

Synthesis of Ce³⁺-doped Terbium Aluminum Garnet Phosphors from Nanostructured Oxides

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The paper describes the synthesis of Ce³⁺-doped terbium aluminum garnet (TAG) phosphors with the use of nanostructured oxides of aluminum and rare earths. Aluminum oxide nanoparticles were obtained by gaseous-disperse synthesis and characterized by X-ray diffraction, differential thermal analysis and scanning electron microscopy. The preparation of cerium-doped terbium oxide nanopowders and luminescent properties of the Tb_{3(1-x)}Ce_{3x}Al₅O₁₂ phosphors are also discussed.

Keywords: Terbium Aluminum Garnet, Synthesis, Nanopowders, Luminescence.

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1. INTRODUCTION

The white light-emitting diodes (LED's) are one of the most promising alternatives to conventional electric light sources, i.e. incandescent lamps, Hg-containing fluorescent lamps. This concept has been commercially realized by using a combination of a blue LED emitting around 460 nm and yttrium aluminum garnet (Y₃Al₅O₁₂, YAG) doped with Ce³⁺ ions as a yellow phosphor. The restricting factors in using such white LED's for general lighting are a low color rendering index (R_a<80) that is caused by a deficit of red component in the emission spectrum of YAG:Ce³⁺ [1,2]. The shortcomings of YAG:Ce³⁺-based white LED's stimulated the search for alternative compositions with the garnet structure [1,2] and, in particular, the attempts to improve the color characteristics of LED's by substitution of Y³⁺ with other rare earth (R) ions. Jang et al. [3] have studied the luminescent properties of Ce³⁺ ions in Tb_{3x}Y_{3(1-x)}Al₅O₁₂ (TYAG) solid solutions. It was found that the Tb³⁺ substitution induces larger crystal field splitting of the Ce³⁺ 5d configuration and shifts the Ce³⁺ emission band towards longer wavelengths. Since this emission is efficiently excited by photons in the 380-460 nm region, efficient white LED's were fabricated by using a combination of (In,Ga)N chips emitting around 460 nm and TYAG:Ce³⁺ as a yellow-orange phosphor. Also, several groups of authors have studied the luminescent properties of Ce³⁺ ions in Tb₃Al₅O₁₂ (TAG) upon excitation in the 240-550 nm region [4-6]. It was shown that there is an efficient energy transfer between Tb³⁺ and Ce³⁺ in TAG and this material can be also of interest for development of new scintillators [5]. As a rule, Ce-containing garnets phosphors are prepared by the direct reaction between starting solid-phase reagents at temperatures, which typically exceed 1500°C. Even then, depending upon the preparation conditions some amounts of impurity phases such as RAlO₃, CeO₂ can be revealed in the final products [2,7].

Beside this, an insufficient mixing and low reactivity of raw materials often result in the significant difference in the Ce³⁺ concentrations within the grains and in the vicinity of grain boundaries [8]. In the present paper, we describe the synthesis of Tb_{3(1-x)}Ce_{3x}Al₅O₁₂ (x= 0-0.03) luminescent materials by solid state reaction between aluminum oxide Al₂O₃ and mixed rare earth oxides. Our approach included the use of a nanosized metastable Al₂O₃, the use of oxalate precursor-derived rare earth oxides, the firing of reaction mixtures in the temperature region of a metastable alumina phase to α-Al₂O₃ transition. It was expected that an acceleration of the diffusion of Al³⁺ and O²⁻ in temperature region of the Al₂O₃ phase transformation would stimulate the solid state reaction. The luminescent properties of the obtained phosphors are also briefly discussed.

2. EXPERIMENTAL

All samples were characterized by X-ray diffraction (XRD) using Cu K_α radiation (Rigaku Ultima IV). Differential thermal analysis (DTA) was performed on a thermal analyzer (LABSYS DSC/DTA/TG) in air at a heating rate of 20°C/min. Morphological investigations were carried out by scanning electron microscopy (SEM) on JEOL JSM 6390LV electron microscope. The emission and excitation spectra in UV-visible region were recorded at 77 K and room temperature using a Fluorolog F1-3 (Horiba Jobin Yvon) spectrofluorometer equipped with a xenon lamp.

3. RESULTS AND DISCUSSION

Nanosized Al₂O₃ was obtained by a gaseous-disperse synthesis. This method is based on the combustion of powdered metals due to exothermic oxidizing reactions between them and a gaseous oxidizer (typically O₂). The details of experimental setup used for the synthesis of nanosized Al₂O₃ can be found in the paper by Poletaev et al. [9]. The dispersed in N₂ aluminum

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particles with an average size of 4.8 μm were injected through an inner tube into O_2 stream. After ignition by an external source, a stable two-phase diffusion flame was observed. The resulting product was collected using a fabric filter. The XRD pattern of the as-prepared Al_2O_3 , shown Fig. 1, indicates that the powder contains γ, δ, θ -phases of Al_2O_3 , which are present in approximately the same quantities.

