (green-emitting), and Tm:Y$_2$O$_3$ (blue-emitting) nanophosphors for FED application as well as upconverting nanophosphors Pr:Y$_2$O$_3$ and Er:Y$_2$O$_3$. Various characteristics of lanthanide-doped nanoparticles were extensively investigated by thermogravimetry (TG), X-ray diffractometer (XRD), X-ray photoelectron spectroscopy (XPS), scanning electronic microscopy (SEM), transmission electronic microscopy (TEM), and photoluminescence instruments (PL). Meanwhile, we investigated the effect of different factors such as the concentration of dopants, calcine temperatures, doping hosts as well as codopants on the luminescent properties of the lanthanide doped nanoparticles.

Microemulsion technique has been proved to be a powerful synthesis method to obtain lanthanide doped nanophosphors with good optical properties. Both Eu:Y$_2$O$_3$ and Tm:Y$_2$O$_3$ nanophosphors prepared in microemulsions had higher quenching concentrations compared to those prepared by conventional synthesis method. Since all of the starting materials are mixed at the molecular level in a solution, a high degree
of homogeneity is achievable. Moreover, the size and shape of nanoparticles formed in microemulsions can be precisely controlled. Lower calcination temperature (800°C) compared to that employed in a conventional solid-state reaction (1400°C-1500°C) also offered nanophosphors smaller particle size and less aggregation than conventional phosphors. All the nanoparticles prepared in this study via microemulsion route have small particle size; most crystalline size was in the range from 10nm to 20 nm.

Eu:Y2O3 nanoparticles are good red-emitting phosphors for FED. These nanoparticles formed typical cubic Y2O3 crystal structure at 600°C. The low process temperature prevented the nanoparticles from aggregating and growing. The nanophosphors had enhanced emission intensities with codopants, such as Al3+ and Ba2+. This finding should be valuable for industry application.

Green-emitting nanophosphors Tb:Y2O3 has been successfully synthesized via microemulsion route for the first time. In order to probe the influence of host materials and codopants on luminescence of Tb, Tb:La2O3, Tb:Gd2O3, Tb, Al:Y2O3, Tb, Bi:Y2O3 and Tb, Ce:Y2O3 were also prepared and investigated. Bi3+ is a favorable codopant to improve green emission and color purity of Tb:Y2O3. Tb3+ has enhanced intensity of emission in La2O3. In terms of XPS study of Tb,Ce:Y2O3, the presence of a large number of Tb4+ and C=O, O-H or H-C=O species was observed, which can greatly decrease the emission efficiency of the Tb,Ce:Y2O3 nanophosphor due to the competitive absorption.

Usually, the quenching effect in Tm:Y2O3 is serious. However, our blue-emitting nanophosphors Tm:Y2O3 has two times higher quenching concentration than that of Tm:Y2O3 film prepared by spray pyrolysis.

As for upconverting nanophosphors, preliminary research was conducted. The structural properties of these upconverting nanophosphors had been investigated by XRD, SEM, TEM and XPS.
CHAPTER 1 INTRODUCTION

1.1. BACKGROUND OF NANOPARTICLES

Nanoparticles represent a state of matter in the transition region between bulk solids and molecular structures [1-5]. Consequently, their physical and chemical properties gradually change from molecular to solid state behavior with increasing particle size. They may form new phases [6] and exhibit enhanced structural, electronic, or optical properties [7-11].

Over the last decade we have witnessed the tremendous development of nanomaterials. They have potential applications in the areas of microelectronics, energy conversion, imaging and display technologies, sensing devices, thin film coatings, and environmental remediation. A variety of multifunctional supermolecules [12], carbon nanotubes [13], supermolecular ensembles [14] and semiconductor nanoparticles [15] have been synthesized and proposed as potential building blocks of optical and electronic devices [16]. Nanoparticles have a large fraction of atoms at or near the particle surface. They can serve as models in the applications of luminescence spectroscopy to study the surface structure and defect chemistry at interior surfaces in bulk materials [17-21]. For an isolated nanoparticle, the phonon spectrum becomes discrete with a gap due to size quantization effect. Rare earth doped insulating nanoparticles provide an ideal model system for studying the fundamental interactions between electronic states and phonons.
Chapter 1. Introduction

since the insulating host eliminates the additional complications of collective electronic interactions [22-23]. Dan Meisel studied electron transfer processes in nanoparticles [24]. The appeal of these systems to the study originates from the simplicity of their preparation and manipulation and the ability to use commonly utilized techniques, particularly those involving kinetic spectrophotometric tools.

In short, nanomaterial has been one of the most exciting, active and challenging research areas during the past decade and it is attracting more and more attention.

1.2. LANTHANIDE-DOPED NANOMATERIALS

The discovery and identification of lanthanides dated back to the early 1800s (1803 for Ce and 1945 for Pm). Lanthanide ions are characterized by an electronic structure consisting of an unfilled inner 4f shell and outer filled 5d and 5p shells. When lanthanide ions are doped in a solid, the effects of the crystalline or ligand field are a small perturbation on the 4f states because of the shielding of the outer electron shells. Optical transitions between 4f levels are parity forbidden; hence they are weak and become allowed only by small admixing of states of opposite parity by odd-order terms in the local field or are induced by vibrations. Optical transitions between 4f and 5d states, on the other hand, are electric-dipole allowed and can be intense in solids. Thus lanthanides exhibit the uncommon features of having both sharp, weak 4f-4f transitions and broad, intense 4f-5d transitions. The observed optical transitions are predominantly electric-dipole in character.
Chapter 1. Introduction

Materials containing lanthanide ions play a critical role in a wide variety of technological applications [25-27]. Their optical applications span the spectral range from the ultraviolet to the infrared region. The widespread utilization of the lanthanides for optical applications was benefited from the concurrence of two developments: (1) an understanding of the optical spectra of the lanthanides derived from many experimental studies and theoretical treatments of crystal fields and of radiative and nonradiative transitions, both conducted primarily in the period from the 1930s through the 1960s, and (2) the availability of high-purity lanthanide materials beginning in the late 1950s. Advances in such diverse fields as phosphors for fluorescent lighting, display monitors, and X-ray imaging [28-30]; scintillators [31]; lasers [32]; and amplifiers for fiber-optic communication [33] rely on the development of improved lanthanide-doped materials that provide enhanced optical performance. The luminescence efficiency of these materials is often limited by the dynamics of the lanthanide ion, which depends on its interactions with the insulating host. Through innovative design and synthesis of the host matrix, the optical response of the dopant population can be influenced. Particularly, in lanthanide-doped nanomaterials successful manipulation of the host structure, while maintaining the material properties required for device construction and operation, is essential to refine the material behavior in existing applications and extend the use of the material into new areas.

The rationale to study nanostructures of lanthanide-doped insulating materials arises because the spectral and dynamic properties of these technologically important materials change when the reduced dimensions affect the chemistry and physical properties of the
host. In a similar manner, the lanthanide dopants can serve as a sensitive probe of the chemistry and structure of its host.

Research is active and ongoing in lanthanide-doped nanomaterials. These materials have found potential optical applications, including lasers [34], solar-energy converters [35], optical amplifiers [33], and photo- or cathodo-excited optical phosphors [36-42]. Preparing lanthanide-doped nanomaterials also provides a new method to develop and study transparent composite materials. The reduced optical scattering of nanoparticles allows the preparation and use of nanocrystals embedded in an amorphous matrix in lasers and amplifiers, which usually require high-quality crystals or glasses. Using nanostructured composites in optical applications could simplify material preparation or allow the use of new host materials for which good crystals cannot be grown. To maintain a concise review, the following paragraphs focuses on the active research in lanthanide-doped nanoparticles, and does not review advances in nanostructured films [43-46], nanocrystal-containing glasses [47-48], and lanthanide-doped fullerenes [49-50] or porous silicon [51-52].

The relationship between the particle size and optical properties is important for the understanding of these materials, and hence optimizing their emissive properties for technological applications. Several groups have reported particle-size-dependent phenomena in lanthanide-doped nanoparticles that affect emission lifetime [17, 20], luminescence quantum efficiency [20, 53, 36], and concentration quenching [54]. In Tb:ZnS, the luminescence lifetime becomes shorter by several orders of magnitude [20,
Chapter 1. Introduction

These effects are postulated to result from mixing of the s-p electrons of the host with the d-f valence electrons of the lanthanide ions due to quantum confinement, causing the normally forbidden d-d or f-f transitions to become allowed [20]. In Eu:Y$_2$O$_3$, as the particle size decreases, the spectra show increased line broadening [17]. Ye et al. reported changes in the charge-transfer excitation spectrum as a function of particle size that are attributed to surface effects. The Eu$^{3+}$ concentration can reach 14% before the onset of concentration quenching [54]. In Tb:Y$_2$O$_3$, the luminescent efficiency was found to increase with the decrease in the particle size from 10nm to 4 nm [55].

The presence of surface defects is a major factor affecting the efficiency of nanocrystalline phosphors [56]. The ability to control these defects could lead to energy-efficient phosphor materials for the next generation of projection and flat-panel displays. L.M. Gan and G.Q. Xu’s group found that the photoluminescence of Mn:ZnS nanoparticles prepared in microemulsion under hydrothermal treatment was enhanced by a factor of 60 as compared to that of the material obtained through the direct aqueous reaction at room temperature. This dramatic increase in photoluminescence yield is attributed to the surface passivation of nanoparticles by the adsorption of surfactants in microemulsion [57]. Pramod K. Sharma et al. used a surface modifier in Eu:Y$_2$O$_3$, and the fluorescence spectra showed approximately a 5-fold enhancement of emission intensity of the $^5$D$_0$$\rightarrow$$^7$F$_2$ transition of Eu$^{3+}$ [58-59]. Q. Li et al. studied the effects of the coating process on nanoscale Eu:Y$_2$O$_3$ powders. Al$^{3+}$ was absorbed on the surface of Eu:Y$_2$O$_3$ nanoparticles in the coating procedure, and the luminescence intensity of
5D0→7F2 transition of Eu3+ was apparently improved after being coated. The luminescence enhancement benefits from surface modifications of the nanoparticles [60].

Codopants sometimes play an important role in improving the optical properties of lanthanide-doped nanoparticles. It was reported that the addition of aliovalent ions affects the luminescence efficiency of Eu:Y2O3 [61] and (Ce,Gd,Tb)MgB2O10 [62]. R. Jagannathan et al. presented the defects-induced enhancement of Eu3+ emission in yttria [62]. Y. Guyot et al. have recorded fluorescence spectra and measured fluorescence lifetimes in yttria single crystals doped with only Tm3+ or Pr3+ ions or codoped with Yb3+, Tb3+ or Ho3+ ions. The effect of the codopants on the infrared emission properties of the Tm3+ ions was studied. They found a very attractive fluorescence around the eye-safe wavelength of 1.55 µm which corresponds to a 3H4→3F4 transition of Tm3+. This transition occurs with a large enough stimulated emission cross section to be practical for laser application. The Tb3+ or the Ho3+ ions were introduced to reduce the problem of bottlenecking due to a longer lifetime of lower laser state than that of the upper state [63]. Research on codopants was also conducted in other nanoparticles [64-65]. These codopants modify the host lattice defect structure or act as sensitizers and coactivators and thus may alter luminescence.

Besides particles size, surface defects, and codopants, a variety of other factors that affect the luminescence properties of lanthanide-doped nanoparticles have also been extensively studied. Eu and Tb doped Y2O3, Y2SiO5 and Y3Al5O12 phosphor materials were prepared by different routes to investigate their effect on luminescent characteristics [67].
Chapter 1. Introduction

Silver’s Group has done a series of research on Er:Y₂O₃. They reported the effects of particle morphology, crystallite size [68] and temperature [69] on the upconversion luminescence properties of these nanoparticles. R. Schmechel et al. probed luminescence properties of nanocrystalline Eu:Y₂O₃ in different host materials [70]. Reduction of intensity from coating MgO or Al₂O₃ on cathodoluminescent phosphors Eu:Y₂O₃ or Tb:Y₂SiO₃ was investigated by W.J. Thomes et al. [71]. B.S. Panigrahi used phenyl phosphonic and phenylphosphinic acids as ligands and obtained enhanced fluorescence and cofluorescence of Tb³⁺ and Eu³⁺ [72]. As mentioned above, Pramod K. Sharma et al. have illustrated the effects of surface defects on the luminescence properties of Eu:Y₂O₃. Their research was also extended to the effects of solvent, host precursor, and dopant concentration on the fluorescence characteristics of Eu:Y₂O₃ [59].

Theoretical study on the lanthanide-doped nanoparticles is critical for researchers to obtain deep understanding of the electronic properties, crystal structure, as well as the optical transition mechanisms of these nanoparticles. The results of such research can be served as valuable references for the synthesis and application of lanthanide-doped nanoparticles.

Many researchers have done extensive study in theoretical field. B.M. Tissue’s group has made a great contribution to the theoretical research of lanthanide-doped nanocrystals. Their work includes: one phonon relaxation processes in Eu:Y₂O₃ nanocrystals [22], electron-phonon interaction in rare earth doped nanocrystals [23], comparison of dynamics of Eu in different Y₂O₃ nanomaterials [73], and laser spectroscopy of
nanocrystalline $\text{Eu}_2\text{O}_3$ and $\text{Eu}_2\text{O}_3$ [74]. The results of the research are helpful for investigating the mechanisms of the electronic relaxation in nanoscale materials and the structure of nanoparticles. G. Blasse et al. found that the electron-phonon coupling for trivalent lanthanides is strong at the beginning and at the end of the lanthanide series and weak in the middle. One can estimate the electron-phonon coupling parameters for lanthanide ions from their measurements [75]. K.C. Mishra et al. studied the electronic structure and optical properties of $\text{Eu}_2\text{O}_3$ using the first-principle molecular-orbital and band-structure methods. Through the calculation of the one-electron energy levels, several properties of the host material and properties of the phosphor based on host-impurity interactions were explained [76]. Based on the electrostatic crystal-field model of M. Faucher, C. Duan et al. calculated the crystal-field energy parameters of nanocrystalline $\text{X}_1\text{Y}_2\text{SiO}_5:\text{Eu}^{3+}$ at two sites both with $C_1$ symmetry. The theoretically simulated spectra and wavefunctions can be used to predict other physical properties, such as the decay time, and nanometric effects on concentration quenching [77]. The energy transfer processes in $\text{Eu}_2\text{O}_3$ were studied in greater detail by D.B.M. Klaassen et al. They quantified the rates for energy transfer from $\text{Eu}^{3+}$ ions at $S_6$ to $\text{Eu}^{3+}$ ions at $C_2$ sites, as well as non-radiative decay rates between the different energy levels of the $\text{Eu}^{3+}$ ions at $C_2$ sites. Hence, a model for the energy flow in $\text{Eu}_2\text{O}_3$ was developed [78]. In Ye Tao’s work, extended X-ray absorption spectroscopy was used to determine the local structure of luminescence centers in $\text{Eu}^{3+}$ doped, Eu-Bi doped, Eu-Tb doped nanoscale yttrium oxide. It was shown that the Eu-O bond distance of the first coordination shell has an important effect on the emission intensity [79]. Sintering behavior of nanocrystalline $\text{Y}_2\text{O}_3$ was investigated by Patricie Merkert et al [80]. The results of their
Chapter 1. Introduction

research are very valuable for researchers to investigate the mechanical properties of nanocrystalline yttrium oxides.

1.3. LANTHANIDE-DOPED NANOPARTICLES USED FOR FLAT PANEL EMISSIVE DISPLAYS

One of the promising applications for lanthanide-doped nanoparticles is as phosphors for flat panel emissive displays [81]. Technology for flat panel displays has evolved rapidly in the past decade as demand has continued to increase [82]. Phosphors are critical to further development in flat panel emissive display technologies. The choice of the type of phosphor and the deposition method provides a great opportunity to improve the performance of a display. Lately, there has been considerable interest in the development of lanthanide-activated oxide-based phosphors for display technology because of their excellent light output and color rendering properties [27, 83, 84]. Field emission displays (FEDs), electroluminescent displays and plasma display panels are three important types of flat panel displays. For portable, battery-operated displays, the devices must be lightweight, thin, and efficient. Liquid crystal displays (LCDs) currently hold most of the market. Among the flat panel emissive displays, FEDs could challenge LCDs. Lanthanide-doped nanoparticles as phosphors for FEDs will be reviewed in this section.

FEDs are operated at low voltages (<1 keV) and high current densities. A scheme of a FED is shown in Figure 1.1. FEDs have ideal display characteristics, such as high luminescent efficiency, high definition, large area, high response speed, high viewing
angle, and low energy consumption. In the past few years, great interest has been focused on the development of phosphors for FEDs. The phosphors most widely investigated for FEDs were the sulfide phosphors such as Zn$_{0.2}$Cd$_{0.8}$S:Ag, Cl (red), Zn$_{0.65}$Cd$_{0.35}$S:Ag, Cl (green), ZnS:Ag, Al (blue), and Y$_2$O$_3$:Eu (red) [85,86]. However, the close proximity of the phosphor particles to the emitter tips requires the phosphor not to outgas or sputter material that will poison the tips. Unfortunately, during operation, such sulfide phosphors degrade and disperse into the vacuum, contaminating the field emitter and thus hindering electron emission. To circumvent these problems associated with sulfide phosphors, the oxide phosphors are preferentially used.

![Figure 1.1 Scheme of a field emission display](image)

Unlike conventional phosphor particles, nanophosphors are attractive for FED applications because their small size allows complete penetration by the low-voltage...
electrons for efficient material utilization. With excellent light output and color rendering properties, lanthanide-activated oxide-based nanophosphors emerge as potential candidates for FEDs.

Eu:Y$_2$O$_3$ is the simplest and efficient red phosphor extensively used in FEDs because of its high stability toward high-energy radiation [87]. J.D. Lee et al have conducted a lot of research on phosphors for FEDs, especially on the red phosphor Eu:Y$_2$O$_3$. They prepared Eu:Y$_2$O$_3$ for FEDs applications using aerosol pyrolysis method and observed the cathodoluminescence of these particles was 130% as bright as commercial products at low-voltage excitation [88-90]. As one of the most promising red phosphors for FEDs application, Eu:Y$_2$O$_3$ has attracted much attention [91-96]. Besides Eu:Y$_2$O$_3$, other red phosphors were developed and studied. SrTiO$_3$:Pr,M (M=Al or Ga) exhibited better luminescent efficiency than Eu:Y$_2$O$_3$ below 400 V [97]. The red-emitting phosphor, Li-doped Gd$_2$O$_3$:Eu, developed in J.C. Parka’s work showed higher brightness compared to the commercial Y$_2$O$_3$:Eu and Y$_2$O$_2$S:Eu phosphors in the voltage range of 500 V–1 kV [98].

As far as green- and blue-emitting oxide phosphors are concerned, Tb:Y$_3$Al$_4$Ga$_2$O$_{12}$ and Ce:Y$_2$SiO$_5$ were widely studied [99-101]. Y. Nakanishi et al. prepared Tm doped Y$_2$O$_3$ blue-emitting phosphor by electron-beam evaporation. The phosphor showed sharp emission at 454 nm, which is attractive for using as a blue-phosphor for FEDs [102]. C.H. Seager and D.R. Tallant studied the interactions of excited activators in rare earth and transition metal doped phosphors and their role in low energy cathodoluminescence.
They performed experiments on several phosphors, including Eu:Y$_2$O$_3$, Tb:Y$_2$SiO$_5$ and Zn$_2$SiO$_4$. The results showed that non-first-order decay processes tend to dominate at higher activator densities. These nonradiative decay routes lead to reduced cathodoluminescence efficiency at electron-beam energy below 5 keV [103].

Many opportunities exist to improve phosphors for FEDs. The major issues are stability under high current densities and efficiency especially of the blue and red phosphors. Table 1.1 summarizes the efficiency of a variety of lanthanide-activated oxide-base phosphors.

<table>
<thead>
<tr>
<th>Material</th>
<th>Color</th>
<th>Efficiency (1m/W)</th>
<th>Voltage</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Eu:Y$_2$O$_3$</td>
<td>red</td>
<td>2.2</td>
<td>500</td>
<td>[104]</td>
</tr>
<tr>
<td>Eu:SnO$_2$</td>
<td>red</td>
<td>2.0</td>
<td>10</td>
<td>[105]</td>
</tr>
<tr>
<td>Tb:Y$_3$Al$_5$O$_12$</td>
<td>green</td>
<td>2.0</td>
<td>500</td>
<td>[106]</td>
</tr>
<tr>
<td>Tb:LaOBr</td>
<td>blue</td>
<td>0.5</td>
<td>300</td>
<td>[107]</td>
</tr>
</tbody>
</table>

1.4. LANTHANIDE-DOPED NANOPARTICLES USED FOR UPCONVERTING PHOSPHORS

An upconverting phosphor is one that converts multiple photons of lower energy to one photon of higher energy. There has been considerable research on upconverting phosphors since initial interest in the 1960s [108]. The first example of upconversion was
Chapter 1. Introduction

reported in 1966 by Auzel for the Yb$^{3+}$, Er$^{3+}$ in CaWO$_4$ [109]. The lanthanide doped materials are ideal for the application of efficient upconversion. Lanthanide ions are unique in that transitions with the $4f^n$ core are substantially independent of outside influences. As a consequence, much of the upconversion research since the 1960s has concentrated on transitions between the $4f^n$ states of the trivalent lanthanide ions. Lanthanides upconverting phosphors have found a variety of applications including solid state lasers, optical wave guides, fiber amplifiers, and immunoassays [110-117].

Compared to other techniques, upconversion offers particular advantages on the application of short wavelength output compact solid state lasers which are one of the most active areas of laser research and development. One advantage over direct UV excitation is to reduce the photoionization induced degradation of hosts. In contrast to nonlinear techniques, upconversion does not need either the stringent constraint of phase matching or of high excitation wavelength stability and the output wavelength is not restricted to a given harmonic. Moreover, upconversion may lead to very simple, inexpensive and reliable compact laser systems.