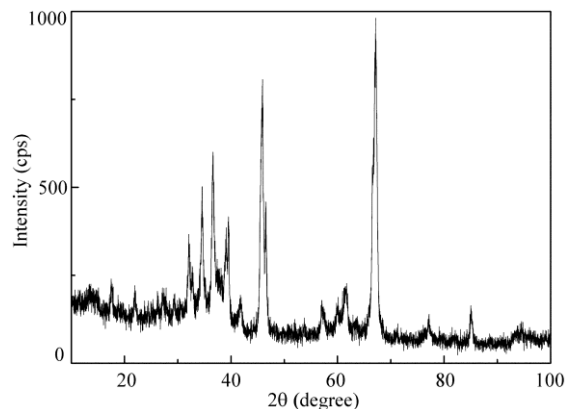


Fig. 1 – Powder X-ray diffraction pattern of as-prepared Al_2O_3

As can be seen from Fig. 2, its crystallites are of spherical in shape with 20-70 nm in diameter, and they exhibit a tendency to adhesion. DTA curve of the as-prepared Al_2O_3 sample revealed a strong exothermic effect in the range 1200-1400°C with a maximum at 1296°C (see Fig. 3), which corresponds to the metastable alumina phase $\rightarrow \alpha\text{-Al}_2\text{O}_3$ phase transition [10]. This phase transformation has been extensively studied, and at present, it is well known that $\alpha\text{-Al}_2\text{O}_3$ is formed through a nucleation and growth process, and depending upon chemical prehistory of the precursor, degree of its crystallinity, the presence of impurities etc. the transition temperature varies from 950 to 1350°C [10].

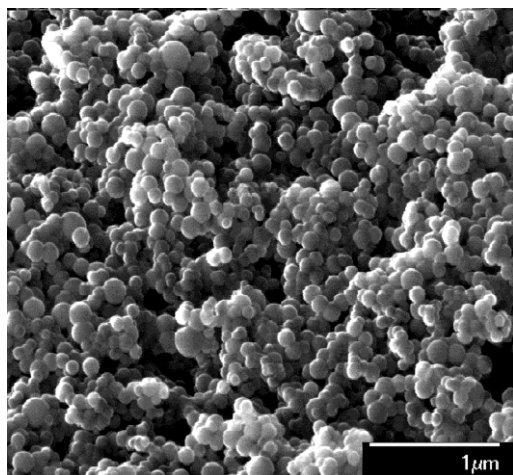


Fig. 2 – SEM photograph of as-prepared Al_2O_3

The second step in the preparation involved the formation of mixed rare earth oxides $\text{Tb}_4\text{O}_7:\text{Ce}$. To this end, the appropriate amounts of Tb_4O_7 (99.99%) and CeO_2 (99.99%) were dissolved in a dilute HNO_3 solution. The hydrous mixed rare earth oxalates $\text{R}_2(\text{C}_2\text{O}_4)_3 \cdot n\text{H}_2\text{O}$ were precipitated from the hot solution

(80 °C) by the slow addition of a concentrated $\text{H}_2\text{C}_2\text{O}_4$ solution. The precipitates were filtered, washed with distilled water, dried and then heated at 850 °C for 1 h in air. It is known that oxalate precursor-derived rare earth oxides typically consist of submicron aggregates of nanosized crystals [11]. After that the calculated amounts of $\text{Tb}_4\text{O}_7:\text{Ce}$ and Al_2O_3 were grinded and thoroughly mixed in ethanol, and the resulting mixtures were fired at a temperature of about 1300 °C for 3-5 h in a reducing medium created by burning activated carbon.

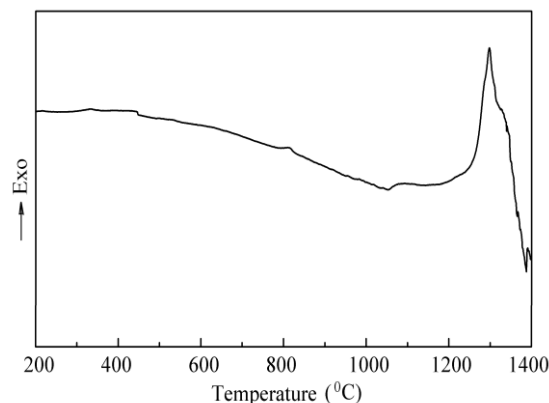


Fig. 3 – DTA curve of nanosized Al_2O_3

The XRD patterns of the as-prepared samples were well matched with JCPDS File No. 76-0111 for TAG. The synthesis procedure used was not further optimized for emission intensity or particle size distribution, but even without this highly efficient luminescent materials were obtained. The emission spectra of TAG:Ce³⁺ depend on cerium concentration and excitation wavelength.