Generally, upconversion processes may be divided into three main classes (the simultaneous multiphoton absorption being ruled out due to its very low efficiency): Excited State Absorption (ESA) or multistep (or sequential) absorption, Energy Transfer Upconversion (ETU) and Photon Avalanche (PA) [118].
Figure 1.2 General energy scheme related to the ESA process

Figure 1.2 shows the general energy scheme related to the successive absorption of two photons. The ion is excited from the ground state to the long-lived intermediate state by the photons of the incident flux $\Phi_1$. After that, the photons of $\Phi_2$ may promote this ion to the upper emitting level. Finally, emission from the emitting level to the ground state may occur. ESA is a single ion process; it is independent of the lanthanide ion concentration in the material.

The different types of ETU processes are summarized in Figure 1.3. In figure 1.3 (a), the sensitizer ion may absorb photons of the incident flux $\Phi$. ET (energy transfer) between the sensitizer in its excited state and the activator in its ground state promotes the activator to its excited state 2; then it is promoted to its excited state 3 by the second ET. In the case of figure 1.3 (b), the photons of $\Phi_2$ instead of ET, excite the activator from state 2 to the higher excited state 3. Figure 1.3 (c) schematizes the case that the sensitizer and the activator are identical ions. Photons of the incident flux $\Phi$ promote both ion 1 and ion 2 to their excited state 2. Then, an ET excites ion 2 to its state 3 while ion 1 goes down to a lower energy state. Figure 1.3 (d) presents the phenomenon when more than
one center takes part in the sensitization process. In this case, two excited ions transfer the energy to one ion which reaches high excited state 3.

PA is among the most efficient types of upconversion. The phenomenon of PA was first discovered in Pr$^{3+}$-based infrared quantum counters [119]. The most simple energy scheme for a PA process is shown in figure 1.4. The photons of the incident flux $\Phi$ promote ion 1 from intermediate level 2 to the upper visible-emitting energy level 3. Besides the visible emission, there is an alternative decay mechanism involving energy transfer from the ion 1 to a neighboring ground state ion 2. As a consequence, one ion initially in the metastable state 2 produces two ions in this state. Under appropriate pumping conditions, the two can produce four, eight, and so on, leading to an avalanche of ion population occupying the metastable level 2. PA requires minimum pump intensity. This threshold condition is unique among the three upconversion mechanisms.
Figure 1.3 General energy scheme related to the ETU process
Pr\(^{3+}\), Nd\(^{3+}\), Ho\(^{3+}\), Er\(^{3+}\) and Tm\(^{3+}\) ions are particularly well-suited for upconversion laser emission, as these ions are characterized by numerous intermediate metastable levels. The metastable state energies are well-matched to the emission wavelengths of several efficient pump laser sources. Many can be populated by absorption from tunable near infrared-emitting lasers such as Ti:sapphire and AlGaAs semiconductor laser diodes. In addition, the trivalent lanthanide ions have several long-lived upper excited states that give rise to strong visible emission. Figure 1.5 shows the partial energy level diagrams for lanthanide ions involved in upconversion.
Chapter 1. Introduction

1.5. MICROEMULSION SYSTEMS FOR PREPARING LANTHANIDE-DOPED NANOPARTICLES

There are a large number of methods for producing nanoparticles, including oxidation of metal nanoparticles [120], vaporization/condensation of ceramics [121], laser ablation [122], laser-driven reaction [123], flame and plasma processing [124-125], solution-phase synthesis [126-129], sol-gel processing [130-132], electrospray and spray pyrolysis [133-135], combustion synthesis [136], high-energy mechanical milling [137], and self-assembly [138-139].
Among these methods, the technique of microemulsion has been developed rapidly since 1982 [128, 140-146]. This technique has several advantages over other techniques. (1) It does not require extreme temperature and pressure conditions. (2) The size and shape of nanoparticles formed in microemulsions can be precisely controlled [140-142]. This is crucial to the research of size-dependent properties. (3) It does not require special equipment. (4) This technique is easy to combine with other powder processing techniques, such as homogeneous co-precipitation, freeze-drying, sol-gel and polymerization, to refine the characteristics of nanoparticles.

1.5.1. Microemulsion

The microemulsion technique is based on the use of microemulsion as microreactors in order to control the growth of the particles. A microemulsion is a thermodynamically stable system with at least three components: two immiscible components (generally water and oil) and a surfactant. The molecule of a surfactant, i.e. a surface-active agent, is composed of a non-polar hydrophobic portion and a polar hydrophilic portion. It is therefore referred to as amphiphilic. Usually, the polar hydrophilic part of the molecule is called the head and the hydrophobic part, which normally includes an elongated alkyl substituent, is called the tail.

The term “microemulsion” was originally proposed by Jack H. Schulman and co-workers in 1959 [147], although the first paper on the topic dates back to 1943 [148]. In general, such a system is a very complicated one in which one can find a variety of complex
structures, e.g., liquid crystals, gels, and vesicles. The microstructure of a microemulsion depends on the composition of the system which has been reviewed by Auvray [149]. There are three main types of microemulsion corresponding to water-swollen micelles (water-in-oil microemulsions), oil-swollen micelles (oil-in-water microemulsions) and bicontinuous structures (bicontinuous microemulsions). The schematic presentations for the o/w droplet, w/o droplet and the bicontinuous structure are shown in Figure 1.6 and Figure 1.7.

![Figure 1.6 Schematic illustrations of (a) oil-in-water microemulsion; (b) water-in-oil microemulsion; and (c) bicontinuous microemulsion [204]](image)
In the water or oil rich regions of the monophasic domain of the phase diagram, microemulsions consist of uniform and spherical droplets surrounded by a surfactant layer and dispersed in a continuous medium. The particle size is \( \sim 10 \) nm, which explains the optical transparency of these systems. In the intermediate regions containing similar amounts of water and oil, the structure is no longer droplets. The surfactant film in these regions has a spontaneous curvature close to zero, which is commonly described as disordered bicontinuous in which aqueous and oily domains are interconnected over macroscopic distances or locally lamellar [150, 151].
Microemulsions form numerous equilibriums. Winsor [152] described four types of phase equilibrium in microemulsions which are designated as WI, WII, WIII and WIV. In a WI system, an o/w microemulsion is in equilibrium with excess oil, while WII consists of a w/o microemulsion in equilibrium with excess water. In WIII system, a middle phase microemulsion coexists with both oil and water excess phases. In WIV system, microemulsion exists as a single-phase. WI and WII have globular form, while WIII middle phase is bicontinuous.

For the purpose of producing nanoparticles, we are interested in water-in-oil microemulsion, which is also known as inverse or reverse microemulsions. Inverse microemulsions have been used as a unique synthetic medium for preparing nanoparticles [143,153]. One of the obvious reasons is that most of the inorganic reactions can take place in the aqueous nanosized droplets of reverse microemulsions. Moreover, the aqueous droplets can limit the uncontrolled growth of solid particles [154].

1.5.2. Formation of microemulsions

The mechanism of microemulsion’s formation has been analyzed by Ostrovsky and Good. The analysis established a boundary of interfacial tension between a thermodynamically stable microemulsion and an unstable macroemulsion. For tensions lower than $10^{-2}$ mN/m, stable microemulsions can be obtained [155]. In other thermodynamic models [156-160], even lower interfacial tension, on the order of $10^{-4}$-$10^{-5}$ mN/m, has been employed to satisfy the stable condition of microemulsions. The adsorption of the surfactant at the
Chapter 1. Introduction

water-oil interface lowers the interfacial tension. It can be described by Gibbs adsorption isotherm for multiple-components systems [161]:

\[d\gamma = -\Sigma \Gamma_i \, du_i = -\Sigma \Gamma_i \, RT \, d \ln a_i\]

where \(\gamma\) is the interfacial tension
\(\Gamma_i\) is the surface excess of component i
\(u_i\) is the chemical potential of i
\(a_i\) is the activity of the solute i

The equation basically dictates that the increase of surfactant activity in the solution would result in a decrease of interfacial tension if the surface excess (i.e. the amount of component i adsorbed per unit area) of the surfactant is positive.

The formation of small microemulsion droplets requires a bending of the interface. It has been shown by Murphy [162] that the bending of an interface requires work to be done against both interfacial tension and bending stress of the interface. At an equilibrium condition with very low interfacial tension, an interface would assume an optimal configuration and curvature, known as the spontaneous curvature, at which the bending energy of the interface is minimized. Bending the interface farther away from this spontaneous curvature will cause an increase in bending energy, which can be represented by a constant K, known as the curvature elasticity (or bending elasticity) of the interface. The constant K with the unit of energy actually dictates the ease of interfacial deformation. A large K value corresponds to a “rigid” interface for which a large amount of energy is required to bend the interface. A small K value represents a
Chapter 1. Introduction

“fluid” interface for which little energy is necessary for bending. Hence K is also called the “rigid constant” of an interface.

Safran and Turkevich [163] have expressed the interfacial free energy $F_1$ of microemulsion droplets in terms of both interfacial tension and bending energy for an uncharged interface:

$$F_1 = n \left[ 4\pi \gamma R^2 + 16 \pi K \left( \frac{1}{R} - \frac{1}{R_0} \right)^2 \right]$$

where $n$ is the number density of droplets
$\gamma$ is the interfacial tension
$R$ is the droplet radius
$R_0$ is the radius of spontaneous curvature

The equation is applicable to ionic w/o or nonionic microemulsions where the electrostatic energy can be neglected. K has been found to be on the order of $10^{-21}$J for microemulsions [164]. When K is close to $kT$, where $k$ is the Boltzmann constant and T is the absolute temperature, the interface is subject to a bending instability resulting from thermal fluctuations. When K is larger than $kT$, oil, water and surfactant may form a birefringent lamellar phase. Only when K is small, are isotropic disordered microemulsions obtained. The addition of cosurfactant is often found to increase the fluidity of the interface, leading to a structural transition from birefringent lamellar phase to isotropic microemulsions. In practice, the fluidity of an interface can be increased by choosing a surfactant and cosurfactant with widely different sizes of the hydrocarbon
moiety, or by setting a temperature so that there is a balance between the hydrophilic and lipophilic properties of the surfactant [165].

The thermal fluctuations of a fluid interface lead to an increase in the entropy of the interfacial film. The decrease in free energy of the system due to this dispersion entropy may exceed the increase of free energy caused by newly created interfacial area due to emulsification, thus resulting in spontaneous formation and stabilization of a microemulsion.

Based on the review above, there are two basic conditions for the formation of microemulsions:

*Large adsorption of surfactant at the water-oil interface*

This can be achieved by choosing a surfactant with proper hydrophilic-lipophilic balance (HLB) value from the system. One can also employ various methods to adjust the HLB, such as adding cosurfactant, changing salinity or temperature.

*High fluidity of the interface*

The interfacial fluidity can be enhanced by using proper cosurfactants or setting an optimum temperature.

1.5.3. Reactions in microemulsions

In water-in-oil microemulsions, the aqueous phase is dispersed as nanodroplets surrounded by a monolayer of surfactant molecules in the continuous hydrocarbon phase.
Chapter 1. Introduction

These aqueous droplets continuously collide, coalesce, and break apart, resulting in a continuous exchange of solute content [166-167]. The collision process depends on the diffusion of the aqueous droplets in the oil phase, and the exchange process depends on the attractive interactions between the surfactants tails and the rigidity of the interface [167].

For reactions in water-in-oil microemulsions involving reactant species totally confined within the dispersed water droplets, a necessary step prior to their chemical reaction is the exchange of reactants by the coalescence of two droplets. When a chemical reaction is fast, its overall reaction rate is to be controlled by the rate of coalescence of droplets [167]. Therefore, properties of interface such as interfacial rigidity are of major importance. A relatively rigid interface decreases the rate of coalescence and hence leads to a low precipitation rate. Thus, by controlling the structure of the interface, one can change the reaction kinetics in microemulsions by an order of magnitude [168]. It has been further shown that the structure of oil, the alcohol, and the ionic strength of the aqueous phase can significantly influence the rigidity of the interface and the reaction kinetics [169].

Figure 1.8 shows a schematic presentation of the process for producing nanoparticles. The process consists of three steps. In step 1, reactants A and B are dissolved into two identical water-in-oil microemulsions. Then, upon mixing, due to collision and coalescence of the droplets, reactants A and B come in contact with each other and form precipitate AB. This precipitate is confined to the interior of the microemulsion droplets.
The synthesis of nanoparticles in microemulsions was first reported by Boutonnet et al. [140]. They obtained monodispersed metal particles of Pt, Pd, Rh and Ir by reducing corresponding salts in waterpools of water-in-oil microemulsions with hydrogen gas. Since then, microemulsions have been used for the synthesis of a variety of nanoparticles.
covering a wide range of applications, including catalysts, ceramics, biological stainers, biomaterials, condensers for electron storage in artificial photosynthesis, and semiconductors [171-184]. Different metallic nanoparticles, such as gold [185], silver [186-187], and copper [187-188], have been successfully prepared in microemulsions. In addition, the microemulsion technique has also been employed to produce many other inorganic nanomaterials, such as silver halides [189], and oxides of Ti [190-191], Zr [192], Fe [193], Si [194-196], Zn [197-199], and Cd [200].

The microemulsion technique is a well-suited method for producing lanthanide-doped nanoparticles. It has remarkable advantages over other methods. Since all of the starting materials are mixed at the molecular level in a solution, a high degree of homogeneity is achievable. Moreover, the size and shape of nanoparticles formed in microemulsions can be precisely controlled. This is crucial to the research of size-dependent properties.

1.6. SCOPE OF THIS THESIS

Lanthanide-doped nanoparticles have been actively investigated because of their broad applications in industry. However, the current theories and experimental databases are inadequate to understand the optical properties of localized luminescent centers in nanostructures. More and more efforts are being made to explore the design of lanthanide-doped nanoparticles by different synthesis methods and to study their physical properties by a variety of characterization techniques.
Chapter 1. Introduction

This thesis reports the synthesis and characterization of a series of lanthanide-doped nanoparticles. The microemulsion technique was employed to prepare these nanoparticles. From the point of view of application, the nanoparticles in this thesis were focused on the nanophosphors used for FEDs (Field emission displays) as well as upconversion materials. The nanophosphors for FEDs included Eu:Y₂O₃ (red-emitting), Tb:Y₂O₃ (green-emitting), and Tm:Y₂O₃ (blue-emitting). In addition, Pr:Y₂O₃ and Er:Y₂O₃ were studied as upconverting phosphors.

Since yttrium oxide is the most attractive matrix for both FEDs and upconversion applications, Y₂O₃ were selected as the main doping host for lanthanide ions in this study. Cubic Y₂O₃ crystallizes in the C bixbyite structure, with a space group Ia3 (T₈) [201]. Y³⁺ ions in the unit cell occupy 24 sites with point symmetry C₂ and 8 sites with S₆.

Figure 1.9 shows S₆ and C₂ symmetry of cubic Y₂O₃. Each lanthanide ion is surrounded
by oxygen ions located at the corners of a cube. Two corners of the cube are not occupied by oxygen ions. The vacancies are either along a body diagonal or along a face diagonal of the cube. Since there is no inversion symmetry at the site of C$_2$ in cubic Y$_2$O$_3$, the uneven crystal field components can mix opposite-parity states into the 4f$^n$-configurational levels if RE$^{3+}$ (Rare Earth) occupy this site. The electric-dipole transitions between levels of the 4f$^n$ are now no longer strictly forbidden and appear as lines in the spectra, the so-called forced electric-dipole transitions. Lanthanide ions are close in ionic radius to yttrium (For example, 0.881 Å for Er$^{3+}$ and 0.892 Å for Y$^{3+}$). Therefore, a large amount of lanthanide ions can be incorporated into the host without significant lattice distortions [202]. Moreover, the high chemical stability, high thermal conductivity, as well as broad transparency range offers Y$_2$O$_3$ remarkable advantages over other kinds of host [203].

The main objectives of this research are as follows:

1) To study the feasibility of preparing lanthanide-doped nanoparticles employing microemulsion techniques.

2) To characterize the lanthide-doped nanoparticles synthesized by microemulsion techniques.

3) To investigate the relationships between optical properties and the particle characteristics of lanthanide-doped nanoparticles prepared in microemulsion systems.

4) To provide a fundamental investigation on the development of novel nanophosphors for FEDs and upconversion applications.
Using thermogravimetry (TG), X-ray diffractometer (XRD), X-ray photoelectron spectroscopy (XPS), scanning electronic microscopy (SEM), transmission electronic microscopy (TEM), and photoluminescence instruments (PL), we extensively studied the various characteristics of lanthanide-doped nanoparticles, including particle size, size distribution, thermal property, crystallinity, and optical properties.

In addition, this thesis focuses on the optical properties of the nanoparticles. We investigated the effect of different factors such as the particle size, the concentration of dopants, calcine temperatures, doping hosts as well as codopants on the luminescent properties of the synthesized lanthanide-doped nanoparticles.

1.7. REFERENCES

Chapter 1. Introduction

Chapter 1. Introduction

Chapter 1. Introduction

Chapter 1. Introduction

      511, 1990.


CHAPTER 2 EXPERIMENTAL

2.1 MATERIALS

Various lanthanides used in this study are shown in Table 2.1. The lanthanide oxides or nitrates were kept in desiccators to avoid contaminations (H₂O and CO₂).

<table>
<thead>
<tr>
<th>Lanthanides</th>
<th>Source</th>
<th>Purity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Europium (III) oxide</td>
<td>Aldrich</td>
<td>99.999%</td>
</tr>
<tr>
<td>Terbium (III) oxide</td>
<td>Fluka</td>
<td>99.9%, contains 0.1% Dy₂O₃, Gd₂O₃, and Y₂O₃</td>
</tr>
<tr>
<td>Gadolinium (III) oxide</td>
<td>Acros</td>
<td>99.9%</td>
</tr>
<tr>
<td>Lathanum (III) oxide</td>
<td>Aldrich</td>
<td>99.9%</td>
</tr>
<tr>
<td>Thulium (III) oxide</td>
<td>Acros</td>
<td>99.9%</td>
</tr>
<tr>
<td>Praseodymium (III, IV) oxide</td>
<td>Aldrich</td>
<td>99.999%</td>
</tr>
<tr>
<td>Erbium (III) oxide</td>
<td>Aldrich</td>
<td>99.9%</td>
</tr>
<tr>
<td>Cerium (III) nitrate</td>
<td>Fluka</td>
<td>99.9%</td>
</tr>
<tr>
<td>Yttrium oxide</td>
<td>Fluka</td>
<td>99.999%</td>
</tr>
</tbody>
</table>

Ammonia hydroxide solution (20%, analytical reagent) was obtained from Merck.

Petroleum ether (boiling point 60-80°C) was from BDH.

Nonionic surfactants: poly(oxyethylene)$_5$ nonyl phenol ether (NP$_5$) and poly(oxyethylene)$_9$ nonyl phenol ether (NP$_9$)

were from Albright & Wilson Asia Pte. Ltd.

Nitric acid (65%) and acetone were from Merck.
All reagents and solvents were used as received. Water was purified by a Milli-Q water purification system (resistance 18.2 kΩ).

Bismuth nitrate was obtained from Fluka.

Aluminium nitrate was from Aldrich.

Barium nitrate was from Aldrich.

2.2 SYNTHESIS

This section consists of two parts, microemulsion systems and synthesis method. In the first part, we introduced the optimal microemulsion system for producing lanthanide-doped nanoparticles after reviewing the previous work on phase behavior of various microemulsion systems. The phase diagram of these systems has previously been established by Dr Fang Jiye and Liu Bing of the same laboratory [1, 2]. For all nanoparticles prepared in this study, the synthesis method is similar. As an example, the synthesis of Eu:Y₂O₃ nanoparticles was described in detail.

2.2.1 Phase behavior of microemulsion systems

Among the various microemulsions employed for synthesizing inorganic nanoparticles, water-in-oil (w/o) inverse microemulsions have been most widely used [3-8]. One of the obvious reasons for this is that most of the inorganic reactions can take place in the aqueous nanosized droplets of w/o microemulsions. In this study, we selected a w/o microemulsion as the reaction medium for synthesizing lanthanide-doped nanocrystals. In
Chapter 2 Experimental

this microemulsion system, Igepal series nonionic surfactants (i.e. polyoxyethylene\(_x\)nonylphenol ether, \(4-(C_9H_{19})C_6H_{14}O(OCH_2CH_2)_yOH\), and they are regarded to as “NP\(_x\)” when \(y=5\), and “NP\(_y\)” when \(y=9\)) was employed. There is a unique advantage of using nonionic surfactants in synthesizing nanophosphors as far as contamination is concerned. The nonionic surfactants are only composed of “organic elements”, such as carbon, hydrogen and oxygen, which could easily be removed by the post-treatment, such as subsequent calcinations step.

When a chemical reaction is performed in a microemulsion media, one of the major concerns is whether the reactants will destabilize the microemulsion. Therefore, the effects of reactants on the stability of microemulsions have to be investigated by establishing appropriate phase diagrams. Besides the type of surfactants and oil phase, the reagents and their concentrations in aqueous phase can also affect the structure of microemulsions, although the characteristics of the resulting product may not be determined solely by the original size of nanodroplets. It is generally accepted that the amount of aqueous phase that can solubilize in an inverse microemulsion system increases with increasing surfactant to oil ratio. Higher percentage of surfactant can result in the formation of a liquid crystalline phase, as shown in Fig. 1.7. But a system containing a very high fraction of surfactant is not a desirable medium for producing fine products. It is therefore not necessary to establish a full phase diagram for the oil-surfactant-aqueous phase system.
2.2.1.1 Systems with cyclohexane-(NP$_5$+NP$_9$) and various aqueous solutions of Alkalies [1]

Figure 2.1 is the basic partial phase diagram for the ternary system containing distilled water, cyclohexane and NP$_5$/NP$_9$ (2:1). The introduction of alkalies into the aqueous phase results in an apparent change in the microemulsion region as to be shown in Figures 2.2 (a-d).

**Figure 2.1** The partial phase diagram at 22$^0$C for the system cyclohexane-NP$_5$/NP$_9$-water [1]
Figure 2.2 (a,b) The partial phase diagrams at 22\(^\circ\)C for the systems cyclohexane-NP\(_5\)/NP\(_9\)-KOH(a) and NaOH(b) at various concentrations [1]
Figure 2.2 (c,d) The partial phase diagrams at 22° C for the systems cyclohexane-NP₅/NP₉-Me₄NOH(c) and NH₄OH(d) at various concentrations [1]
Figures 2.2 (a-d) show the transparent microemulsion regions for the systems containing aqueous solutions of KOH, NaOH, NH₃H₂O and Me₄NOH of various concentrations, respectively. The microemulsion region in each of these systems reduces with increasing concentration of alkali at a given weight ratio of surfactant to cyclohexane. These cations can form strong complexes with the ethylene oxide units of mixed surfactants. In addition, hydroxide (OH⁻) may serve as a weak bridge by linking the complex cations of the neighboring surfactant molecules. The rigidity of the interfacial films of the w/o microemulsion droplets is thus increased and this favors the formation of smaller droplets of microemulsions. Therefore, the microemulsion region reduces significantly as the concentration of alkali is increased. However, the effect of ammonia concentration on the reduction of microemulsion region is not so significant. This is because ammonia solution is a weak base that weakly dissociates into ionic species. With this special property, ammonia is a good precipitant for reactions in inverse microemulsions with higher concentrations of reactants.

2.1.1.2 Systems with petroleum ether-ZnCl₂ solution-NP₅/NP₉ with various weight ratios of NP₅ to NP₉ [2]

A very pronounced alteration in the region of microemulsion can be observed in Fig. 2.3 (a) and Fig. 2.3 (b). The transparent region increases dramatically as the ratio changes from 8:1 to 2:1, while a phase separation can be observed as the ratio increases to 1:1. It can be concluded the optimal ratio of NP₅ to NP₉ is 2:1.
Figure 2.3 (a) Partial phase diagram for the system PE-ZnCl$_2$ aqueous solution-NP$_5$/NP$_9$ in the ratio of 8:1 and 4:1 respectively [2]

Figure 2.3 (b) Partial phase diagram for the system PE-ZnCl$_2$ aqueous solution-NP$_5$/NP$_9$ in the ratio of 2:1 [2]
Refer to the review in Section 1.5.2, the alteration in the region of microemulsion can be easily understood. NP9 serves as a cosurfactant in this microemulsion system. Since it has different size of the hydrocarbon moiety compared to NP5, the fluidity of an interface between the aqueous and oil phase can be increased dramatically, leading to a structural transition from birefringent lamellar phase to isotropic microemulsions. In addition, the introduction of NP9 in the ratio of 2:1 results in an optimal HLB (hydrophilic-lipophilic balance) value of the mixed surfactant.

2.1.1.3 Systems with cyclohexane-(NP5+NP9) and various aqueous solutions of salts

Figures 2.4 (a-c) show the transparent microemulsion regions for the systems containing various aqueous inorganic salts with different concentrations. It can be seen that an aqueous solution containing a cation of higher valence together with an anion of lower valence enlarges the inverse microemulsion region with increasing the salt concentration. On the other hand, a lower valence cation together with a higher valence anion dramatically reduces the microemulsion regions by increasing the salt concentration. The reduction in microemulsion regions is due to the strong association of divalent-metal ions with the ethylene oxides of the surfactant and subsequently, resulting in intermolecular associations with the neighboring surfactant molecules via multi-valent anions. The formation of these complexes increases the rigidity of the interfacial film of microemulsion droplets that can only be formed for much smaller droplets containing low aqueous salt solution.
Figure 2.4a The partial phase diagram for the systems cyclohexane-NP$_5$/NP$_9$-Na$_3$PO$_4$ with different concentrations [1]

Figure 2.4b The partial phase diagram for the systems cyclohexane-NP$_5$/NP$_9$-K$_2$CO$_3$ with different concentrations [1]
Chapter 2 Experimental

Figure 2.4c The partial phase diagram for the systems cyclohexane-NP$_5$/NP$_9$-Fe(NO$_3$)$_3$ with different concentrations [1]

2.1.1.4 The optimal microemulsion system for producing Lanthenide-doped nanoparticles

Based on the study of the microemulsion phase behaviors, it is established that larger inverse microemulsion regions can be obtained when the aqueous solutions contain either lanthenides nitrates or ammonia solution. The best weight ratio of NP$_5$ to NP$_9$ is 2:1. Since the microemulsion system cyclohexane-NP$_5$/NP$_9$-aqueous solution is stable at 22$^\circ$C, while Petroleum ether-NP$_5$/NP$_9$-aqueous solution system forms at 30$^\circ$C, we
selected PE as the oil phase. With this understanding, higher yields of lanthanide-doped nanoparticle precursors can thus be obtained.

2.2.2 Synthesis method

Figure 2.5 describes the synthesis method used in this project.

Figure 2.5 The flowchart of synthesizing lanthanide-doped nanophosphors

The synthesis of Eu:Y₂O₃ nanoparticles was introduced in detail as follows:

The microemulsion used petroleum ether (PE) as oil phase and NP₅:NP₉=2:1 mixture as surfactants. Based on the phase diagram, the formula of the system was selected as PE: Surfactant: aqueous = 42:18:40 (wt%). Two types of microemulsions, 1 and 2, were prepared separately. The only difference between them is that the aqueous solution in 1
contains 0.1M Y(NO$_3$)$_3$ and 0.01M Eu(NO$_3$)$_3$, whereas 2 contains ammonium hydroxide. The nonionic surfactants are more stable than ionic surfactants at various pHs. The stability of microemulsions is greatly influenced by temperature. They were kept at 30$^\circ$C to prevent phase separation or phase conversion. Microemulsions 1 and 2 were mixed together with continuous stirring at 30$^\circ$C till the pH value reaching 10. Then, the Eu doped Yttrium hydroxide precursor was washed by acetone and water 3-4 times to remove most of the oil and surfactant molecules adsorbed on the surface of the particles. The washed particles were collected and dried in a rotary evaporator at 40$^\circ$C-70$^\circ$C. The dried particles were calcinated at different temperatures.

In co-doped synthesis process, the codopants (Al$^{3+}$, Ba$^{2+}$, Ce$^{3+}$, etc) were dissolved in nitric acid and then mixed with Y(NO$_3$)$_3$ and Lanthanide nitrates. The mixture was finally incorporated into microemulsion 1 to react with microemulsion 2.

2.3 CHARACTERIZATION TECHNIQUES

2.3.1 Thermal Analysis

Thermal analysis is a collection of techniques for measuring the physical properties of a substance as a function of temperature. It is particularly useful in determining thermally driven changes, including phase change and reaction that alter the weight of the sample [9, 10]. In this study, lanthanide-doped nanoparticles were characterized using thermal gravimetric analysis (TGA). TGA was carried out on a TA Instrument (Model Universal
V1, 10 B). About 5 mg of powder was loaded at room temperature into a standard platinum crucible. The crucible was then heated to 1000°C at a constant rate of 5°C/min in air.

### 2.3.2 Elemental analysis

IRIS AP Duo (from Thermo Jarrell Ash) was used to determine the Lanthenides contents of various samples. The IRIS Optical Emission Spectrometers are a family of inductively coupled argon plasma (ICAP) optical emission spectrometers (OES) which use Echelle optics and a unique Charge Injection Device (CID) solid state detector to provide complete and continuous wavelength coverage over the typical analytical wavelength range. Typically, OES can analyze samples in the concentration range from low ppb to % levels. IRIS AP Duo equipped with Axial Plasma and Auxiliary Optics for radial viewing of the higher wavelengths where matrix interferences are more prevalent in the axial plasma.

### 2.3.3 XPS measurement

X-ray photoelectron spectroscopic (XPS) measurements were made on a VGESCALAB MkII spectrometer with a Mg Kα X-ray source (1253.6 eV photons) and a hemispherical energy analyzer. Samples were mounted on standard sample studs by a double-sided adhesive tape. The X-ray source was run at 12 KV and 10mA. Pass energy of 20 eV and a rate of 0.05 eV/step were used for all the high-resolution XPS spectra acquisition with a
binding energy width of 12 eV. The pressure in the analysis chamber was maintained at \(10^{-8}\) mbar or lower during measurements. All spectra were obtained at a take-off angle of 75°C to the sample surface and were curve fitted with the XPSPEAK 3.1 software.

### 2.3.4 X-ray Diffraction

Since the specific interference (diffraction) pattern is unique for a particular crystalline material, XRD is a standard method for identifying phases in crystalline materials. By XRD technique, we can also estimate the mean crystalline size of the nanoparticles. In this study, the XRD experiments were carried out on a Simens D5005 Diffractometer (40 kV, 40mA) using Ni-filtered Cu Kα radiation. The intensity of the diffracted X-ray from the samples was measured by a scintillation counter.

### 2.3.5 Scanning Electron Microscope

Among the commonly used imaging techniques, scanning electron microscope (SEM) is the most often used [11], and it is widely employed in characterizing various materials. SEM may be used to study the surface, or the near surface structure of bulk and powdered materials. All samples were coated with gold in order to minimize the charging problems. In this work, JEOL and Hitachi scanning electron microscope were employed. Electrons from an electron gun are accelerated to the energy between 2 KeV and 40 KeV. Condenser lenses will demagnify the electron beam before it scans the specimen by the scan coils, while a detector counts the number of low energy secondary electrons or other
radiation, given off from each point on the surface. The cathode ray tube (CRT) is scanning across the screen at the same time. The amplified current from the detector will modulate the brightness of the spot. Any signal is an interaction between the incident electrons and specimen. Thus, any radiation from the specimen can be used to provide signal to modulate CRT, providing contrast in the image. Usually secondary electrons, backscattered electrons and x-ray signal are utilized.

2.3.6 Transmission Electron Microscope

Transmission electron microscope (TEM) is a very useful technique for studying the nanostructure of materials [12-15]. In this study, JEOL (100CX) was used to study the particle size of nanoparticles. TEM technique requires specialized specimen preparation. For powdered materials, fine particles are dispersed into distilled water or ethanol, and the suspension is dropped onto a carbon film deposited on the copper grid, followed by removing the solvent. The JEOL TEM was operated at a voltage of 100 kV and a vacuum of \(10^{-5}\) torr or higher.

2.3.7 Photoluminescence measurement

The photoluminescence measurements were performed by Spex 1934D3 spectrophotometer. The excitation source was a 150W xenon lamp. The experimental parameters are as follows: Scan increment: 0.5; integrated time: 0.1s; Slit widths: ex. 1nm, em. 1nm; and scan region: 200-800nm.
2.4 REFERENCES


CHAPTER 3 RED-EMITTING NANOPHOSPHOR Eu:Y$_2$O$_3$

The Eu:Y$_2$O$_3$ phosphor has found application as the red component in cathode-ray tubes and fluorescent lighting devices since the 1960s [1-2]. This material fulfills all the requirements for a good red-emitting phosphor. It exhibits a sharp emission line at 613 nm and all other emission lines are weak. It can be easily excited by 254 nm radiation [3].

To develop the luminescent materials with high chemical purity, homogeneity, and high luminescence efficiency, many researchers have done extensive research on nano-size Eu:Y$_2$O$_3$. B. M. Tissue’s group carried out a series of studies on the luminescent properties of Eu:Y$_2$O$_3$ nanocrystals and their comparison to bulk monoclinic Eu:Y$_2$O$_3$ [4-7]. A. Konrad, et al, found that nanoparticles synthesized by chemical vapor method showed blue-shifted absorption bands with respect to coarsely grained material [8]. Pramod K. Sharma, et al, studied the size effect on the fluorescence properties of nano-sized Eu:Y$_2$O$_3$ synthesized by wet chemical method [9]. Takayuki Hirai et al obtained Eu:Y$_2$O$_3$ phosphor particles by calcination of composite Y-Eu oxalate particles prepared in emulsion liquid membrane systems. The particles showed photoluminescence at 614nm [10]. To enhance the Eu emission intensity, many researchers have codoped with either other rare earth or transition metal ions [11-12].

The synthesis of Eu:Y$_2$O$_3$ is typically carried out through the decomposition of co-precipitated oxalates from purified solutions of yttrium and europium nitrates [1, 13]. This process involves firing the dried oxalates at 600$^\circ$C, followed by a high temperature
fire at 1400°C-1500°C for several hours. Other different methods to synthesize Eu:Y$_2$O$_3$ nanoparticles have been developed, including solution-phase synthesis [9], combustion synthesis [14], chemical vapor synthesis [8], and hydrolysis technique [15].

As reviewed in Chapter 1, Eu:Y$_2$O$_3$ nanoparticles synthesized in this study are to be used as red-emitting phosphors for FEDs. Phosphors obtained by conventional methods have little or no control over the particle morphology, due to the high temperature solid-state reaction. To achieve a better quality of phosphors, low temperature synthesizing methods are desired.

Microemulsion technique has been developed and reported in this study. In a microemulsion synthesis process, all starting materials were mixed at a molecular level in a solution, so that doping of Eu$^{3+}$ was easy and effective [16, 17]. The surface area of the powders produced from microemulsion route is very high [18], possibly resulting in a better thermal conductivity when excited by high-energy electrons (cathode ray tube and field emission displays) or photons (plasma display). Moreover, the quenching concentration of Eu has been raised remarkably. These results can be applicable in development of field emission displays. In this study, Eu, Al:Y$_2$O$_3$ and Eu, Ba:Y$_2$O$_3$ were prepared to investigate the influence of codopants on luminescence of Eu:Y$_2$O$_3$ nanophosphors.
3.1 RESULTS AND DISCUSSIONS

3.1.1 Elemental analysis of Eu:Y$_2$O$_3$ nanoparticles

In order to confirm the actual concentration of Eu ions doped in Y$_2$O$_3$, the elemental analysis was conducted by ICP technique. Table 3.1-3.3 shows the results of the elemental analysis of some of the nanoparticles prepared.

**Table 3.1** Elemental analysis of Eu:Y$_2$O$_3$ nanoparticles (1%)

<table>
<thead>
<tr>
<th>Elements</th>
<th>Theoretical value (wt%)</th>
<th>Experimental value (wt%)</th>
<th>Eu:Y (mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Y</td>
<td>77.70</td>
<td>70.18</td>
<td>0.96%</td>
</tr>
<tr>
<td>Eu</td>
<td>1.33</td>
<td>1.16</td>
<td></td>
</tr>
</tbody>
</table>

**Table 3.2** Elemental analysis of Eu:Y$_2$O$_3$ nanoparticles (8%)

<table>
<thead>
<tr>
<th>Elements</th>
<th>Theoretical value (wt%)</th>
<th>Experimental value (wt%)</th>
<th>Eu:Y (mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Y</td>
<td>71.09</td>
<td>63.09</td>
<td>7.9%</td>
</tr>
<tr>
<td>Eu</td>
<td>9.72</td>
<td>8.52</td>
<td></td>
</tr>
</tbody>
</table>

**Table 3.3** Elemental analysis of Eu:Y$_2$O$_3$ nanoparticles (15%)

<table>
<thead>
<tr>
<th>Elements</th>
<th>Theoretical value (wt%)</th>
<th>Experimental value (wt%)</th>
<th>Eu:Y (mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Y</td>
<td>65.52</td>
<td>55.93</td>
<td>15.7%</td>
</tr>
<tr>
<td>Eu</td>
<td>16.80</td>
<td>15.08</td>
<td></td>
</tr>
</tbody>
</table>
Chapter 3 Red-emitting nanophosphor Eu:Y$_2$O$_3$

The experimental values of Y and Eu were lower than the theoretical values. It is due to the contamination of H$_2$O, and CO$_2$. From the results of the elemental analysis, it can be seen that the molar ratio of Eu to Y fit the theoretical values very well. It can be concluded that microemulsion technique is an effective way to dope impurities into nanocrystals.

3.1.2 Thermal decomposition of the precursor of Eu:Y$_2$O$_3$ nanoparticles

The TGA curve (Fig.3.1) recorded the phase transitions of the Eu:Y$_2$O$_3$ nanoparticles from room temperature (28°C) to 1000°C. It was observed that the powder undergoes three transitions in different temperature regions. The first occurs below 230°C, which is due to the loss of water molecules associated with the particles. The second is from 230°C to 400°C corresponding to the removal of organic materials. From 500°C to 600°C, there is the third transition that represents the conversion of hydroxide to oxide. In the range of 600°C to 1000°C, there is very little change of weight for the samples. The whole transition process can be expressed as follows:

\[
Y_{1-x}Eu_x(OH)_3H_2O \rightarrow Y_{1-x}Eu_x(OH)_3 \rightarrow \text{Eu:Y}_2\text{O}_3
\]

The results of TGA analysis indicate that the precursor of Eu:Y$_2$O$_3$ nanoparticles converts to Eu:Y$_2$O$_3$ at around 600°C.
Chapter 3 Red-emitting nanophosphor Eu:Y₂O₃

**Figure 3.1** TGA curve of the Eu:Y₂O₃ nanoparticles
3.1.3 Crystallinity and crystalline size of Eu:Y₂O₃ nanoparticles

The X-ray diffraction (XRD) patterns (Fig. 3.2) show that the nanoparticles calcinated at 600°C or above have good crystallinity of Y₂O₃. There is little difference among XRD curves of the samples calcinated at 600°C, 800°C, and 1000°C. This result is agreeable with the results of thermal analysis. The XRD lines match well with the standard lines given in JCPDS (82-2415) data files. The comparison of XRD lines between the nanoparticles calcined at 600°C and the standard data file is shown in Table 3.5 These results indicate that the crystallization temperatures of the nanoparticles prepared by the microemulsion technique are far below the temperatures employed in a solid-state reaction (1400°C-1500°C) [1, 13, 19].

The size of crystallites in the sample can be estimated by the Scherrer equation:

\[ L = \frac{K\lambda}{\beta \cos \theta} \]

where K (=0.9) is the Scherrer shape factor; \( \lambda \) (=1.54) is the wavelength of X-ray; \( \theta \), the Bragg angle; and \( \beta \), the pure line broadening. The results are shown in Table 3.4.

<table>
<thead>
<tr>
<th>Sample (°C)</th>
<th>FWHM(L) (°)</th>
<th>FWHM(R) (°)</th>
<th>2θ (°)</th>
<th>B</th>
<th>β</th>
<th>L, crystalline size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>600</td>
<td>0.242</td>
<td>0.211</td>
<td>29.0884</td>
<td>0.0079</td>
<td>0.0078</td>
<td>18</td>
</tr>
<tr>
<td>800</td>
<td>0.293</td>
<td>0.280</td>
<td>29.1245</td>
<td>0.0100</td>
<td>0.0099</td>
<td>14</td>
</tr>
<tr>
<td>1000</td>
<td>0.276</td>
<td>0.265</td>
<td>29.2330</td>
<td>0.0094</td>
<td>0.0094</td>
<td>15</td>
</tr>
</tbody>
</table>

The crystalline sizes of Eu:Y₂O₃ nanoparticles with different calcination temperatures were obtained by averaging from three main diffraction peaks (2θ=29, 48 and 57): 16, 16 and 15 nm for 600, 800 and 1000°C, respectively.
Chapter 3 Red-emitting nanophosphor Eu:Y$_2$O$_3$

B is the measured half-width of the experiment profile, $B = \frac{(FMHM_L + FMHM_R)}{180\pi}$

$\beta^2 = B^2 - b_0^2$, $b_0$ is the instrumental broadening, here $b_0=0.0011$.

Table 3.5 The comparison of XRD lines between the sample calcined at 600$^\circ$C and standard cubic Y$_2$O$_3$

<table>
<thead>
<tr>
<th>d (sample)</th>
<th>d (standard)</th>
<th>h</th>
<th>k</th>
<th>l</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.3316</td>
<td>4.3281</td>
<td>2</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>3.0629</td>
<td>3.0604</td>
<td>2</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>2.6529</td>
<td>2.6504</td>
<td>4</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>2.4973</td>
<td>2.4988</td>
<td>4</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>2.3728</td>
<td>2.3706</td>
<td>4</td>
<td>2</td>
<td>0</td>
</tr>
<tr>
<td>2.2613</td>
<td>2.2603</td>
<td>3</td>
<td>3</td>
<td>2</td>
</tr>
<tr>
<td>2.0797</td>
<td>2.0791</td>
<td>1</td>
<td>3</td>
<td>4</td>
</tr>
<tr>
<td>1.9379</td>
<td>1.9356</td>
<td>5</td>
<td>2</td>
<td>1</td>
</tr>
<tr>
<td>1.8753</td>
<td>1.8741</td>
<td>4</td>
<td>4</td>
<td>0</td>
</tr>
<tr>
<td>1.8204</td>
<td>1.8181</td>
<td>4</td>
<td>3</td>
<td>3</td>
</tr>
<tr>
<td>1.7216</td>
<td>1.7198</td>
<td>6</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>1.6790</td>
<td>1.6762</td>
<td>0</td>
<td>2</td>
<td>6</td>
</tr>
<tr>
<td>1.6345</td>
<td>1.6358</td>
<td>1</td>
<td>4</td>
<td>5</td>
</tr>
<tr>
<td>1.5991</td>
<td>1.5982</td>
<td>6</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>1.5658</td>
<td>1.5631</td>
<td>1</td>
<td>3</td>
<td>6</td>
</tr>
<tr>
<td>1.5287</td>
<td>1.5302</td>
<td>4</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td>1.5009</td>
<td>1.4993</td>
<td>5</td>
<td>4</td>
<td>3</td>
</tr>
<tr>
<td>1.4706</td>
<td>1.4702</td>
<td>0</td>
<td>4</td>
<td>6</td>
</tr>
<tr>
<td>1.4420</td>
<td>1.4427</td>
<td>2</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>1.4096</td>
<td>1.4167</td>
<td>6</td>
<td>4</td>
<td>2</td>
</tr>
<tr>
<td>1.3450</td>
<td>1.3467</td>
<td>2</td>
<td>3</td>
<td>7</td>
</tr>
<tr>
<td>1.3247</td>
<td>1.3252</td>
<td>8</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>1.3052</td>
<td>1.3049</td>
<td>8</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>1.2874</td>
<td>1.2856</td>
<td>8</td>
<td>2</td>
<td>0</td>
</tr>
<tr>
<td>1.2632</td>
<td>1.2671</td>
<td>3</td>
<td>5</td>
<td>6</td>
</tr>
<tr>
<td>1.2465</td>
<td>1.2494</td>
<td>8</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>1.2318</td>
<td>1.2324</td>
<td>8</td>
<td>3</td>
<td>1</td>
</tr>
<tr>
<td>1.2165</td>
<td>1.2161</td>
<td>6</td>
<td>6</td>
<td>2</td>
</tr>
<tr>
<td>1.1847</td>
<td>1.1853</td>
<td>0</td>
<td>4</td>
<td>8</td>
</tr>
<tr>
<td>1.1444</td>
<td>1.1432</td>
<td>7</td>
<td>6</td>
<td>1</td>
</tr>
<tr>
<td>1.1180</td>
<td>1.1175</td>
<td>1</td>
<td>5</td>
<td>8</td>
</tr>
</tbody>
</table>
Figure 3.2 XRD spectra of the Eu:Y$_2$O$_3$ nanoparticles with various calcination temperatures
3.1.4 Morphology of the Eu:Y$_2$O$_3$ nanoparticles

Since the luminescence of a phosphor depends on the shape, size, crystallinity, defects, and grain boundaries, the morphology of the prepared samples was studied using scanning electron microscopy (SEM).