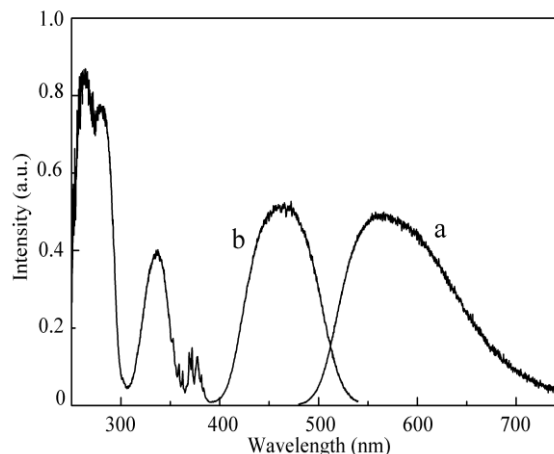


Fig. 4 – Emission and excitation spectra of $\text{Tb}_{3(1-x)}\text{Ce}_{3x}\text{Al}_5\text{O}_{12}$ ($x = 0.03$). The emission spectrum (a) was recorded upon excitation at 450 nm and the excitation spectrum (b) was recorded for the Ce^{3+} emission at 560 nm

As can be seen from Fig. 4, upon excitation at 450 nm the emission band of $\text{Tb}_{3(1-x)}\text{Ce}_{3x}\text{Al}_5\text{O}_{12}$ ($x = 0.03$) extends from 480 to 750 nm and has a maximum at about 563 nm. At 77 K the spectrum shows the doublet structure and can be reasonably decomposed into Gaussian-type bands with maxima at 534 and 583 nm, which are

due to transitions from the lowest Ce³⁺ 5d excited state to the 4f ground state levels 2F_{5/2} and 2F_{7/2}. The positions of these maxima are in agreement with the results reported for the Ce³⁺ emission in TAG at 10 K [3]. The excitation spectrum of Tb_{3(1-x)}Ce_{3x}Al₅O₁₂ ($x = 0.03$) recorded for the Ce³⁺ emission at 560 nm is also shown in Fig. 4. No doubt that the broad band with a maximum at 465 nm is mainly caused by the 4f→5d transition to the lowest component of the Ce³⁺ 5d configuration, while the narrow ones are due to the 4f₈→4f₈ transitions of Tb³⁺ ions. The band at 334 nm is a superposition of bands with maxima at 325 and 338 nm arising from spin-forbidden 4f₈→4f_{75d} transition of Tb³⁺ ions and 4f→5d transition of Ce³⁺ ions, respectively, so that its shape and relative intensity depend on the emission wavelength and temperature. The spectrum also contains overlapping bands with maxima at 277 and 262 nm, which must be attributed to the 4f₈ → 4f_{75d} transitions of the Tb³⁺ ions [5]. The substitution of Tb³⁺ for Y³⁺ in the garnet structure results in broadening the emission band and shifting its maximum towards the longer wavelengths. At room temperature the full width at half maximum of the Ce³⁺ emission increases from 3460 cm⁻¹ (YAG) to ~3800 cm⁻¹ for TAG. When the larger Tb³⁺ ion occupies the Y³⁺ position, the dodecahedral site is expanded and distorted, so that these results can be explained by

an increase in both the crystal field splitting of the Ce³⁺ 5d configuration and Stokes shift of the emission. Indeed, because the lowest Ce³⁺ excitation band of Tb_{3(1-x)}Ce_{3x}Al₅O₁₂ ($x = 0.03$) is situated at 465 nm (Fig. 4), the Stokes shift of the emission amounts to 2780 cm⁻¹. This value is comparable but somewhat larger than that reported for the Ce³⁺ emission in YAG (2400 cm⁻¹) [12]. The quantum efficiency of luminescence (η) of the Tb_{3(1-x)}Ce_{3x}Al₅O₁₂ ($x = 0.03$) sample was determined as described in Refs. [1, 2] using a commercial YAG:Ce³⁺ phosphor for LED's with $\eta = 0.90$ as a standard. For the excitation at 460 nm, the found value of 0.83 ± 0.04 is comparable but somewhat larger than that ($\eta = 0.76$) reported in the literature for the Ce³⁺ emission in TAG prepared at 1500oC [4].

4. CONCLUSIONS

TAG:Ce³⁺ phosphors have been successfully prepared with the use of nanostructured oxides of aluminum and rare earths. Spherical Al₂O₃-particles with a diameter ranging from 20 nm to 70 nm were obtained by gaseous-disperse synthesis. It was shown that the Ce³⁺ ions in TAG exhibit the efficient broad band emission with a maximum at about 563 nm and the quantum efficiency of luminescence of the Tb_{3(1-x)}Ce_{3x}Al₅O₁₂ ($x = 0.03$) phosphor was found as high as 0.83.

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