The micrographs (Fig.3.3, Fig.3.4) show that a continuous network of particles was formed at 600 and 800$^\circ$C. Pores and voids can be clearly seen. This is similar to that of the combustion-synthesized powders [20, 21]. It may result from the escaping gases during calcination. The nanoparticles prepared in microemulsions adsorbed the surfactants that can act as fuels in calcination process. As shown in Fig. 3.1, the surfactants can be burned away at above 230$^\circ$C.

The agglomeration was due to sintering of the particles. Under 600$^\circ$C-800$^\circ$C of calcination temperatures, the agglomeration of the particles is unavoidable.
Figure 3.3 SEM micrograph of Eu:Y$_2$O$_3$ nanoparticles calcined at 600°C

Figure 3.4 SEM micrograph of Eu:Y$_2$O$_3$ nanoparticles calcined at 800°C
3.1.5 Transmission electronic microscopy

By transmission electronic microscopy (TEM), we studied the particle size with a higher resolution and accuracy. It can be seen from the micrographs (Fig. 3.5, Fig. 3.6, and Fig. 3.7) that the particles are in the range of several nm to tens of nm. This result is consistent with what we obtained from XRD analysis. Most of the particles agglomerate into a larger size (tens of nm or hundreds of nm) during the calcination process. Therefore, the particle size of the samples we observed in TEM micrographs includes both crystallite size and agglomeration size, which is in the range of several nm to hundreds of nm. In addition, nanoparticles calcinated at 800 or 1000°C have a narrower distribution of particle size than that of nanoparticles calcinated at 600°C. The size distribution was obtained from TEM micrographs (Including the micrographs not shown here). 50 particles of the different samples are chosen and the bar height represents the number of particles.
Chapter 3 Red-emitting nanophosphor Eu:Y$_2$O$_3$

Figure 3.5 TEM micrograph and size distribution of nanoparticles calcined at 800\(^\circ\)C

Figure 3.6 TEM micrograph and size distribution of nanoparticles calcined at 1000\(^\circ\)C

Figure 3.7 TEM micrograph and size distribution of nanoparticles calcined at 600\(^\circ\)C
3.1.6 Photoluminescent properties

3.1.6.1 The emission of Eu:Y$_2$O$_3$

Figures 3.8 and 3.9 show the excitation and emission spectra of Eu:Y$_2$O$_3$ nanoparticles.

![Excitation spectrum of Eu:Y$_2$O$_3$ nanoparticles](image1)

**Figure 3.8** Excitation spectrum of Eu:Y$_2$O$_3$ nanoparticles

![Emission spectrum of Eu:Y$_2$O$_3$ nanoparticles](image2)

**Figure 3.9** Emission spectrum of Eu:Y$_2$O$_3$ nanoparticles
The excitation spectrum was taken at an emission wavelength of 610 nm. The most intense peak is at 393.5 nm, which is ascribed to electronic transitions within 4f$^6$ shell of Eu$^{3+}$. Upon excitation at 393 nm, trivalent europium-activated Y$_2$O$_3$ yields intense red emission at ~591 nm, 610nm and ~630nm. Figure 3.10 shows the partial energy level diagram of the Eu$^{3+}$ ion in the solid matrix. The emission of Eu$^{3+}$ usually consists of lines in the red spectral range, corresponding to transitions from the excited $^5D_0$ level to the $^7F_J$ ($J=0, 1, 2, 3, 4, 5, 6$) levels of the 4f$^6$ configuration. These lines have found important applications in lighting and display.

![Energy Level Diagram](image)

**Figure 3.10** Partial energy level diagram of the Eu$^{3+}$ ion in solid matrix
Although such types of transitions are forbidden by Laporte’s selection rule, they are observed as forced electric dipole transition when Eu$^{3+}$ occupies acentric sites of cubic Y$_2$O$_3$ [22]. The theory has been discussed in Section 1.6 of Chapter 1.

### 3.1.6.2 The influence of calcination temperature on the emission of Eu:Y$_2$O$_3$

All the samples with different concentrations of Eu showed similar relationship between emission intensity and calcination temperatures. Fig. 3.11 is an example for 8%(mol%) of Eu. From Fig.3.11, it can be found that the main emission of the solid sample without calcinations (precursors) peaks at 613nm ($^5$D$_0 \rightarrow ^7$F$_2$) with a very low intensity. In addition, the transitions of $^5$D$_0 \rightarrow ^7$F$_1$ at 589nm, 594nm, $^5$D$_0 \rightarrow ^7$F$_3$ at 650 nm, $^5$D$_0 \rightarrow ^7$F$_4$ at 699nm and $^5$D$_0 \rightarrow ^7$F$_5$ at 750nm are clearly observable [23]. After calcination at 600°C to 1000°C for 2 hours, the main emission intensity increases by thirteen to seventeen times and the peaks shift from 613nm to 610nm. The other transitions are dramatically suppressed [Fig.3.12].

From crystallographic studies in Section 1.6 of Chapter 1, Eu$^{3+}$ occupies two types of sites in cubic Y$_2$O$_3$: C$_2$ and S$_6$. $^5$D$_0 \rightarrow ^7$F$_2$ originates from Eu activators at C$_2$ sites. With the increase of calcination temperature, the cubic crystals are formed [Section 3.1.2, 3.1.3]. Because the ratio of S$_6$ and C$_2$ is 1:3 in cubic Y$_2$O$_3$ [24], the emission corresponding to $^5$D$_0 \rightarrow ^7$F$_2$ transition at 610nm becomes more dominant, whereas the other sets of emission was suppressed. Since the firing temperatures employed in this experiment are lower than those prepared by a solid-state reaction process, there is less
possibility of forming multiphase systems [25]. The peak shift from precursors to cubic Eu₂O₃ was attributed to a change in the crystalline field.

**Figure 3.11** Emission spectra of precursors of Eu:Y₂O₃ and Eu:Y₂O₃ calcined at various temperatures for 2 hours
From XRD, TEM, and Photoluminescence studies, it can be concluded that 800°C is the optimum calcination temperature for this type of nanophosphor prepared by microemulsions.

Figure 3.12 Variation of peak intensities of the transitions of $^5D_0 \rightarrow ^7F_2$, $^5D_0 \rightarrow ^7F_1$, and $^5D_0 \rightarrow ^7F_3$ of Eu:Y$_2$O$_3$ with various calcination temperatures

3.1.6.3 The influence of Eu$^{3+}$ concentration on the emission of Eu:Y$_2$O$_3$

The emission intensity is related to the concentration of Eu$^{3+}$ activator. However, when the activator concentration increases to a certain level, the luminescence begins to be quenched [Fig.3.13, 3.14]. In this case, the pairing or aggregation of activator atoms at high concentration may change a fraction of the activators into quenchers and induce the quenching effect. The migration of excitation by resonant energy transfer between the Eu$^{3+}$ activators can sometimes be so efficient that it may carry the energy to a distant killer or to a quenching center existing at the surface of the crystal.
Chapter 3 Red-emitting nanophosphor Eu:Y$_2$O$_3$

From Fig. 3.13, it can be seen that for this type of nanophosphors quenching starts at a Eu concentration of 10% (mol%), while a value of 6%-8% was obtained for the phosphors prepared by the conventional method [26]. This observation is attributed to a reduced energy-transfer rate due to interface effect of the nanoscale material, so that less energy can migrate to the quenching sites. The enhancement of quenching concentration also suggests that the close proximity of the crystals does not introduce a large number of surface quenching defects. This benefited from the advantage of microemulsion technique. Since all of the starting materials are mixed at the molecular level in a solution, a high degree of homogeneity is achievable. Moreover, the size and shape of nanoparticles formed in microemulsions can be precisely controlled. Lower calcination temperature (800$^\circ$C) compared to that employed in a conventional solid-state reaction (1400$^\circ$C-1500$^\circ$C) also offered Eu:Y$_2$O$_3$ nanoparticles smaller particle size and less aggregation than conventional phosphors.

![Concentration quenching curve of microemulsion-prepared Eu:Y$_2$O$_3$ nanoparticles](image)

**Figure 3.13** Concentration quenching curve of microemulsion-prepared Eu:Y$_2$O$_3$ nanoparticles
Figure 3.14 Emission spectra of Eu:Y$_2$O$_3$ with various Eu concentrations
3.1.6.4 The influence of codopants on the emission of Eu:Y$_2$O$_3$

Al$^{3+}$ and Ba$^{2+}$ were doped into Eu:Y$_2$O$_3$ as codopants. The molar ratio of codopants to Eu$^{3+}$ was 1:2. The effect of Al$^{3+}$ and Ba$^{2+}$ on the emission intensity of Eu:Y$_2$O$_3$ was studied.

![Emission spectra of precursors of Eu:Al:Y$_2$O$_3$ and Eu:Al:Y$_2$O$_3$ with various calcination temperatures](image)

**Figure 3.15** Emission spectra of precursors of Eu:Al:Y$_2$O$_3$ and Eu:Al:Y$_2$O$_3$ with various calcination temperatures
Figure 3.16 Emission spectra of precursors of Eu:Ba:Y$_2$O$_3$ and Eu:Ba:Y$_2$O$_3$ with various calcination temperatures
From the emission spectra of Eu:Y$_2$O$_3$ [Fig.3.15, Fig. 3.16], it can be found that there is no peak shift after codoped with Al$^{3+}$ and Ba$^{2+}$. The codopants did not influence the crystal structure of Eu:Y$_2$O$_3$. The emission intensities of Eu:Y$_2$O$_3$, Eu:Al:Y$_2$O$_3$ and Eu:Ba:Y$_2$O$_3$ show the same trend as a function of calcination temperatures [Fig.3.17]. It should also be noted that the emission intensity was slightly enhanced with codopants. One possible reason is that codopants can effectively disperse the clustered Eu$^{3+}$ ions in Y$_2$O$_3$, leading to lower effect of concentration quenching of Eu.
As mentioned in Section 1.6 of Chapter 1, each of rare-earth ions is surrounded by oxygen ions located at the corners of a cube. Two corners of the cube are not occupied by oxygen ions. The vacancies are either along a body diagonal or along a face diagonal of the cube. This results in a situation that is quite favorable for accommodating larger interstitial sites having sizes comparable to that of oxygen in the anionic sublattice. These interstitial sites are arranged in the form of non-intersecting strings running through the crystal thus providing open pathways for interstitial diffusion [27]. The effect of codopants in the yttria lattice can lead to two possibilities (taking Ba\(^{2+}\) as an example):

\[
2\text{MO} + 1/2\text{O}_2 (g) \Rightarrow 2\text{M}_\text{Y} \cdot' + \text{Y}_2\text{O}_3 + 2\text{h}^\cdot \quad (3.1)
\]

\[
2\text{MO} + \text{O}_i \Rightarrow 2\text{M}_\text{Y} \cdot' + \text{Y}_2\text{O}_3 \quad (3.2)
\]

where M= Ba, the dot denotes a positive effective charge, a prime denotes a negative effective charge, M\(_{\text{Y}}\) \(\cdot'\) denotes a codopant ion occupying a trivalent yttrium site and the suffix i denotes the ion in the interstitial position. According to the equation (3.1), two electron holes (2\(\text{h}^\cdot\)) are produced with the substitution of codopants in the yttrium sublattice. The equation (3.2) depicts that the oxygen interstitial is consumed by codopants occupying a trivalent yttrium site. With the knowledge of electrical conductivity it has been confirmed that scheme (3.1) is more predominant than (3.2) [28]. Codopants induced excitons can effectively feed various lower energy levels of Eu\(^{3+}\), leading to enhancement in emission intensity. In addition, the decrease in the interstitial oxygen results in a decrease in the competitive absorption and hence yielding higher luminescence quantum yield.
3.1.6.5 Lifetime of Eu:Y$_2$O$_3$ nanophosphors

Lifetime spectroscopy is a nondestructive materials characterization tool and has been used to study a variety of materials including metals and semiconductors [29, 30]. This technique is sensitive to local variations in electron density and can therefore detect the defect structures [31]. By monitoring $^5\text{D}_0 \rightarrow ^7\text{F}_2$ fluorescence excited with 393 nm, we measured the decay curves of Eu:Y$_2$O$_3$ nanophosphors with various Eu concentrations and calcination temperatures. The Lifetimes were obtained from a single-exponential fit to the decay curves. Figure 3.18 to Figure 3.21 depicts the results.

There is a similar relationship between the lifetime and the calcination temperature for all the samples with different concentrations of Eu. Figure 3.18 and 3.19 show the result for Eu:Y$_2$O$_3$ nanophosphors with 2%(mol%) of Eu. It can be seen that lifetimes became longer with the increased calcination temperatures.

For the two-level system (excited state and ground state), the population of the excited state decreases according to [3]

$$\frac{dN_e}{dt} = -N_e P_{eg} \quad (3.3)$$

the value of $N_e$ gives the number of luminescent ions in the excited state after an excitation pulse, $t$ is the time, and $P_{eg}$ is the probability for spontaneous emission from the excited to the ground state.
Integration of the equation (1) yields

\[ N_e(t) = N_e(0)e^{-t/\tau_R} \quad (3.4) \]

which is also written as

\[ N_e(t) = N_e(0)e^{-t/\tau_R} \quad (3.5) \]

Where \( \tau_R = 1/P_{eg} \) is the radiative lifetime. After a time \( \tau_R \), the population of the excited state has decreased to \( 1/e \) (37%).

Some information about the crystal structure of \( Y_2O_3 \) is quite useful in explaining the change of lifetimes with various calcination temperatures. It is known that the occurrence of two oxygen vacancies along the body and face diagonals leads to \( S_6 \) and \( C_2 \) symmetries for the rare-earth ions (\( Y^{3+} \) and \( Eu^{3+} \)) sites, respectively. The relative concentration of these two sites is in a ratio of 1:3 respectively. According to the theory of Judd [32] and Ofelt [33], the transition of \( ^5D_0 \rightarrow ^7F_2 \) in \( Eu^{3+} \) on \( C_2 \) site becomes electric dipole allowed due to an admixture of opposite parity \( 4f^{(n-1)}5d \) states by an odd parity crystal field component. Since \( S_6 \) sites have inversion symmetry, \( ^5D_0 \rightarrow ^7F_2 \) transition is expected to be absent.

In addition, such “forced” electric dipole transitions are hypersensitive to changes in the crystal field. Therefore, it is reasonable to assume that the increased lifetimes originate
from very small changes in the crystal field. It is probably due to the increased lattice constant in Eu:Y$_2$O$_3$ nanoparticles which reduces the odd parity crystal field component.

Another possible reason for the increased lifetimes is the effect of strains in the lattice or the breakdown of the regular Coulomb potentials at the surface of the nanoparticles on the luminescence decay [34-36]. The existence of grain boundaries and internal surfaces will contribute to the measured defect spectrum of the material. The measured lifetime of nanophosphors is a value representing the combined effects of $^5D_0 \rightarrow ^7F_2$ transition and surface states. With the increased firing temperatures, the intergranular regions also increased, resulting in a longer lifetime.
Figure 3.18 $^5\text{D}_0 \rightarrow ^7\text{F}_2$ decay curves of nanocrystalline Eu:Y$_2$O$_3$ calcined at various temperatures.

Figure 3.19 Lifetimes of Eu:Y$_2$O$_3$ (Eu 2%) as a function of various calcination temperatures.
3.1.6.6 Total decay rates as a function of Eu$^{3+}$ concentration

We measured the decay curves of the $^5D_0$ ($S_6$) emission for samples with various Eu$^{3+}$ concentrations at room temperature [Figure 3.20]. From the integrated decay curves, the total decay rate, $K_{\text{tot}}$ was obtained.

$$K_{\text{tot}} = \frac{1}{\int_0^\infty I(t)dt}$$

where $I(t)$ is the normalized decay curve, i.e. $I(t=0)=1$

The total decay rate of the $^5D_0$ ($S_6$) level as a function of Eu$^{3+}$ concentration is given in Figure 3.21 and Table 3.6. The radiative decay rate was the reciprocal of the lifetime.

<table>
<thead>
<tr>
<th>Eu$^{3+}$ concentration (mol%)</th>
<th>Total decay rate ($10^2$ s$^{-1}$)</th>
<th>Radiative decay rate ($10^2$ s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>3.47</td>
<td>3.61</td>
</tr>
<tr>
<td>3</td>
<td>3.38</td>
<td>3.51</td>
</tr>
<tr>
<td>4</td>
<td>3.36</td>
<td>3.62</td>
</tr>
<tr>
<td>5</td>
<td>2.63</td>
<td>2.87</td>
</tr>
<tr>
<td>6</td>
<td>2.53</td>
<td>2.92</td>
</tr>
<tr>
<td>7</td>
<td>2.76</td>
<td>3.22</td>
</tr>
<tr>
<td>8</td>
<td>2.38</td>
<td>2.78</td>
</tr>
<tr>
<td>9</td>
<td>2.38</td>
<td>2.80</td>
</tr>
</tbody>
</table>
Chapter 3 Red-emitting nanophosphor Eu:Y$_2$O$_3$

Figure 3.20 $^5$D$_0 \rightarrow ^7$F$_2$ decay curves of Eu:Y$_2$O$_3$ nanophosphors with various Eu concentration (mol%)

Figure 3.21 Decay rate as a function of Eu$^{3+}$ concentration
Figure 3.22 Simplified scheme of decay process of $^5D_0 \rightarrow ^7F_2$ transition in Eu:Y$_2$O$_3$ nanoparticles

Previous work by Heber et al. [37] gives evidence for energy transfer from $^5D_0$ ($S_6$) to $^5D_0$ ($C_2$). D.B.M. Klaassen et al [38] calculated the decay rate $K$ of process 1 [Figure 3.22]. $K_1 = Cx^\gamma$, $x$ is the concentration of Eu$^{3+}$, $C$ and $\gamma$ are constants, where $C=51.7$ (s$^{-1}$) and $\gamma=1.42$. With the increased Eu concentration, the energy transfer rate of process 1 increases.

It can be observed that there is little but not significant change in decay rates with various Eu$^{3+}$ concentrations. This may be attributed to the different crystal fields in different samples.
3.2 SUMMARY

Red-emitting nanophosphors Eu:Y$_2$O$_3$ were synthesized via the microemulsion route. The average crystalline size of these nanoparticles was below 20nm. The precursor of this type of nanophosphors formed the typical cubic Y$_2$O$_3$ crystal structure under calcination at around 600$^0$C. After calcinations, the nanophosphors showed morphology of a continuous network of particles, which is similar to that of the combustion-synthesized powders. With the increased calcination temperatures, both the fluorescence intensity and lifetimes of the nanophosphors increased. The increasing intensity originates from the enhanced concentration of C$_2$ sites, while the longer lifetimes are due to the effects of surface states, strains in lattice as well as the change of crystal field as the firing temperature increased. The nanophosphors had enhanced emission intensities with codopants, such as Al$^{3+}$ and Ba$^{2+}$. It may be ascribed to the increased concentration of electron holes induced by codopants, decreased effect of concentration quenching of Eu$^{3+}$ and decreased amount of interstitial oxygens. With the increased Eu$^{3+}$ concentration, the energy transfer rate of Eu$^{3+}$(S$_6$) to Eu$^{3+}$(C$_2$) increases. However, varying Eu$^{3+}$ concentrations had no significant influence on decay rates. The variations may be attributed to different crystal fields in different samples.

The emission efficiency of phosphor materials is an issue of major concern in design of field emission display. Unfortunately, the emission efficiency of rare-earth-activated phosphor appears to be limited by concentration quenching of the activators [39]. Compared with the phosphors prepared by conventional method, the quenching
concentration of Eu in these nanoparticles has been raised remarkably. They start quenching at 25%-40% higher concentration of Eu. This property may benefit from the interface effect of nanophosphors which reduced the energy-transfer rate from activators to quenching sites. Based on the results of this study, the phosphor with 10%(mol%) of Eu and calcinated at 800°C for 2 hours has the optimum luminescent properties. Eu:Y₂O₃ nanoparticles prepared in this study could be a promising red-emitting nanophosphor for field emission display.

3.3 REFERENCES:


CHAPTER 4 GREEN-EMITTING NANOPHOSPHOR

Tb:Y$_2$O$_3$

Typical green-emitting phosphors for display devices include Cu, Al:ZnS; Au, Cu, Al:ZnS; Cu, Al:(ZnCd)S; Cu:ZnS; Mn:Zn$_2$SiO$_4$; Tb:Gd$_2$O$_2$S; Tb:Y$_3$Al$_5$O$_{12}$; Tb:Y$_2$SiO$_5$ and Tb:Y$_2$O$_3$. The emission color of the green has been chosen as a compromise between obtaining a larger area of color reproduction in the chromaticity diagram and more equal electron beam currents for exciting the three color phosphors to produce reference white. For this concern, efforts have been made to shift the emission peak of 530 nm of green-emitting Cu,Cl (or Al):ZnS to a longer wavelength (530 nm-560 nm) either by employing a solid solution Zn$_{1-x}$Cd$_x$S or by introducing a deeper acceptor such as Au [1]. However, it is difficult to maintain a pure white color at high brightness, since the efficiencies of the green ZnS phosphors are reduced, while that of the red Eu$^{3+}$ phosphor remains relatively constant with increase in current density. To minimize this problem, linear-responding green phosphor, Tb:Y$_2$O$_2$S, was used and showed a significant improvement [2]. Although the emission colors of Tb$^{3+}$-activated phosphors are not ideal, their linear green emission with respect to the excitation power has attracted more and more attention.

For applications of display devices such as high definition and projection televisions, light valve projectors, image intensifiers, electroluminescence panels, plasma and field emission displays, it is essential that the phosphor particles be small in order to reproduce images with high-resolution. Conventional phosphor production through high temperature solid-state reactions typically results in particle sizes of 5-20 μm. Simply
milling down the phosphor results in a substantial decrease in luminescence efficiency. This is normally attributed to an increase in non-radiative recombination via surface defect states as particle size decreases [3]. Moreover, phosphors obtained by the conventional method show little or no control over the particle morphology.

In order to prepare nanophosphors with high luminescence efficiency, various synthesis methods have been studied. Rao prepared yttrium-based phosphors by sol-gel processes. The phosphors show that crystallization took place at lower temperatures and the luminescent efficiency was comparable to commercially available phosphors. And the particles fired at higher temperature were more spherical [4]. E.T. Goldburt et al found that the luminescent efficiency in nanocrystalline Tb:Y$_2$O$_3$ synthesized by sol-gel process increased with the decrease in the particle size from 100 to 40 Å. The light output per Tb$^{3+}$ ion in nanocrystalline Tb:Y$_2$O$_3$ exceeded that in the standard Tb:LaOBr [5]. The sol-gel technique may also be used to produce other nanoparticles of rare-earth doped yttia [6-8].

B. Bihari et al, synthesized nanocrystalline Eu$_2$O$_3$ and Eu:Y$_2$O$_3$ by gas-phase condensation [9]. The nanoparticles form in the monoclinic crystal structure. This phase requires high temperature or pressure to form bulk Eu$_2$O$_3$ and Eu:Y$_2$O$_3$.

Colloidal chemical routes to the production of luminescent semiconductor nanoparticles from solution are well known. This method has been widely investigated as the electronic and optical properties of such materials differ greatly from the bulk as the particle size
approaches that of the excitonic Bohr radius and the electrons and holes are subject to quantum confinement effects [10-12]. A wide variety of nanoparticles have been synthesized, for example, CdS [13], CdSe [14], ZnO [15], and Mn:ZnS [16].

The hydrothermal method and combustion synthesis are some other means to obtain nanophosphors with controlled morphology [17, 18].

In order to develop a prominent green-emitting phosphor for display devices, we used micromulsion technique for the first time to synthesize Tb:Y$_2$O$_3$ nanophosphors. The green-emitting Tb:Y$_2$O$_2$S has been replaced by Tb:Y$_2$O$_3$ because of its inferior efficiency at high temperatures. These nanophosphors were studied by various characterization techniques, such as TGA, XRD, SEM, TEM, XPS and PL (Photoluminescence). The dependence of firing temperatures, doping hosts, and codopants on luminescent properties was investigated. To study Tb$^{3+}$ emission in different host materials, Tb:La$_2$O$_3$ and Tb:Gd$_2$O$_3$ nanoparticles were synthesized by the same microemulsion technique and characterized by TGA, XRD, TEM, SEM and PL. Tb, Al:Y$_2$O$_3$, Tb, Bi:Y$_2$O$_3$ and Tb, Ce:Y$_2$O$_3$ were prepared to investigate the influence of codopants on Tb:Y$_2$O$_3$ emission. Tb, Ce:Y$_2$O$_3$ was studied by XRD, XPS, SEM, and TEM in detail. And the emission spectra of Tb, Al:Y$_2$O$_3$, Tb, Bi:Y$_2$O$_3$ and Tb, Ce:Y$_2$O$_3$ were obtained by PL measurement.
4.1 RESULTS AND DISCUSSIONS

4.1.1 Thermal decomposition of the precursors of Tb:Y₂O₃ and Tb:La₂O₃ nanoparticles

Figure 4.1 shows TGA curve of Tb:Y₂O₃. It can be seen that the thermal behavior of Tb:Y₂O₃ had changed very little compared to that of Eu:Y₂O₃ [Fig. 3.1]. Below 250°C, the weight change corresponds to the removal of water molecules associated with the particles. From 250°C to around 460°C, surfactants and other organic materials were burned out, leading to >20% of weight loss for the nanoparticles. There is little weight change when the nanoparticles were heated over 730°C. The weight change from 460°C to 730°C was due to the conversion of hydroxide to oxide. The results of TGA analysis indicate that the precursor completely converted to Tb:Y₂O₃ over 730°C.
Figure 4.1 TGA curve of Tb:Y$_2$O$_3$
Figure 4.2 TGA curve of Tb:La$_2$O$_3$
The TGA curve of Tb:La$_2$O$_3$ [Fig. 4.2] presents a different behavior from that of Tb:Y$_2$O$_3$ [Fig. 4.1] as well as Eu:Y$_2$O$_3$ [Fig. 3.1]. There is an apparent weight change in the region from 700$^0$C to 800$^0$C. Based on the results of XRD study, which will be discussed in next section (4.1.2), we can interpret the TGA results as follows:

Tb:La$_2$O$_3$ has the same thermal behavior as that of Tb:Y$_2$O$_3$ below 460$^0$C, the decomposition is due to the removal of water molecules associated with the particles and organic materials. As for the weight loss in the region from 460$^0$C to 700$^0$C, the main contribution is the conversion of hexagonal hydroxide to cubic oxide [19]. With the increased calcination temperatures, cubic oxide structure is replaced by hexagonal oxide. Calcined at over 800$^0$C, Tb:La$_2$O$_3$ nanoparticles show the dominant hexagonal oxide structure [see also in Section 4.1.2.3, Fig 4.7].

### 4.1.2 Crystallization and crystalline size

#### 4.1.2.1 Tb:Y$_2$O$_3$ and Tb, Ce: Y$_2$O$_3$ (calcined at 800$^0$C)

Both of Tb:Y$_2$O$_3$ and Tb, Ce: Y$_2$O$_3$ nanoparticles calcined at 800$^0$C had the cubic crystal structure. Their XRD lines matched well with the lines of standard cubic yttrium oxide given in JCPDS-File No. 05-574 (D) [Fig. 4.4]. It is also observed that crystallization of Tb:Y$_2$O$_3$ was far better than that of Tb, Ce: Y$_2$O$_3$ [Fig. 4.3]. When Ce$^{3+}$ ions are codoped into Tb:Y$_2$O$_3$ nanoparticles, some of them will occupy in the sites of Y$^{3+}$ and Tb$^{3+}$, leading to the change in crystal structure due to the different bond length of Ce-O from
Y-O and Tb-O. In this study, the molar ratio between Ce and Tb is 1:1, thus the codopants (Ce) had remarkable influence on crystalline size of Tb:Y$_2$O$_3$ nanophosphors. The calculation method of crystalline size has been described in Chapter 3 [Section 3.1.3]. The results for Tb:Y$_2$O$_3$ and Tb, Ce: Y$_2$O$_3$ are presented in Table 4.1.

<table>
<thead>
<tr>
<th>Sample</th>
<th>FWHM</th>
<th>$2\theta$</th>
<th>B</th>
<th>$\beta$</th>
<th>L, crystalline size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tb:Y$_2$O$_3$</td>
<td>0.427</td>
<td>29.024</td>
<td>0.0075</td>
<td>0.0074</td>
<td>19</td>
</tr>
<tr>
<td>Tb,Ce:Y$_2$O$_3$</td>
<td>0.825</td>
<td>29.077</td>
<td>0.0144</td>
<td>0.0144</td>
<td>10</td>
</tr>
</tbody>
</table>

By averaging from three main diffraction peaks ($2\theta$=29, 48 and 57), the crystalline sizes of Tb:Y$_2$O$_3$ and Tb,Ce:Y$_2$O$_3$ are 18 and 10 nm, respectively.

![Figure 4.3 Comparison of XRD spectra between Tb:Y$_2$O$_3$ and Tb,Ce:Y$_2$O$_3$ nanoparticles](image)
Figure 4.4 XRD spectra of Tb:Y$_2$O$_3$ and Tb,Ce:Y$_2$O$_3$ nanoparticles
4.1.2.2 Tb:Gd$_2$O$_3$ (calcined at 800$^\circ$C)

![Tb:Gd$_2$O$_3$ XRD spectrum](image)

**Figure 4.5** XRD spectrum of Tb:Gd$_2$O$_3$ nanoparticles and standard Gd$_2$O$_3$

In Fig. 4.5, the XRD lines of Tb:Gd$_2$O$_3$ fit well with the lines of standard cubic gadolinium oxide given in JCPDS-File No. 12-0797 (*). The cubic Gd$_2$O$_3$ structure is closely related to the fluorite structure with two anions per one cation, shown in Fig. 4.6. The cations form an fcc lattice, while the anions fill all the tetrahedral sites. Therefore, each cation has eight anion neighbors and each anion has four cation neighbors. The sesquioxide structure is derived by removing two oxygen anions out of the unit cell, thus reducing the number of anions and doubling the lattice constant [20, 21]. This change in the anion content in the structure leaves the cations in an octahedral coordination with some disorder and vacancies in the occupied tetrahedral sites. Table 4.2 shows that the crystalline size of these nanophosphors is around 10 nm.
Table 4.2 Crystalline size of Tb:Gd$_2$O$_3$ nanoparticle

<table>
<thead>
<tr>
<th>Sample</th>
<th>FWHM $\theta$</th>
<th>$2\theta$</th>
<th>B</th>
<th>$\beta$</th>
<th>L, crystalline size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tb:Gd$_2$O$_3$</td>
<td>0.683</td>
<td>28.480</td>
<td>0.0119</td>
<td>0.0168</td>
<td>9</td>
</tr>
</tbody>
</table>

The crystalline size of Tb:Gd$_2$O$_3$ nanoparticle was further estimated by averaging from four main diffraction peaks ($2\theta$=28, 33, 47 and 56). The result is 8 nm.

4.1.2.3 Tb:La$_2$O$_3$

From Fig. 4.7, it can be observed that the precursor of Tb:La$_2$O$_3$ nanoparticles is actually Tb:La(OH)$_3$. The XRD lines of Tb:La$_2$O$_3$ (no calcination) show that there is a dominant hexagonal lanthanum hydroxide crystal structure (JCPDS-File No. 36-1481(*)), while the lines corresponding to hexagonal lanthanum oxide (JCPDS-File No.02-0688(D)) were remarkably depressed. In the XRD curve of Tb:La$_2$O$_3$ (calcined at 800$^\circ$C), the characteristic lines corresponding to hexagonal lanthanum oxide structure (JCPDS-File
Figure 4.7 XRD spectra of precursors of Tb:La$_2$O$_3$, Tb:La$_2$O$_3$ with various calcination temperatures and standard La$_2$O$_3$
No.05-0602 (*) had strong intensities. The lines corresponding to cubic lanthanum oxide structure were also found but with very low intensities. The XRD spectrum of Tb:La$_2$O$_3$ (calcined at 1000$^0$C) shows only the lines of hexagonal lanthanum oxide structure. The results of XRD study agree well with those of TGA.

![Crystal Structure](image)

**Figure 4.8** The crystal structure of hexagonal La$_2$O$_3$

The crystal structure of hexagonal La$_2$O$_3$ is illustrated in Fig.4.8 [23]. And the structure of cubic La$_2$O$_3$ belongs to the C-type structure of the classification of rare-earth sesquioxides established by Goldschmidt [24]. According to Caro [25], this structure can also be described from an arrangement of OL$\text{a}_4$ tetrahedra sharing corners.

The crystalline sizes are presented in Table 4.3. The particle size increases greatly with the increased calcination temperature from 800$^0$C to 1000$^0$C.
### Table 4.3 Crystalline sizes of Tb:La$_2$O$_3$ nanoparticles

<table>
<thead>
<tr>
<th>Sample</th>
<th>FWHM ($^\circ$)</th>
<th>2$\theta$ ($^\circ$)</th>
<th>B</th>
<th>$\beta$</th>
<th>L, crystalline size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>800$^\circ$C</td>
<td>0.584</td>
<td>29.987</td>
<td>0.0102</td>
<td>0.0101</td>
<td>14</td>
</tr>
<tr>
<td>1000$^\circ$C</td>
<td>0.198</td>
<td>29.987</td>
<td>0.0035</td>
<td>0.0033</td>
<td>43</td>
</tr>
</tbody>
</table>

The crystalline sizes of Tb:La$_2$O$_3$ nanoparticles were further calculated by averaging from three main diffraction peaks (2$\theta$=30, 40 and 55) and the results were 12 and 35 nm for 800 and 1000$^\circ$C, respectively.

### 4.1.3 Morphology

SEM micrographs of various Tb actived-nanophosphors are presented in Figure 4.9. Pores and voids can be observed. As mentioned in Chapter 3, it is ascribed to the escaping gases during calcination. Some rod-like particles are found in the micrograph of Tb:La$_2$O$_3$ calcined at 1000$^\circ$C. It may be the consequence of grain growth at high temperatures. The XRD study also shows that the crystalline size increases from 14 nm to 44 nm with the increased calcination temperature from 800$^\circ$C to 1000$^\circ$C.

### 4.1.4 Transmission electronic microscopy

Figure 4.10 shows the TEM micrographs of Tb:Y$_2$O$_3$ and Tb,Ce:Y$_2$O$_3$ (800$^\circ$C). It can be seen that the particles agglomerate and the size of a single particle is in the range from several nm to tens of nm. The crystalline sizes obtained from XRD study are 19 nm and 10 nm, respectively. It is in agreement with what is observed in TEM micrographs.
From Fig. 4.11, we can estimate the particle size of Tb:La$_2$O$_3$. The average size of the nanoparticles in the micrographs is about 20 nm. It should be noted that rod-like particles are clearly observable in Tb:La$_2$O$_3$ (1000°C). As mentioned in 4.1.3, the grain growth at high temperatures results in the occurrence of nanorods. The existence of nanorods leads to greatly increased crystalline size [Table 4.3].
Chapter 4 Green-emitting nanophosphor Tb:Y$_2$O$_3$

Figure 4.9 SEM micrographs of various Tb actived-nanophosphors

- Tb:Y$_2$O$_3$ calcined at 800$^\circ$C
- Tb:Ce:Y$_2$O$_3$ calcined at 800$^\circ$C
- Tb:Gd$_2$O$_3$ calcined at 800$^\circ$C
- Tb:La$_2$O$_3$ no calcination
- Tb:La$_2$O$_3$ calcined at 800$^\circ$C
- Tb:La$_2$O$_3$ calcined at 1000$^\circ$C
Chapter 4 Green-emitting nanophosphor Tb:Y$_2$O$_3$

*Figure 4.10* TEM micrographs of Tb:Y$_2$O$_3$ and Tb,Ce:Y$_2$O$_3$

Tb:Y$_2$O$_3$ calcined at 800$^\circ$C

Tb,Ce:Y$_2$O$_3$ Calcined at 800$^\circ$C

Figure 4.10 TEM micrographs of Tb:Y$_2$O$_3$ and Tb,Ce:Y$_2$O$_3$
Figure 4.11 TEM micrographs of Tb:La$_2$O$_3$ (800°C) and Tb:La$_2$O$_3$ (1000°C)
4.1.5 X-ray photoelectron spectroscopic (XPS) study of Tb,Ce:Y$_2$O$_3$ nanophosphors

![XPS wide scan spectrum of Tb,Ce:Y$_2$O$_3$ calcined at 800°C](image)

**Figure 4.12** XPS wide scan spectrum of Tb,Ce:Y$_2$O$_3$ calcined at 800°C

The signals corresponding to the characteristic features of Y3d, Tb4d, C1s, O1s and Ce3d are clearly observable in figure 4.12. Their peak positions are given in Table 4.4. To compensate for surface charging effects in the insulating samples, all binding energies were corrected with reference to the saturated hydrocarbon C1s peak at 285.0 eV.
### Table 4.4 Elements in Tb,Ce:Y$_2$O$_3$ nanoparticles

<table>
<thead>
<tr>
<th>Elements</th>
<th>Peak position (eV)</th>
<th>Corrected position (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C1s</td>
<td>292.5</td>
<td>285.0</td>
</tr>
<tr>
<td>Y3d</td>
<td>164.3</td>
<td>156.8</td>
</tr>
<tr>
<td>O1s</td>
<td>539.0</td>
<td>531.5</td>
</tr>
<tr>
<td>Tb4d</td>
<td>165.2</td>
<td>157.7</td>
</tr>
<tr>
<td>Ce3d</td>
<td>893.5</td>
<td>886.0</td>
</tr>
</tbody>
</table>

To identify the chemical state of the elements in Tb,Ce:Y$_2$O$_3$ nanoparticles, detailed analysis of XPS spectra was carried out. The core level spectra of C1s, Y3d, O1s, Tb4d and Ce3d were fitted employing Gaussian sum functions.

![Figure 4.13 XPS spectrum of C1s of Tb,Ce:Y$_2$O$_3$](image)
Chapter 4 Green-emitting nanophosphor Tb$_2$Y$_2$O$_3$

The XPS spectrum of C1s exhibits the expected adsorption of adventitious carbon [Fig. 4.13]. The presence of some adventitious carbon is probably due to storage in the desiccators. It should be noted that this adsorbent is primarily hydrocarbons whose binding energy was 285.0 eV. The adventitious carbon also exhibits significant COOH containing species (at 290.8 eV).

![Figure 4.14 XPS spectrum of Y3d of Tb,Ce:Y$_2$O$_3$](image)

The doublets of Y3d signals [Y(3d$_{3/2}$), Y(3d$_{5/2}$)] are located at 158.8 and 156.8 eV [Figure 4.14] in agreement with literature data on Y$_2$O$_3$ reference compounds [26]. The Y(3d$_{5/2}$) peak corresponds to Y-O bond in an Y$_2$O$_3$ crystal. There is no obvious shift in binding energy of Y3d with doping Tb$^{3+}$ and Ce$^{3+}$ in Y$_2$O$_3$ crystal.
The fitted peaks of O1s are found at 529.2 eV and 531.5 eV [Fig. 4.15]. We assign the signal at lower binding energy (529.2 eV) to surface lattice oxygen and the signal at higher binding energy (531.5 eV) to adsorbed oxygen species such as O\(^{-}\), O\(_2\)^{2-}, or O\(^{2-}\) [27–30]. The high surface area of nanoparticles produces a high reactivity and results in an accelerated rate of reaction with atmospheric water and CO\(_2\). Therefore, the fitted peak at 531.5 eV could be attributed to C=O, O-H or H-C=O. The existence of these bonds will greatly decrease the emission efficiency of the Tb,Ce:Y\(_2\)O\(_3\) nanophosphor due to the competitive absorption. In addition, these bonds can also quench the emitter Tb\(^{3+}\) results in a decrease both in the emission yield and intensity.
There were three peaks shown in Figure 4.16. The strongest signal at 157.7 eV was mainly attributed to Y3d, while there was a contribution of Tb4d. (Tb:Y=1:100) The peaks at 148.5 eV and 171.2 eV were due to Tb4d. We can further assign the signals at 157.7 and 171.2 eV to the characteristic features of Tb$^{4+}$ and the signal at 148.5 eV to Tb$^{3+}$ [31, 32]. XPS results indicated that a large number of Tb$^{3+}$ had been oxidized to Tb$^{4+}$. The oxidization probably occurred during calcination process.

From Fig. 4.17, one can observe the doublets of Ce3d corresponding to the 3$d_{3/2}$ and 3$d_{5/2}$ contributions, respectively. The 3$d_{5/2}$ was at ca. 886 eV, while 3$d_{3/2}$ was located at ca. 905 eV. States at 886 eV and 905 eV belong to unique photoelectron features from the Ce$^{3+}$ state [33].
4.1.6 Photoluminescence properties

4.1.6.1 Emission of Tb:Y$_2$O$_3$

The emission of Tb$^{3+}$ is due to transitions $^5D_4 \rightarrow ^7F_J$ that are mainly in the green emission region. At low concentration of Tb, there is a considerable contribution to the emission from the higher-level emission $^5D_3 \rightarrow ^7F_J$, mainly in the blue region. Since the J values involved in the transitions are high, the crystal field splits the levels into many sublevels, leading to a complicated emission spectrum. Figure 4.18 exhibits a schematic model for photoluminescence of Tb$^{3+}$. The emission spectrum of the Tb:Y$_2$O$_3$ nanophosphor calcined at 800$^\circ$C, Tb 1%(mol) is shown in figure 4.19.
Figure 4.18 A schematic model for photoluminescence of Tb$^{3+}$

For the nanophosphor Tb$:$Y$_2$O$_3$ calcined at 800$^\circ$C with Tb 1%(mol%), three emission bands with peaks at 451, 467-491, and 544 were detected in PL spectrum [Fig. 4.19]. They correspond to $^5$D$_3\rightarrow^7$F$_4$, $^5$D$_4\rightarrow^7$F$_6$ and $^5$D$_4\rightarrow^7$F$_5$, respectively. Generally, it is difficult to observe the emission from $^5$D$_3\rightarrow^7$F$_J$ transitions of Tb$^{3+}$, because the relaxation of $^5$D$_3$ to $^5$D$_4$ is very fast [34, 35]. This relaxation is a cross-relaxation process through energy transfer from $^5$D$_3\rightarrow^5$D$_4$ to $^7$F$_6\rightarrow^7$F$_0$. However, at low concentration of Tb$^{3+}$, the distance between neighboring ions is large, resulting in an inefficient transfer and enabling the $^5$D$_3\rightarrow^7$F$_J$ transitions [35].
Figure 4.19 Emission spectrum of Tb:Y$_2$O$_3$ nanophosphor calcined at 800°C with Tb 1%(mol%)

4.1.6.2 The influence of codopants on the emission of Tb:Y$_2$O$_3$

Figure 4.20 shows the luminescence spectra obtained after excitation at 330 nm for Tb:Y$_2$O$_3$ with different codopants. Luminescence from both the $^5D_3$ and the $^5D_4$ states to the $^7F_J$ (J=0,1,2,3,4,5,6) multiplets is observed. The ratio R of the intensities of the two luminescence bands is measured by integrating the areas in the range 450-480 nm for the transitions $^5D_3$-$^7F_J$ and 480-550 nm for $^5D_4$-$^7F_J$, respectively.
Figure 4.20 Luminescence spectra of Tb:Y$_2$O$_3$ with different codopants
\[
R = \frac{\sum_j I(^5D_4 \rightarrow ^7F_j)}{\sum_j I(^5D_3 \rightarrow ^7F_j)}, \quad (J=1,2,3,4,5,6)
\]

Table 4.5 Integrated intensity of Tb:Y\textsubscript{2}O\textsubscript{3} with different codopants

<table>
<thead>
<tr>
<th>Samples</th>
<th>I (^5\text{D}_3) (10\textsuperscript{7})</th>
<th>I (^5\text{D}_4) (10\textsuperscript{7})</th>
<th>R</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tb:Y\textsubscript{2}O\textsubscript{3}</td>
<td>1.24</td>
<td>4.13</td>
<td>3.3</td>
</tr>
<tr>
<td>Tb, Al:Y\textsubscript{2}O\textsubscript{3}</td>
<td>1.71</td>
<td>4.19</td>
<td>2.5</td>
</tr>
<tr>
<td>Tb, Bi:Y\textsubscript{2}O\textsubscript{3}</td>
<td>1.30</td>
<td>4.48</td>
<td>3.5</td>
</tr>
<tr>
<td>Tb, Ce:Y\textsubscript{2}O\textsubscript{3}</td>
<td>1.29</td>
<td>4.20</td>
<td>3.3</td>
</tr>
</tbody>
</table>

Both of the intensities of blue (I \(^5\text{D}_3\)) and green (I \(^5\text{D}_4\)) emission increased after codoping Al, Bi, or Ce into Tb:Y\textsubscript{2}O\textsubscript{3}. Similar phenomena have been reported for SiO\textsubscript{2} glass containing rare-earth element ions, such as Eu\textsuperscript{3+}, Tb\textsuperscript{3+} or Sm\textsuperscript{3+} doped sol-gel-derived glass [36, 37, 38]. Some Tb\textsuperscript{3+} ions are considered to form clusters in Tb:Y\textsubscript{2}O\textsubscript{3}, resulting in self-quenching of luminescence [39, 40]. The addition of codopants promoted better dispersion of Tb\textsuperscript{3+} ions, which made more optical active centers.

Table 4.5 also shows that the value of R decreased with incorporation of Al and Ce. That means codopants of Al and Ce intensified the \(^5\text{D}_3\) emission of Tb:Y\textsubscript{2}O\textsubscript{3}. Similar effects have been reported for the ions Tb\textsuperscript{3+} in silica-xerogels codoped with Al\textsuperscript{3+} [38]. For a specific host, the radiative emission probability of an excited state is influenced by energy-transfer processes [41]. The intensity of the \(^5\text{D}_3\) emission decreases with increasing Tb\textsuperscript{3+} concentration due to energy-transfer among Tb ions [42-44]. An excited
Tb$^{3+}$ ion, the donor in the $^5D_3$ state, relaxes non-radiatively to the $^5D_4$ state, whereas another Tb$^{3+}$ ion, the acceptor, in the ground state is excited to the $^7F_0$ state. The rate of this cross-relaxation process increases with a decreasing donor-acceptor distance and hence the $^5D_3$ emission decreases. On the contrary, with the fixed concentration of Tb$^{3+}$ ions, the addition of Ce and Al increased the donor-acceptor distance and thus increased the $^5D_3$ emission.

Surprisingly, for Tb, Bi:Y$_2$O$_3$, the $^5D_3$ emission was suppressed. From figure 4.20, it can be seen that emission at 482, 491 nm, corresponding to the transitions of $^5D_4\rightarrow ^7F_6$, were enhanced significantly. This demonstrates that a large number of Tb$^{3+}$ ions in the $^5D_3$ state relaxed non-radiatively to the $^5D_4$ state. As discussed in section 3.1.6.4, for Tb:Y$_2$O$_3$, each of rare-earth ions is surrounded by oxygen ions located at the corners of a cube. Two corners of the cube are not occupied by oxygen ions. The vacancies are either along a body diagonal or along a face diagonal of the cube [Figure 1.9]. This results in a situation that is quite favorable for accommodating larger interstitial sites having sizes comparable to that of oxygen in the anionic sub-lattice. The work of Li et al indicates that for M$^{3+}$ dopant radii less than the host Zr$^{4+}$ cation radii, the oxygen vacancies associate with the dopant. However, for M$^{3+}$ dopant radii greater than the host Zr$^{4+}$ cation radii, the oxygen vacancies associate with the host [45]. Bi$^{3+}$ is a highly polarizable cation due to its lone pair of electrons, and has greater radii than rare earth ions (Y$^{3+}$ and Tb$^{3+}$). Therefore, when Bi$^{3+}$ was codoped into Tb:Y$_2$O$_3$, Tb-oxygen vacancies interactions had a higher probability of occurrence. Based on XPS study in section 4.1.5, we know that
there is a large number of Tb\(^{4+}\) in Tb:Y\(_2\)O\(_3\). The interaction between Tb and oxygen vacancies can lead to the reduction of Tb\(^{4+}\) to Tb\(^{3+}\):

\[
\text{Tb}^{4+} + \text{O}^{2-} \rightarrow \text{Tb}^{3+} + \text{O}^{-}
\]

The increasing number of Tb\(^{3+}\) caused enhanced intensities both of blue and green emission. Since the bigger Bi\(^{3+}\) could not disperse Tb\(^{3+}\) as fully as Al\(^{3+}\) and Ce\(^{3+}\) did, most of the increasing Tb\(^{3+}\) populated in the excited state of \(^5\text{D}_4\), leading to a higher value of R. For application for green emitting nanophosphors, Bi\(^{3+}\) is a favorable codopant to improve green emission and color purity of Tb:Y\(_2\)O\(_3\).

### 4.1.6.3 Emission of Tb\(^{3+}\) in different host materials

It is well known that the emission of luminescent dopant atoms depends critically on properties of the host lattice [46-52]. Non-radiative decay processes and their temperature dependence are influenced by crystal properties such as the dopant site symmetry and size. In this work, we investigated emission of Tb\(^{3+}\) in Y\(_2\)O\(_3\), La\(_2\)O\(_3\) and Gd\(_2\)O\(_3\). Figure 4.21 shows the luminescence spectra of Tb:Gd\(_2\)O\(_3\), Tb:La\(_2\)O\(_3\) as well as Tb:La\(_2\)O\(_3\) calcinated at different temperatures. The intensities of green emission for different samples are listed in Table 4.6.
Figure 4.21 Tb$^{3+}$ emission in different host materials
Table 4.6 Intensity of green emission of Tb$^{3+}$ ($I^{5}D_{4}$-$^{7}F_{J}$) in different host materials

<table>
<thead>
<tr>
<th>Sample</th>
<th>Intensity (a.u.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tb:Y$_2$O$_3$ (800$^0$C)</td>
<td>4.13 E7</td>
</tr>
<tr>
<td>Tb:Gd$_2$O$_3$ (800$^0$C)</td>
<td>4.09 E7</td>
</tr>
<tr>
<td>Tb:La$_2$O$_3$ (800$^0$C)</td>
<td>4.43 E7</td>
</tr>
<tr>
<td>Tb:La$_2$O$_3$(1000$^0$C)</td>
<td>4.62 E7</td>
</tr>
<tr>
<td>Tb:La$_2$O$_3$(no calcination)</td>
<td>4.20 E7</td>
</tr>
</tbody>
</table>

The green emission of Tb:Gd$_2$O$_3$ has almost the same intensity as Tb:Y$_2$O$_3$. That can be ascribed to identical site symmetries for Tb$^{3+}$ ions provided by Y$_2$O$_3$ and Gd$_2$O$_3$, both of which exists as cubic phase crystals [Section 4.1.2]. Tb$^{3+}$ has enhanced intensity of emission in La$_2$O$_3$. As mentioned in section 4.1.2, La$_2$O$_3$ exists as hexagonal crystal structure. The parameters for one crystal cell are: a=b=3.937 Å and c=6.130 Å. However, for cubic Y$_2$O$_3$, O-O distance ranges from 2.89 to 2.96 Å [53]. It can be inferred that Tb-Tb distance is greater in La$_2$O$_3$ than in Y$_2$O$_3$, which can reduce the occurrence of Tb$^{3+}$ ion’s concentration quenching. Less self-quenching caused stronger emission.

The emission intensity increased with increased calcination temperatures for Tb:La$_2$O$_3$. As mentioned in section 4.1.2, Tb:La$_2$O$_3$ with no calcination is actually Tb:La(OH)$_3$. In this case, OH$^{-}$ played a role as an effective quencher for emissive Tb$^{3+}$. With increasing calcination temperatures, hexagonal lanthanum hydroxide crystal structure converted to hexagonal lanthanum oxide structure, leading to enhanced emission intensities of Tb$^{3+}$. 

123
4.2 SUMMARY

Green-emitting nanophosphors Tb:Y$_2$O$_3$ has been successfully synthesized via microemulsion route for the first time. The average particle size is 20 nm. Tb:Y$_2$O$_3$ nanoparticles have a similar thermal decomposition behavior as Eu:Y$_2$O$_3$ nanoparticles [Chapter 3]. Water molecules, surfactants and other organic materials were removed completely at around 460$^0$C, and the particles formed typical cubic crystal structure of Y$_2$O$_3$ over 730$^0$C. In the case of Tb:La$_2$O$_3$, there is an apparent weight change in the region from 700$^0$C to 800$^0$C, which is due to the conversion of cubic oxide to hexagonal oxide structure. The codopants (Ce) had remarkable influence on crystalline size of Tb:Y$_2$O$_3$ nanophosphors. The crystalline size of Tb,Ce:Y$_2$O$_3$ is 10 nm, whereas 18 nm for Tb:Y$_2$O$_3$. Tb:Gd$_2$O$_3$ (8 nm) and Tb:La$_2$O$_3$ (12 nm) have different average particle size from that of Tb:Y$_2$O$_3$ due to the different crystal structures. Some rod-like particles are found in the TEM micrograph of Tb:La$_2$O$_3$ calcined at 1000$^0$C. It may be the consequence of grain growth at high temperatures. XPS study of Tb,Ce:Y$_2$O$_3$ shows the presence of a large number of Tb$^{4+}$ and C=O, O-H or H-C=O species, which can greatly decrease the emission efficiency of the Tb,Ce:Y$_2$O$_3$ nanophosphor due to the competitive absorption.

Since a relative low concentration of Tb$^{3+}$ (1%, mol%) was doped into Y$_2$O$_3$, La$_2$O$_3$ or Gd$_2$O$_3$ in this study, emission corresponding to $^5$D$_3$-$^7$F$_j$ was clearly observable. Both of the intensities of blue (I $^5$D$_3$) and green (I $^5$D$_4$) emission increased after codoping Al, Bi, or Ce into Tb:Y$_2$O$_3$. That can be ascribed to better dispersion of Tb$^{3+}$. Bi$^{3+}$ is a favorable
codopant to improve green emission and color purity of Tb:Y₂O₃. Tb³⁺ has enhanced intensity of emission in La₂O₃. Tb-Tb distance is greater in La₂O₃ than in Y₂O₃, which can reduce the occurrence of Tb³⁺ ion’s concentration quenching and therefore enhance the intensity of emission.

4.3 REFERENCES

Chapter 4 Green-emitting nanophosphor Tb:Y$_2$O$_3$

CHAPTER 5 BLUE-EMITTING NANOPHOSPHOR

Tm:Y$_2$O$_3$

The conventional blue phosphors for cathode ray tubes (CRT) are not applicable to the field emission display (FED) [1, 2]. One serious impediment to the success of FED is the lack of stable phosphors under high-electron-density excitation. The most efficient blue phosphors currently available are metal sulfides. They have been recognized as having superior luminescent properties at low-voltage excitation. However, at high-current-density excitation, these phosphors degrade and as a result, the luminescent yield decreases with formation of a dead layer on the surface [3]. In addition, the degradation leads to contamination of the cathode components and decrease the lifetime of the display [4].

Recently, there has been considerable interest in the development of rare-earth-activated oxide-based phosphors for display technology because of their excellent light output and color rendering properties [5-7]. Moreover, oxide phosphors emerge as potential candidates for FEDs because of their stability toward high-current-density excitation. As far as blue-emitting oxide phosphors are concerned, Y$_2$SiO$_5$:Ce are widely studied [8-10]. Besides Y$_2$SiO$_5$:Ce, various rare-earth-activated oxide-based phosphors have been investigated. Tm:BaAl$_2$O$_4$ films were deposited by a spray pyrolysis method. The film had the main wavelength at 462 nm, and the highest cathodoluminescence luminance and efficiency at 5 kV and 57 $\mu$ Acm$^{-2}$ were 25 cd m$^{-2}$ and 0.11 lm W$^{-1}$, respectively [11]. Tadtsugu Minami et al prepared Tm-activated vanadium oxide-based phosphor thin films and observed a very high photoluminescence intensity in blue emission in Tm:Gd$_{0.5}$-V$_{0.5}$-
O [12]. F. S. Ermeneux et al investigated growth and fluorescence properties of Tm doped YVO₄ and Y₂O₃ single crystals. These systems present broad and intense absorption bands around 800 nm which is very attractive for diode pumping with relaxed temperature control and large stimulated emission cross sections in the eye-safe spectral range [13].

Lately, there has been significant research interest in the development of Tm:Y₂O₃ thin film phosphor for FED applications because of its simple host structure and efficient luminescence. Y. Nakanishi et al [14] prepared Tm-doped blue-emitting thin-film phosphor by electron-beam evaporation. The film shows sharp emission at 454 nm. The CL luminescence is found to increase with substrate, deposition, and annealing temperatures. In Arnaud Huignard’s work [15], Tm:Y₂O₃ thin film have been grown by the pulsed laser deposition (PLD) technique on various single-crystal substrates heated at 700°C. The recording of the visible fluorescence spectra of the Tm doped Y₂O₃ thin films, as well as the measurements of the fluorescence lifetimes of the ¹D₂ and ¹G₄ Tm emitting levels, gave results very similar to those obtained on bulk crystals. Doping percentage in Tm of 0.5 and 1% were found to limit Tm-Tm interactions inside the films and to give relatively high visible luminescence intensities. Spray pyrolysis was used to prepare thin films of Tm: Y₂O₃ by J. H. Hao et al in 2001 [16]. The intensity of the blue phosphor must be improved without resorting to annealing temperatures higher than 600°C.

In this study, we have investigated Tm:Y₂O₃ nanoparticles as a blue emitting phosphor for FEDs. For the first time, Tm:Y₂O₃ nanoparticles were synthesized by microemulsion
technique. They have been extensively studied by various characterization techniques, such as TGA, XRD, SEM, TEM, XPS and PL. We proposed a promising candidate of blue emitting nanophosphors for FEDs.

5.1 RESULTS AND DISCUSSIONS

5.1.1 Elemental analysis of Tm:Y₂O₃ nanoparticles

In order to determine the actual concentration of Tm ions doped in various samples of Tm:Y₂O₃, elemental analysis was conducted by ICP technique. The results were shown in table 5.1-5.3.

<table>
<thead>
<tr>
<th>Table 5.1 Elemental analysis of Tm:Y₂O₃ nanoparticles (0.5%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Elements</td>
</tr>
<tr>
<td>Y</td>
</tr>
<tr>
<td>Tm</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Table 5.2 Elemental analysis of Tm:Y₂O₃ nanoparticles (1%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Elements</td>
</tr>
<tr>
<td>Y</td>
</tr>
<tr>
<td>Tm</td>
</tr>
</tbody>
</table>
Table 5.3 Elemental analysis of Tm:Y$_2$O$_3$ nanoparticles (2%)

<table>
<thead>
<tr>
<th>Elements</th>
<th>Theoretical value (wt%)</th>
<th>Experimental value(wt%)</th>
<th>Tm:Y (mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Y</td>
<td>76.46</td>
<td>67.50</td>
<td>1.9%</td>
</tr>
<tr>
<td>Tm</td>
<td>2.92</td>
<td>2.47</td>
<td></td>
</tr>
</tbody>
</table>

The experimental values of Y and Tm were lower than the theoretical values. It is due to the contamination of H$_2$O and CO$_2$. From the results of the elemental analysis, it can be seen that the molar ratio of Tm to Y fit the theoretical values very well. It can be concluded that microemulsion technique is an effective and exact way to dope impurities into nanocrystals.

5.1.2 Thermal decomposition of the precursor of Tm:Y$_2$O$_3$ nanoparticles

Tm:Y$_2$O$_3$ exhibits a similar thermal decomposition behavior as that of Eu:Y$_2$O$_3$ [Figure 3.1] and Tb:Y$_2$O$_3$ [Figure 4.1]. There are three main weight change stages in Figure 5.1. Below 140$^\circ$C, water molecules associated with the precursor of Tm:Y$_2$O$_3$ were removed completely. The second remarkable weight loss occurred from 200 to 400$^\circ$C, corresponding to the departure of surfactants and other organic materials. Around 600$^\circ$C, there was an exothermic transition representing the conversion of hydroxide to oxide structure. There was no significant weight change upon further heating from 760 to 1000$^\circ$C. That indicates that the completion of thermal decomposition of the precursor.
5.1.3 Crystallization and crystalline size

Figure 5.2 presents XRD pattern of Tm:Y$_2$O$_3$ nanoparticles. Similar to Tb:Y$_2$O$_3$, XRD lines of Tm:Y$_2$O$_3$ matched well with the lines of standard cubic yttrium oxide given in JCPDS-File No. 05-574 (D). The sample had a defective fluorite structure having relatively strong intensities at 29.08$^0$, 33.72$^0$, 48.46$^0$ and 57.52$^0$ corresponding to (222), (400), (440) and (622) diffraction lines. The relatively strong intensities and narrow full width at half maximum demonstrates a good crystallization of Tm:Y$_2$O$_3$ nanoparticles. The crystalline size of the sample was calculated using the method presented in Chapter 3 [section 3.1.3]. The result was shown in Table 5.4.
Chapter 5 Blue-emitting nanophosphor Tm:Y$_2$O$_3$

![XRD pattern of Tm:Y$_2$O$_3$ nanoparticles](image)

**Figure 5.2** XRD patterns of Tm:Y$_2$O$_3$ nanoparticles

<table>
<thead>
<tr>
<th>Sample</th>
<th>FWHM ($\theta$)</th>
<th>$2\theta$ ($^\circ$)</th>
<th>B</th>
<th>$\beta$</th>
<th>L, crystalline size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tm:Y$_2$O$_3$</td>
<td>0.352</td>
<td>29.073</td>
<td>0.0061</td>
<td>0.0060</td>
<td>24</td>
</tr>
</tbody>
</table>

The crystalline size of Tm:Y$_2$O$_3$ was further calculated by averaging from three main diffraction peaks ($2\theta=29$, 48 and 57). The result was 19 nm.

### 5.1.4 Morphology

Figure 5.3 presents SEM micrographs of Tm:Y$_2$O$_3$ calcinated at $800^\circ$C. There is aggregation shown in the micrographs. Pores and voids can also be observed. The pores and voids were caused by escaping gases during calcination. The nanoparticles prepared in microemulsions adsorbed the surfactants that can act as fuels in calcination process. As
shown in Fig. 5.1, the surfactants can be burned away completely at above 230°C. The agglomeration was due to sintering of the particles. Under 600°C-800°C of calcination temperatures, the agglomeration of the particles is unavoidable.

5.1.5 Transmission electronic microscopy

By transmission electronic microscopy (TEM), we studied the particle size with a higher resolution and accuracy. It can be seen from the micrographs (Figure 5.4) that the particles are in the range of several nm to tens of nm. This result is consistent with what we obtained from XRD analysis. Most of the particles agglomerate into a larger size (tens of nm or hundreds of nm) during the calcination process. Therefore, the particle size of the samples we observed in TEM micrographs includes both crystallite size and agglomeration size, which is in the range of several nm-hundreds of nm.
Figure 5.3 SEM micrographs of Tm:Y$_2$O$_3$ (800$^\circ$C)
Figure 5.4 TEM micrographs of Tm:Y\textsubscript{2}O\textsubscript{3}
5.1.6 X-ray photoelectron spectroscopic (XPS) study of Tm:Y$_2$O$_3$ nanophosphors

![XPS wide scan spectrum of Tm:Y$_2$O$_3$](image)

**Figure 5.5** XPS wide scan spectrum of Tm:Y$_2$O$_3$

The XPS wide scan spectrum of Tm:Y$_2$O$_3$ [Figure 5.5] shows that there are four elements in the nanoparticles, including Y, Tm, O and C. Their peak positions are given in Table 5.5. All the other positions are corrected with reference to C1s (285 eV) due to surface charging effects.

<table>
<thead>
<tr>
<th>Elements</th>
<th>Peak position (eV)</th>
<th>Corrected position (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C1s</td>
<td>293.0</td>
<td>285.0</td>
</tr>
<tr>
<td>Y3d</td>
<td>164.8</td>
<td>156.8</td>
</tr>
<tr>
<td>O1s</td>
<td>537.2</td>
<td>529.2</td>
</tr>
<tr>
<td>Tm4d</td>
<td>179.1</td>
<td>171.1</td>
</tr>
</tbody>
</table>
Chapter 5 Blue-emitting nanophosphor Tm:Y$_2$O$_3$

Detailed study on XPS spectra of Tm:Y$_2$O$_3$ was carried out to obtain a better understanding of the chemical state of the elements in the nanoparticles. The core level spectra of Y3d, Tm4d, C1s, and O1s were fitted employing Gaussian sum functions.

The high surface area of nanoparticles produces a high reactivity and results in an accelerated rate of reaction with atmospheric water and CO$_2$. From figure 5.6, it can be observed that the fitted peaks of O1s are found at 529.2 eV and 531.6 eV. The signal at lower binding energy (529.2 eV) can be assigned to surface lattice oxygen and the signal at higher binding energy (531.6 eV) to adsorbed oxygen species such as O$, \text{O}_2^{2-}, \text{or O}^{2-}$ [18–21]. The fitted peak at 531 eV could be attributed to C=O, O-H or H-C=O. In addition, the XPS spectrum of C1s exhibits the adsorption of adventitious carbon. The fitted peaks of C1s were obtained at 285.0 and 290.6 eV, which could be attributed to C=O and COOH, respectively.

Similar to the XPS spectra of Tb:Y$_2$O$_3$, the XPS spectrum of Y3d in Tm:Y$_2$O$_3$ shows the doublets of Y3d signals [Y(3d$_{3/2}$), Y(3d$_{5/2}$)] at 158.7 and 156.8 eV. The signal corresponding to Y(3d$_{5/2}$) is dominant, which could be assigned to Y-O bond. The 4d spectrum of Tm is shown in Figure 5.6. The binding energies of the Tm 4d peaks are 171.1 and 192.0 eV. These values are in good agreement with the binging energies reported in previous work [22, 23]. The 4d spectrum shows dominant signals at 171 and 192 eV, which can be assigned to the characteristic features of Tm$^{3+}$ [23-34].
Figure 5.6 C1s, Y3d, O1s and Tm4d spectra of Tm:Y2O3 nanoparticles
5.1.7 Photoluminescence properties of Tm:Y$_2$O$_3$

5.1.7.1 Emission of Tm:Y$_2$O$_3$

It is well known that Tm has complicated energy levels due to strong deviation from R-S coupling in the 4f configuration [Figure 5.7]. Hence, the relaxation of the excited states of Tm ions may take place via a large number of relaxation paths [Figure 5.8], giving rise to ultraviolet, visible, and infrared emission with moderate intensity [35]. In Y$_2$O$_3$ nanoparticles, Tm shows emission at the blue region with strong intensity and very low intensity at the near-infrared region [Figure 5.9]. Although f-f transitions are forbidden by Laporte’s selection rule, they are observed as a forced electric dipole transition when thulium occupies acentric sites as observed for Eu ion in Y$_2$O$_3$ [Chapter 3]. Some information on the crystal structure of bixybyite-type Y$_2$O$_3$ is quite useful in explaining the dominant $^1$D$_2$-$^3$F$_4$ (electric dipole) transition at low concentration of Tm [36]. In cubic Y$_2$O$_3$, the oxygen vacancy along the body and face diagonals leads to two types of yttrium sites, viz., C$_2$ and S$_6$ symmetries in the ratio of 1:3 [37]. In particular, the former one, lacking inversion symmetry, is quite suitable for forced electric dipole transition for Tm ions. When thulium is doped in yttrium oxide, because of its favorable size with yttrium, isomorphic substitution is easily possible and occupies with equal probability two different Y$^{3+}$ sites in the lattice. Hence, it can be expected that both magnetic and electric dipole transitions are possible between 400 to 800 nm. Moreover, the S$_6$ site is three times less in number compared with the C$_2$ site and has low absorption strength, leading to the emission from the $^1$D$_2$-$^3$F$_4$ electric dipole transition.
Figure 5.7 Diagram of energy levels and $4f - 4f$ inner shell transitions of Tm$^{3+}$ in Al$_x$Ga$_{1-x}$N:Tm [38]

Figure 5.8 Possible cross-relaxation mechanisms from the $^1D_2$ and $^1G_4$ thulium emitting levels [15]
Figure 5.9 shows the photoluminescence (PL) emission spectrum of Tm:Y$_2$O$_3$ nanoparticles upon excitation with a wavelength of 305 nm. Major PL emission peaks were observed in the blue region (452, 467, 472 and 483 nm) and 583 nm. The 452 and 467 nm emission are well known and attributed to $^1D_2\rightarrow^3F_4$ [14, 38, 39]. For the 472 and 483 nm emission, we believe that it is due to $^1G_4\rightarrow^3H_6$ [39]. There is another intense emission at 583 nm shown in Figure 5.9. It could be corresponding to $^1I_6\rightarrow^3F_3$. Emission in the blue region is the focus of this work.
5.1.7.2 The influence of Tm$^{3+}$ concentration on the emission of Tm:Y$_2$O$_3$

Figure 5.10 illustrates the effect of Tm$^{3+}$ concentration on the photoluminescence intensities of Tm:Y$_2$O$_3$. In the emission spectra, both line position and linewidth remained the same as the Tm$^{3+}$ concentration changed, indicating that the nature of the thulium activation did not change with varying concentrations. Table 5.6 lists the intensities of blue emission with various Tm$^{3+}$ concentrations. The blue emission was obtained by integrating the areas in the range 447-485 nm.

<table>
<thead>
<tr>
<th>Concentration (mol%)</th>
<th>Intensity (a.u.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5%</td>
<td>2.59 E7</td>
</tr>
<tr>
<td>1%</td>
<td>2.75 E7</td>
</tr>
<tr>
<td>2%</td>
<td>2.90 E7</td>
</tr>
</tbody>
</table>

Tm-Tm interactions inside the Y$_2$O$_3$ films became more important at higher thulium concentration. Previous work reported that, to obtain the maximum intensity at 462nm, the concentration of Tm in the Y$_2$O$_3$ phosphor films prepared by spray pyrolysis was limited to 1% [11, 15, 16]. However, for the Tm:Y$_2$O$_3$ nanoparticles synthesized in microemulsion, the intensities of blue emission kept increasing up to 2%. A possible explanation of enhanced quenching concentration of Eu:Y$_2$O$_3$ nanoparticles synthesized
in microemulsions has been presented in Chapter 3 [Section 3.1.6.3]. It can be applied to interpret quenching results of Tm:Y$_2$O$_3$ nanoparticles.

![Emission spectra of Tm:Y$_2$O$_3$ nanoparticles with various Tm$^{3+}$ concentration (mol%), calcinated at 800$^\circ$C](image)

**Figure 5.10** Emission spectra of Tm:Y$_2$O$_3$ nanoparticles with various Tm$^{3+}$ concentration (mol%), calcinated at 800$^\circ$C
Chapter 5 Blue-emitting nanophosphor Tm:Y$_2$O$_3$

5.2 SUMMARY

For the first time, blue-emitting nanophosphors Tm:Y$_2$O$_3$ were successfully produced in microemulsion. The average particle size is around 20 nm. The blue-emitting nanophosphors exhibited a similar thermal decomposition behavior as the red-emitting and green-emitting nanophosphors [Chapter 3, 4]. Water molecules, surfactants and other organic materials were removed completely at around 400$^0$C, and the particles formed typical cubic crystal structure of Y$_2$O$_3$ over 760$^0$C. Agglomeration of the particles occurred during the sintering process. XPS study of the nanophosphors shows that there were C=O, O-H or H-C=O which can greatly decrease the emission efficiency of the nanophosphor due to the competitive absorption. It can be attributed to absorption of CO$_2$ and H$_2$O.

The nanophosphors Tm:Y$_2$O$_3$ exhibited a strong emission in the blue region. The blue emission can be attributed to $^1D_2$$\rightarrow^3F_4$ and $^1G_4$$\rightarrow^3H_6$. The effect of Tm$^{3+}$ concentration on the blue emission intensities of nanophosphors Tm:Y$_2$O$_3$ had been studied. The blue emission intensities of the nanophosphors prepared in micromulsion kept increasing up to 2%, whereas the limited Tm concentration to obtain maximum blue emission intensity in Tm:Y$_2$O$_3$ film prepared by spray pyrolysis is 1%. It can be concluded that the microemulsion technique is a powerful method to synthesize nanophosphors with good optical properties.
5.3 REFERENCES


CHAPTER 6 PRELIMINARY WORK ON UPCONVERTING NANOPHOSPHORS

There has been considerable research on upconverting phosphors since initial interest in the late 1950s [1-3]. Possible applications of upconverting phosphors include three-dimensional displays [4-6], fiber optic amplifiers that operate at wavelengths of 1.55, 1.46 and 1.31 μm [7-9], upconversion lasers [5] and remote sensing thermometers for high-temperature applications [10-11]. Considering the interest in the signal amplification in telecommunication systems at a wavelength of 1.3 and 1.5 μm, Er doped SiO₂ have been successfully used in the third window of telecommunications (1.5 μm) while Pr doped ZBLAN (ZrF₄•BaF₂•LaF₃•AlF₃•NaF) fibers are considered to be one of the most promising candidate materials for the second window (1.3 μm) [12]. Among the vast number of different types of upconverting materials, yttrium oxide thin films have received particular attention due to their diverse physical, chemical and optical properties [13]. It is reasonable that many researchers have made efforts to investigate Er:Y₂O₃ and Pr:Y₂O₃ in order to develop promising upconverting materials.

J. Silver et al reported a series of research on Er:Y₂O₃. The urea homogeneous precipitation method was used to prepare spherical Er:Y₂O₃ particles. The effect of particle morphology and crystallite size on the upconversion luminescence properties of erbium and ytterbium codoped yttrium oxide phosphors [11] and temperature dependent upconversion luminescence properties of erbium in yttrium oxide [10] were investigated. The results revealed that two hot bands can be observed, and that they arise from the two
different Er\(^{3+}\) lattice sites in Er:Y\(_2\)O\(_3\). The wavelength positions of these emission lines showed no observable shifts with temperature. J. A. Capobianco et al investigated optical spectroscopy of nanocrystalline cubic Er:Y\(_2\)O\(_3\) obtained by combustion synthesis [14]. These materials showed a very high surface area and a small apparent density. Diffuse reflectance spectra indicated that these nanoparticles had a blue shift of the intrinsic absorption of the host, compared to bulk samples with the same dopant concentration. This behavior could have a significant influence on the quantum yield of the emission upon UV excitation. Solid-state reaction method was used to prepared Er:Y\(_2\)O\(_3\) by A. N. Georgobiani et al [15]. The phosphors showed sharp emission peaks in the visible and IR (1.5\(\mu\)m) regions. The optimal Er content is 10\% (at.\%) and the shape of the emission bands is independent on Er concentration. Ph. Lecoeur et al undertook structural and optical characterizations of Er:Y\(_2\)O\(_3\) thin films deposited by pulsed laser deposition from metal targets [16]. They found that the guiding properties of Er:Y\(_2\)O\(_3\) films are not only dependent on the crystalline quality of the samples but also on the surface roughness of the film. As our best knowledge, there are relatively few research reported on Pr:Y\(_2\)O\(_3\).

Although the halide phosphors are more efficient than Er:Y\(_2\)O\(_3\) and Pr:Y\(_2\)O\(_3\), they are sensitive to CO\(_2\) and water, thus require protection from the atmosphere [11]. This fact instigated us to investigate nanosized Er:Y\(_2\)O\(_3\) and Pr:Y\(_2\)O\(_3\) prepared by microemulsion technique. In this preliminary work, the upconverting nanophosphors Er:Y\(_2\)O\(_3\) and Pr:Y\(_2\)O\(_3\) were synthesized in microemulsions for the first time. Structural characterizations were carried out by XRD and XPS. However, optical properties have not been studied due to lack of instruments.
6.1 RESULTS AND DISCUSSIONS

6.1.1 Elemental analysis of Er:Y\textsubscript{2}O\textsubscript{3} and Pr:Y\textsubscript{2}O\textsubscript{3} nanoparticles

In this work, Er and Pr were doped into Y\textsubscript{2}O\textsubscript{3} with a concentration of 1% (mol%). In order to determine the actual concentration of Er and Pr ions doped in the samples of Er:Y\textsubscript{2}O\textsubscript{3} and Pr:Y\textsubscript{2}O\textsubscript{3}, the elemental analysis was conducted by ICP technique. Table 6.1-6.2 shows the results of the elemental analysis.

| Table 6.1 Elemental analysis of Er:Y\textsubscript{2}O\textsubscript{3} nanoparticles (1%) |
|-------------------------------|-------------------------------|-------------------------------|-----------------|
| Elements | Theoretical value (wt%) | Experimental value (wt%) | Er:Y (mol) |
| Y | 77.61 | 66.61 | 0.95% |
| Er | 1.46 | 1.19 | |

| Table 6.2 Elemental analysis of Pr:Y\textsubscript{2}O\textsubscript{3} nanoparticles (1%) |
|-------------------------------|-------------------------------|-------------------------------|-----------------|
| Elements | Theoretical value (wt%) | Experimental value (wt%) | Pr:Y (mol) |
| Y | 77.79 | 65.74 | 1.03% |
| Pr | 1.23 | 1.07 | |

The experimental values of Y, Er and Pr were lower than the theoretical values. It is due to the contamination of H\textsubscript{2}O and CO\textsubscript{2}. From the results of the elemental analysis, it can be seen that the molar ratio of Pr and Er to Y fit the theoretical values very well. It can be concluded that microemulsion technique is an effective and exact way to dope impurities into nanocrystals.
6.1.2 Crystallization and crystalline size

The crystallinity and structure of Er:Y$_2$O$_3$ and Pr:Y$_2$O$_3$ were characterized by X-ray diffraction using CuK$\alpha$ radiation. The XRD spectra are shown in figure 6.1. Both Er:Y$_2$O$_3$ and Pr:Y$_2$O$_3$ exhibited similar diffraction patterns as that of standard cubic yttrium oxide [JCPDS-File No. 05-574 (D)]. Peaks were found at around 29$^0$, 33$^0$, 48$^0$ and 57$^0$, which can be ascribed to (222), (400), (440) and (622) diffraction lines of Y$_2$O$_3$ respectively. This result is agreement with what reported in A. Brigida’s work [17]. The crystalline size of the sample was calculated using the method presented in Chapter 3 [section 3.1.3]. The result was shown in Table 6.3.

<table>
<thead>
<tr>
<th>Sample</th>
<th>FWHM ($^0$)</th>
<th>$2\theta$ ($^0$)</th>
<th>B</th>
<th>$\beta$</th>
<th>L, crystalline size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Er:Y$_2$O$_3$</td>
<td>0.552</td>
<td>29.043</td>
<td>0.0096</td>
<td>0.0096</td>
<td>15</td>
</tr>
<tr>
<td>Pr:Y$_2$O$_3$</td>
<td>0.585</td>
<td>28.973</td>
<td>0.0102</td>
<td>0.0102</td>
<td>14</td>
</tr>
</tbody>
</table>

In order to provide better estimate, the crystalline sizes of Er:Y$_2$O$_3$ and Pr:Y$_2$O$_3$ were further calculated by averaging from three main diffraction peaks ($2\theta$=29, 48 and 57). The average crystalline sizes were 14 and 13 nm for Er:Y$_2$O$_3$ and Pr:Y$_2$O$_3$ respectively.
Figure 6.1 XRD patterns of Er\(_2\)O\(_3\) and Pr\(_2\)O\(_3\) nanoparticles
6.1.3 Morphology and Transmission electronic microscopy

SEM micrographs of Er:Y$_2$O$_3$ and Pr:Y$_2$O$_3$ nanoparticles are shown in figure 6.2. Aggregation of particles is clearly observed. The size of agglomerates is between 100 and 300 nm. Some agglomerates exist in the form of nanoflakes. The nanoflakes formed in the calcination process. TEM micrographs are presented in figure 6.3. Aggregation is also shown in TEM micrographs. Although the particles agglomerate, it can be seen the size of individual particle size is tens of nm.

6.1.4 X-ray photoelectron spectroscopic (XPS) study of upconverting phosphors

Pr:Y$_2$O$_3$ and Er:Y$_2$O$_3$ nanophosphors were investigated by XPS. The information obtained from XPS study can offer us better understanding on the electronic structure and chemical state of the elements in these upconverting nanophosphors. Figures 6.4 shows the XPS wide scanning spectra of Pr:Y$_2$O$_3$ and Er:Y$_2$O$_3$. Tables 6.4 and 6.5 list the elements as well as their peak positions of Pr:Y$_2$O$_3$ and Er:Y$_2$O$_3$ respectively. To compensate for surface charging effects in the insulating samples, all binding energies were corrected with reference to the saturated hydrocarbon C1s peak at 285.0 eV.
**Figure 6.2** SEM micrographs of upconverting nanophosphors

(Top-Er:Y$_2$O$_3$; bottom-Pr:Y$_2$O$_3$)
Figure 6.3 TEM micrographs of upconverting nanophosphors

(Top-Er:Y$_2$O$_3$; bottom-Pr:Y$_2$O$_3$)
Figure 6.4 XPS wide scan spectrum of upconverting nanophosphors

( Top-Pr:Y$_2$O$_3$; bottom-Er:Y$_2$O$_3$)
Table 6.4 Elements in Pr:Y$_2$O$_3$ nanoparticles

<table>
<thead>
<tr>
<th>Elements</th>
<th>Peak position (eV)</th>
<th>Corrected position (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C1s</td>
<td>292.3</td>
<td>285.0</td>
</tr>
<tr>
<td>Y3d</td>
<td>164.4</td>
<td>157.1</td>
</tr>
<tr>
<td>O1s</td>
<td>536.2</td>
<td>528.9</td>
</tr>
<tr>
<td>Pr3d</td>
<td>939.4</td>
<td>932.1</td>
</tr>
</tbody>
</table>

Table 6.5 Elements in Er:Y$_2$O$_3$ nanoparticles

<table>
<thead>
<tr>
<th>Elements</th>
<th>Peak position (eV)</th>
<th>Corrected position (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C1s</td>
<td>292.4</td>
<td>285.0</td>
</tr>
<tr>
<td>Y3d</td>
<td>164.4</td>
<td>157.0</td>
</tr>
<tr>
<td>O1s</td>
<td>536.8</td>
<td>529.4</td>
</tr>
<tr>
<td>Er4d</td>
<td>178.9</td>
<td>169.5</td>
</tr>
</tbody>
</table>

The core level spectra of Pr:Y$_2$O$_3$ and Er:Y$_2$O$_3$ are shown in Figures 6.5 and 6.6, respectively. In the Pr 3$d$ profiles of Pr:Y$_2$O$_3$, a doublet is observed at binding energies of ca. 957.3 and 932.1 eV, representing 3$d_{3/2}$ and 3$d_{5/2}$, respectively. According to Matsumura et al. (18) and Sarma and Rao (19), the signals at ca. 932.1 and 957.3 eV were assigned to Pr$^{3+}$.

The signals at ca. 169.5 and 199.7 eV in the Er 4$d$ profiles can be assigned to 4$d$ level of Er$^{3+}$ [20]. The observed variation between the signals of Y3d, C1s and O1s in Pr:Y$_2$O$_3$ and Er:Y$_2$O$_3$ is very small. It can be concluded that different dopants (Er and Pr) have no remarkable influence on the electronic structure of Y$^{3+}$ and O$^{2+}$. As discussed in chapter 4
and 5, the XPS spectra of C1s exhibit the adsorption of adventitious carbon while the signals of O1s reveal adsorbed oxygen species such as O\(^-\), O\(^{2-}\), or O\(^{2-}\) [21-24].

6.2 SUMMARY

Microemulsion technique to synthesize upconverting nanophosphors Er:Y\(_2\)O\(_3\) and Pr:Y\(_2\)O\(_3\) was reported in this work for the first time. The structural properties of these upconverting nanophosphors had been investigated by XRD, SEM, TEM and XPS. The average crystalline size of Er:Y\(_2\)O\(_3\) and Pr:Y\(_2\)O\(_3\) nanophosphors is 15 and 14 nm, respectively. Aggregation of particles is clearly observed in micrographs of SEM and TEM. Some agglomerates exist in the form of nanoflakes. Both of Er:Y\(_2\)O\(_3\) and Pr:Y\(_2\)O\(_3\) showed XRD patterns of standard cubic yttrium oxide. In the Er:Y\(_2\)O\(_3\) and Pr:Y\(_2\)O\(_3\) nanoparticles, there are a little amount of adventitious carbon and oxygen species which may undermine the optical properties of these nanophosphors.
Figure 6.5 XPS spectra of C1s, Y3d, O1s and Pr3d in Pr:Y$_2$O$_3$ nanoparticles
Figure 6.6 XPS spectra of C1s, Y3d, O1s and Er4d in Er:Y$_2$O$_3$ nanoparticles
6.3 REFERENCES


CHAPTER 7 CONCLUSIONS AND RECOMMENDATIONS

In this project, microemulsion technique has been developed to synthesize rare earth doped nanophosphors. Two series of rare earth doped nanophosphors have been successfully synthesized in microemulsions. Considering the application for field emission displays, we have prepared nano-sized Eu:Y$_2$O$_3$, Tb:Y$_2$O$_3$ and Tm:Y$_2$O$_3$, which are proposed as promising red-emitting, green-emitting and blue-emitting nanophosphors, respectively. Upconverting nanophosphors Er:Y$_2$O$_3$ and Pr:Y$_2$O$_3$ are the other series of rare earth doped nanophosphors prepared by microemulsion technique. It should be noted that the synthesis of Tb:Y$_2$O$_3$, Tm:Y$_2$O$_3$, Er:Y$_2$O$_3$ and Pr:Y$_2$O$_3$ nanoparticles by microemulsion technique is reported for the first time.

7.1 RED-EMITTING NANOPHOSPHORS Eu:Y$_2$O$_3$

Eu:Y$_2$O$_3$ nanoparticles obtained in microemulsions are distributed from several to tens of nanometer in diameter as determined by TEM. The average particle size is below 20 nm. During the calcination process, water and surfactant molecules were removed completely at around 400$^\circ$C and cubic yttrium oxide structure formed around 600$^\circ$C. Aggregation was clearly observable.

Compared with the phosphors prepared by conventional method, the quenching concentration of Eu in these nanoparticles has been raised remarkably. The nanophosphors synthesized in this study starts quenching at 25%-40% higher
concentration of Eu compared to that reported [Reference 27, Chapter 3]. With the increased calcinations temperatures, both the fluorescence intensity and lifetimes of the nanophosphors increased. The increasing intensity originates from the enhanced concentration of $C_2$ sites, while the longer lifetimes are due to the effects of surface states, strains in lattice as well as the change of crystal field as the firing temperature increased. The nanophosphors had enhanced emission intensities with codopants, such as $Al^{3+}$ and $Ba^{2+}$. It may be ascribed to the increased concentration of electron holes induced by codopants, decreased effect of concentration quenching of $Eu^{3+}$ and decreased amount of interstitial oxygens. With the increased $Eu^{3+}$ concentration, the energy transfer rate of $Eu^{3+}(S_6)$ to $Eu^{3+}(C_2)$ increases. However, varying $Eu^{3+}$ concentrations had no significant influence on decay rates. The variations may be attributed to the different crystal fields in different samples.

### 7.2 GREEN-EMITTING NANOPHOSPHORS $Tb:Y_2O_3$

In this part, in order to probe the relationship between structure and optical properties, we investigated several systems, including $Tb:Y_2O_3$, $Tb,Ce:Y_2O_3$, $Tb,Gd_2O_3$, $Tb:La_2O_3$, $Tb,Bi:Y_2O_3$, and $Tb,Al:Y_2O_3$. The average particle size of $Tb:Y_2O_3$ was 20 nm and decreased to 10 nm with the addition of codopants $Ce^{3+}$. It may result from the different bond length of $Ce$-$O$, $Y$-$O$ and $Tb$-$O$. $Tb:La_2O_3$ exists as hexagonal lanthanum oxide structure, which formed at a calcination temperature of 800$^0$C. With the increased calcination temperature, the average particle size increased remarkably from 14 nm (800$^0$C) to 43 nm (1000$^0$C). $Tb:Gd_2O_3$ has a smaller average particle size of 8.5 nm. XPS
study revealed that the situation of Tb\textsuperscript{3+} oxidation was serious. There were a large number of Tb\textsuperscript{4+} ions inside Tb:Y\textsubscript{2}O\textsubscript{3} nanoparticles. The XPS spectra also showed that there were contaminations of C=O, O-H or H-C=O species in Tb:Y\textsubscript{2}O\textsubscript{3} due to storage.

Since a relative low concentration of Tb\textsuperscript{3+} (1\%, mol\%) was doped into Y\textsubscript{2}O\textsubscript{3}, La\textsubscript{2}O\textsubscript{3} or Gd\textsubscript{2}O\textsubscript{3} in this study, emission corresponding to \textsuperscript{5}D\textsubscript{3}-\textsuperscript{7}F\textsubscript{J} was clearly observable. Both of the intensities of blue (I \textsuperscript{5}D\textsubscript{3}) and green (I \textsuperscript{5}D\textsubscript{4}) emission increased after codoping with Al, Bi, or Ce into Tb:Y\textsubscript{2}O\textsubscript{3}. This can be ascribed to a better dispersion of Tb\textsuperscript{3+}. Bi\textsuperscript{3+} is a favorable codopant to improve green emission and color purity of Tb:Y\textsubscript{2}O\textsubscript{3}. Tb\textsuperscript{3+} has enhanced intensity of emission in La\textsubscript{2}O\textsubscript{3}. Tb-Tb distance is greater in La\textsubscript{2}O\textsubscript{3} than in Y\textsubscript{2}O\textsubscript{3}, which can reduce the occurrence of Tb\textsuperscript{3+} ion’s concentration quenching and therefore enhance the intensity of emission.

### 7.3 BLUE-EMITTING NANOPHOSPHORS Tm:Y\textsubscript{2}O\textsubscript{3}

The average particle size of blue-emitting nanophosphors Tm:Y\textsubscript{2}O\textsubscript{3} is 20 nm. Tm:Y\textsubscript{2}O\textsubscript{3} nanophosphors exhibited a similar thermal decomposition behavior as the red-emitting and green-emitting nanophosphors. Agglomeration of the particles occurred during the sintering process. XPS study of the nanophosphors shows that there were C=O, O-H or H-C=O which can greatly decrease the emission efficiency of the nanophosphor due to the competitive absorption. It can be attributed to absorption of CO\textsubscript{2} and H\textsubscript{2}O.
Chapter 7 Conclusions and recommendations

The nanophosphor Tm:Y$_2$O$_3$ exhibited a strong emission in blue region. The blue emission can be attributed to $^1D_2\rightarrow^3F_4$ and $^1G_4\rightarrow^3H_6$. The effect of Tm$^{3+}$ concentration on the blue emission intensities of nanophosphors Tm:Y$_2$O$_3$ had been studied. The blue emission intensities of the nanophosphors prepared in micromulsion kept increasing up to 2%, whereas the limited Tm concentration to obtain maximum blue emission intensity in Tm:Y$_2$O$_3$ film prepared by spray pyrolysis is 1%. It can be concluded that the microemulsion technique is a powerful method to synthesize nanophosphors with high emission efficiency.

7.4 PRELIMINARY WORK ON UPCONVERTING NANOPHOSPHORS

In this preliminary work, upconverting nanophosphors Er:Y$_2$O$_3$ and Pr:Y$_2$O$_3$ were successfully prepared in microemulsions and the average size of the nanoparticles is 15, 14 nm, respectively. The structural properties of these upconverting nanophosphors had been investigated by XRD, SEM, TEM and XPS. Aggregation of particles is clearly observed in micrographs of SEM and TEM. Some agglomerates exist in the form of nanoflakes. Both Er:Y$_2$O$_3$ and Pr:Y$_2$O$_3$ showed XRD patterns of standard cubic yttrium oxide. In the Er:Y$_2$O$_3$ and Pr:Y$_2$O$_3$ nanoparticles, there are a little amount of adventitious carbon and oxygen species which may undermine the optical properties of these nanophosphors.
7.5 RECOMMENDATIONS FOR FURTHER STUDY

The research on rare earth doped nanophosphors conducted in this project is by no means exhaustive due to the limited instruments and research time. The following subjects are suggested for further development:

(i) Aggregation of particles occurred in all systems investigated in this study. Further development on microemulsion technique is needed. AOT could be a promising surfactant employing in microemulsion systems, which can reduce particle aggregation. In addition, powerful milling process should be carried out to obtain proper homogenization and reduce aggregation.

(ii) Photoluminescence property of green-emitting nanophosphors Tb:Y₂O₃ with higher concentration of Tb³⁺ should be investigated.

(iii) Optical property of Tb:Y₂O₃ and Pr:Y₂O₃ nanophosphors calcinated under H₂ flow should be investigated. H₂ atmosphere could avoid the oxidation of Tb³⁺ and Pr³⁺.

(iv) Optical property of upconverting nanophosphors should be completed.

This study has set up a valuable background for us to extend research interest on current hot research areas. We propose two subjects for future work. One is blue, green and red upconversion emission from lanthanide-doped LuPO₄ and YbPO₄ nanocrystals. Er³⁺ (for near IR to green) and Tm³⁺ (for near IR to blue and red) are the most efficient upconversion phosphors. These nanomaterials may be applied for the labeling of biomolecules and the amplification of signals transmitted through fiber cables. The other
subject is light emission from lanthanide doped III-N semiconductors. The proposed semiconductors are GaN, AlN and AlGaN. The research on these nanomaterials is of significant current interest for applications in electroluminescence devices.
PUBLICATIONS

1. Synthesis and characterization of Eu:Y_{2}O_{3} nanoparticles

*Nanotechnology* 13 (3): 318-323 Jun 2002

Huang, H.; Xu, G. Q.; Chin, W. S.; Gan, L. M.; Chew, C. H.

2. Characterization and optical properties of Tb:Y_{2}O_{3} nanoparticles synthesized in microemulsions

(Submitted for publication)

Huang, H.; Xu, G. Q.; Chin, W. S.

3. The influence of codopants on the luminescence of lanthanide-doped yttrium oxide nanoparticles

(Submitted for publication)

Huang, H.; Xu, G. Q.; Chin, W. S.

4. Luminescence of Tb^{3+} in different host materials

(Submitted for publication)

Huang, H.; Xu, G. Q.; Chin, W. S.

5. Luminescence and characterization of Tm:Y_{2}O_{3} nanoparticles prepared by microemulsion technique

(Submitted for publication)

Huang, H.; Xu, G. Q.; Chin, W. S.
APPENDIX 1 LIST OF FIGURES

Figure 1.1 Scheme of a field emission display ..........................................................10
Figure 1.2 General energy scheme related to the ESA process ..............................14
Figure 1.3 General energy scheme related to the ETU process ............................16
Figure 1.4 General energy scheme for the simplest PA process ..........................17
Figure 1.5 Partial energy level diagrams for lanthanide ions involved in upconversion .................................................................18
Figure 1.6 Schematic illustrations of (a) oil-in-water microemulsion; (b) water-in-oil microemulsion; and (c) bicontinuous microemulsion ........................20
Figure 1.7 Schematic illustration of some phase equilibria of microemulsions encountered in multicomponent systems ...........................................21
Figure 1.8 Schematic presentation of reactions in mixed inverse microemulsions ..........................27
Figure 1.9 Crystal structures of Y$_2$O$_3$ ......................................................................29
Figure 2.1 The partial phase diagram at 22$^\circ$C for the system cyclohexane-NP$_5$/NP$_9$-water .................................................................44
Figure 2.2 (a,b) The partial phase diagrams at 22$^\circ$C for the systems cyclohexane-NP$_5$/NP$_9$-KOH(a) and NaOH(b) at various concentrations 45
Figure 2.2 (c,d) The partial phase diagrams at 22$^\circ$C for the systems cyclohexane-NP$_5$/NP$_9$-Me$_4$NOH(c) and NH$_4$OH(d) at various concentrations ......................................................46
Figure 2.3 (a) Partial phase diagram for the system PE-ZnCl$_2$ aqueous solution-NP$_5$/NP$_9$ in the ratio of 8:1 and 4:1 respectively .................................48
Figure 2.3 (b) Partial phase diagram for the system PE-ZnCl$_2$ aqueous solution-NP$_5$/NP$_9$ in the ratio of 2:1 .................................................................48
Figure 2.4 (a) The partial phase diagram for the systems cyclohexane-NP$_5$/NP$_9$-Na$_3$PO$_4$ with different concentrations ............50
Figure 2.4 (b) The partial phase diagram for the systems cyclohexane-NP$_5$/NP$_9$-K$_2$CO$_3$ with different concentrations ......................50
Figure 2.4 (c) The partial phase diagram for the systems cyclohexane-NP$_5$/NP$_9$-Fe(NO$_3$)$_3$ with different concentrations ...............51
Figure 2.5 The flowchart of synthesizing lanthanide-doped nanophosphors ........52
Appendix 1 List of Figures

Figure 3.1 TGA curve of the Eu:Y\(_2\)O\(_3\) nanoparticles.................................................62
Figure 3.2 XRD spectra of the Eu:Y\(_2\)O\(_3\) nanoparticles with various calcination temperatures..................................................................................65
Figure 3.3 SEM micrograph of Eu:Y\(_2\)O\(_3\) nanoparticles calcined at 600\(^\circ\)C ..............67
Figure 3.4 SEM micrograph of Eu:Y\(_2\)O\(_3\) nanoparticles calcined at 800\(^\circ\)C ...........67
Figure 3.5 TEM micrograph and distribution of nanoparticles calcined at 800\(^\circ\)C ...69
Figure 3.6 TEM micrograph and distribution of nanoparticles calcined at 1000\(^\circ\)C ..69
Figure 3.7 TEM micrograph and distribution of nanoparticles calcined at 600\(^\circ\)C ....69
Figure 3.8 Excitation spectrum of Eu:Y\(_2\)O\(_3\) nanoparticles ........................................70
Figure 3.9 Emission spectrum of Eu:Y\(_2\)O\(_3\) nanoparticles .............................................70
Figure 3.10 Partial energy level diagram of the Eu\(^{3+}\) ion in solid matrix ..................71
Figure 3.11 Emission spectra of precursors of Eu:Y\(_2\)O\(_3\) and Eu:Y\(_2\)O\(_3\) calcined at various temperatures for 2 hours.........................................................73
Figure 3.12 Variation of peak intensities of the transitions of \(^5\)D\(_0\) \(\rightarrow\) \(^7\)F\(_2\), \(^7\)D\(_0\) \(\rightarrow\) \(^7\)F\(_1\) and \(^5\)D\(_0\) \(\rightarrow\) \(^7\)F\(_3\) of Eu:Y\(_2\)O\(_3\) with various calcination temperatures ...74
Figure 3.13 Concentration quenching curve of microemulsion-prepared Eu:Y\(_2\)O\(_3\) nanoparticles .................................................................................................75
Figure 3.14 Emission spectra of Eu:Y\(_2\)O\(_3\) with various Eu concentrations ..............76
Figure 3.15 Emission spectra of precursors of Eu:Al:Y\(_2\)O\(_3\) and Eu:Al:Y\(_2\)O\(_3\) with various calcination temperatures .................................................................77
Figure 3.16 Emission spectra of precursors of Eu:Ba:Y\(_2\)O\(_3\) and Eu:Ba:Y\(_2\)O\(_3\) with various calcination temperatures .................................................................78
Figure 3.17 Peak intensities of the transition of \(^5\)D\(_0\) \(\rightarrow\) \(^7\)F\(_2\) as a function of calcination temperatures for the three nanophosphors .................79
Figure 3.18 \(^5\)D\(_0\) \(\rightarrow\) \(^7\)F\(_2\) decay curves of nanocrystalline Eu:Y\(_2\)O\(_3\) calcined at various temperatures .....................................................................................84
Figure 3.19 Lifetimes of Eu:Y\(_2\)O\(_3\) (Eu 2\%) as a function of various calcination temperatures .........................................................................................................................84
Figure 3.20 \(^5\)D\(_0\) \(\rightarrow\) \(^7\)F\(_2\) decay curves of Eu:Y\(_2\)O\(_3\) nanophosphors with various Eu concentration (mol\%) .............................................................................86
Figure 3.21 Decay rate as a function of Eu\(^{3+}\) concentration .........................................86
Figure 3.22 Simplified scheme of decay process of \(^5\)D\(_0\) \(\rightarrow\) \(^7\)F\(_2\) transition in Eu:Y\(_2\)O\(_3\) nanoparticles ........................................................................................................87
Appendix 1 List of Figures

Figure 4.1 TGA curve of Tb:Y$_2$O$_3$ ................................................................. 96
Figure 4.2 TGA curve of Tb:La$_2$O$_3$ ................................................................. 97
Figure 4.3 Comparison of XRD spectra between Tb:Y$_2$O$_3$ and Tb,Ce:Y$_2$O$_3$ nanoparticles ................................................................. 99
Figure 4.4 XRD spectra of Tb:Y$_2$O$_3$ and Tb,Ce:Y$_2$O$_3$ nanoparticles .......... 100
Figure 4.5 XRD spectrum of Tb:Gd$_2$O$_3$ nanoparticles and standard Gd$_2$O$_3$ .... 101
Figure 4.6 The fluorite crystal structure ............................................................. 102
Figure 4.7 XRD spectra of precursors of Tb:La$_2$O$_3$ and Tb:La$_2$O$_3$ with various calcination temperatures and standard La$_2$O$_3$ ........................................ 103
Figure 4.8 The crystal structure of hexagonal La$_2$O$_3$ ........................................ 104
Figure 4.9 SEM micrographs of various Tb actived-nanophosphors .................. 107
Figure 4.10 TEM micrographs of Tb:Y$_2$O$_3$ and Tb,Ce:Y$_2$O$_3$ ......................... 108
Figure 4.11 TEM micrographs of Tb:La$_2$O$_3$ (800°C) and Tb:La$_2$O$_3$ (1000°C) .... 109
Figure 4.12 XPS wide scan spectrum of Tb,Ce:Y$_2$O$_3$ calcined at 800°C .......... 110
Figure 4.13 XPS spectrum of C1s of Tb,Ce:Y$_2$O$_3$ ............................................. 111
Figure 4.14 XPS spectrum of Y3d of Tb,Ce:Y$_2$O$_3$ .......................................... 112
Figure 4.15 XPS spectrum of O1s of Tb,Ce:Y$_2$O$_3$ .......................................... 113
Figure 4.16 XPS spectrum of Tb4d of Tb,Ce:Y$_2$O$_3$ ........................................ 114
Figure 4.17 XPS spectrum of Ce3d of Tb,Ce:Y$_2$O$_3$ ........................................ 115
Figure 4.18 A schematic model for photoluminescence of Tb$^{3+}$ .................... 116
Figure 4.19 Emission spectrum of Tb:Y$_2$O$_3$ nanophosphor calcined at 800°C with Tb 1%(mol%) ................................................................. 117
Figure 4.20 Luminescence spectra of Tb:Y$_2$O$_3$ with different codopants .......... 118
Figure 4.21 Tb$^{3+}$ emission in different host materials ....................................... 122
Figure 5.1 TGA curve of the Tm:Y$_2$O$_3$ nanoparticles ...................................... 132
Figure 5.2 XRD patterns of Tm:Y$_2$O$_3$ nanoparticles ....................................... 133
Figure 5.3 SEM micrographs of Tm:Y$_2$O$_3$ (800°C) ........................................ 135
Figure 5.4 TEM micrographs of Tm:Y$_2$O$_3$ .................................................... 136
Figure 5.5 XPS wide scan spectrum of Tm:Y$_2$O$_3$ ........................................... 137
Figure 5.6 C1s, Y3d, O1s and Tm4d spectra of Tm:Y$_2$O$_3$ nanoparticles .......... 139
Figure 5.7 Diagram of energy levels and 4f–4f inner shell transitions of Tm$^{3+}$ in Al$_x$Ga$_{1-x}$N:Tm ................................................................. 141
Figure 5.8 Possible cross-relaxation mechanisms from the $^1$D$_2$ and $^1$G$_4$ thulium emitting levels ................................................................. 141
Appendix 1 List of Figures

**Figure 5. 9** Photoluminescence emission spectrum of Tm:Y$_2$O$_3$..............................142

**Figure 5. 10** Emission spectra of Tm:Y$_2$O$_3$ nanoparticles with various Tm$^{3+}$
concentration (mol%), calcinated at 800°C .........................................................144

**Figure 6. 1** XRD patterns of Er:Y$_2$O$_3$ and Pr:Y$_2$O$_3$ nanoparticles......................152

**Figure 6. 2** SEM micrographs of upconverting nanophosphors .............................154

**Figure 6. 3** TEM micrographs of upconverting nanophosphors .............................155

**Figure 6. 4** XPS wide scan spectrum of upconverting nanophosphors .....................156

**Figure 6. 5** XPS spectra of C1s, Y3d, O1s and Pr3d in Pr:Y$_2$O$_3$ nanoparticles .......159

**Figure 6. 6** XPS spectra of C1s, Y3d, O1s and Er4d in Er:Y$_2$O$_3$ nanoparticles ......160
## APPENDIX 2 LIST OF TABLES

| Table 1. 1 | Phosphor efficiency | 12 |
| Table 2. 1 | Characteristics of various lanthanides | 41 |
| Table 3. 1 | Elemental analysis of Eu:Y$_2$O$_3$ nanoparticles (1%) | 60 |
| Table 3. 2 | Elemental analysis of Eu:Y$_2$O$_3$ nanoparticles (8%) | 60 |
| Table 3. 3 | Elemental analysis of Eu:Y$_2$O$_3$ nanoparticles (15%) | 60 |
| Table 3. 4 | Crystalline sizes of Eu:Y$_2$O$_3$ with different calcination temperatures | 63 |
| Table 3. 5 | The comparison of XRD lines between the sample calcined at 600$^\circ$C and standard cubic Y$_2$O$_3$ | 64 |
| Table 3. 6 | Decay data of Eu:Y$_2$O$_3$ with different Eu$^{3+}$ concentration | 85 |
| Table 4. 1 | Crystalline sizes of Tb:Y$_2$O$_3$ and Tb,Ce:Y$_2$O$_3$ nanoparticles | 99 |
| Table 4. 2 | Crystalline size of Tb:Gd$_2$O$_3$ nanoparticle | 102 |
| Table 4. 3 | Crystalline sizes of Tb:La$_2$O$_3$ nanoparticles | 105 |
| Table 4. 4 | Elements in Tb,Ce:Y$_2$O$_3$ nanoparticles | 111 |
| Table 4. 5 | Integrated intensity of Tb:Y$_2$O$_3$ with different codopants | 119 |
| Table 4. 6 | Intensity of green emission of Tb$^{3+}$ (I$^5D_4$-$^7F_3$) in different host materials | 123 |
| Table 5. 1 | Elemental analysis of Tm:Y$_2$O$_3$ nanoparticles (0.5%) | 130 |
| Table 5. 2 | Elemental analysis of Tm:Y$_2$O$_3$ nanoparticles (1%) | 130 |
| Table 5. 3 | Elemental analysis of Tm:Y$_2$O$_3$ nanoparticles (2%) | 130 |
| Table 5. 4 | Crystalline size of Tm:Y$_2$O$_3$ | 133 |
| Table 5. 5 | Elements in Tm:Y$_2$O$_3$ nanoparticles | 137 |
| Table 5. 6 | Blue emission intensities of Tm:Y$_2$O$_3$ nanophosphors with various Tm$^{3+}$ concentrations | 143 |
| Table 6. 1 | Elemental analysis of Er:Y$_2$O$_3$ nanoparticles (1%) | 150 |
| Table 6. 2 | Elemental analysis of Pr:Y$_2$O$_3$ nanoparticles (1%) | 150 |
| Table 6. 3 | Crystalline size of Er:Y$_2$O$_3$ and Pr:Y$_2$O$_3$ | 151 |
| Table 6. 4 | Elements in Pr:Y$_2$O$_3$ nanoparticles | 157 |
| Table 6. 5 | Elements in Er:Y$_2$O$_3$ nanoparticles | 157 |