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Physics Procedia 2 (2009) 587–601

Physics Procedia

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Melt synthesis of oxide red phosphors $La_2WO_6:Eu^{3+}$

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Keywords: melt synthesis, tungstate, La_2WO_6, red phosphor

Abstract

To synthesize various complex oxide materials and their solid solutions, we have applied a novel “melt-synthesis technique” rather than conventional solid-state reaction techniques. The synthesis of well-crystalline multi-component phosphor materials is sometimes difficult using conventional solid-state reaction techniques

doi:10.1016/j.phpro.2009.07.045

because the reaction rates are slow as a result of slow mutual diffusion among solid-state species, thereby creating an inhomogeneous product. However, the melt reaction is rapid and homogeneous as it proceeds because of a solution reaction with fast diffusion. Red-phosphor La_2WO_6:Eu^{3+} samples with 25 mol% Eu^{3+} were prepared in a short time using melt synthesis. Red emission was observed at 618 nm typical for the Eu^{3+} center. Melt-synthesized samples exhibited much higher emission intensities than those obtained for the sample prepared using a solid-state reaction.

Introduction

Rare-earth tungsten oxides are of considerable interest as laser hosts, phosphors, ferroelectrics, and nuclear or refractory materials. Nassau studied crystallographic and physical properties of $R_2(MO_4)_3$ (R= rare earth, M= W, Mo) [1]. Yoshimura reported a high-temperature phase diagram of the La_2O_3-WO_3 system with eight compounds (Fig. 1) [2]. Furthermore, Yanovskii and Voronkova studied the phase diagram with nine compounds [3]. These studies have been a standard for fundamental comprehension for the La_2O_3-WO_3 system. Recently, several studies have investigated rare-earth-doped La_2O_3-WO_3 compounds available for laser host materials. In fact, $La_2W_3O_{12}$ is well known as a candidate for laser host crystals, suggesting that the material is stable under near-UV-light exposure, similar to Yb^{3+}:$La_2(WO_4)_3$ [4] and Nd^{3+}:$La_2(WO_4)_3$ [5,6].

In contrast, $(La, Eu)_2W_3O_{12}$ is known as a red phosphor [7,8], but fewer reports describe photoluminescence (PL) properties under near-UV-light excitation [9]. Recently, many studies have investigated phosphors for white LEDs as energy-saving illumination.

Herein, we report the PL properties of tungstate red phosphors of La_2WO_6:Eu^{3+}. The 4f–4f absorption transitions of Eu^{3+} occur at around 395 nm and 4f–4f emission transitions occur at around 610 nm, almost independent of host crystal optical phenomena. The oscillator strength of the 4f–4f transition is much weaker than that of 4f–5d or the charge-transfer transition. Generally, complex oxides are not easily synthesized using conventional solid-state reaction techniques because mutual diffusion among solid-state species is too slow to form homogeneous compounds or solid solutions. In contrast, the melt reaction is extremely fast and homogeneous because of a solution reaction with fast diffusion in the liquid phase. Therefore, the melt synthesis technique is suitable for synthesizing multi-component oxides where homogeneous cation mixing is necessary. During melt synthesis, the mixture of oxides or their precursors is melted in a very short period of time (1–60 s) using a strong light radiation in an arc-imaging furnace. Combining these advantages of the melt synthesis with the arc-imaging furnace, we prepared La_2WO_6:Eu^{3+} phosphors at a rapid rate, with necessary homogeneous Eu^{3+} doping.

Experimental

The starting materials were high-purity oxide (Eu_2O_3 (99.99%, Shin-Etsu Chemical Co. Ltd.), WO_3 (99.99%, Kojundo Chemical Lab. Co. Ltd.), and La_2O_3 (99.99%, Shin-Etsu Chemical Co. Ltd.)) powders. They were mixed by dry mixing and wet mixing in a high-purity alumina mortar. The mixed powder or a molded sample was placed on a copper hearth and melted in air under normal pressure using an arc-imaging furnace, as described in earlier reports [10, 11]. By exposure of the focused radiation of a 10 kW Xe lamp, the sample was melted into a 3–5 mm spherical globule on the copper hearth and then cooled rapidly by closing a shutter to cut off the radiation. After closing the shutter, the change from the molten state at around 2,000°C to a solid state with a dark color at around

600°C generally took 5–15 s. Therefore, the cooling rate was estimated as higher than 100°C/s. For comparison, samples of $La_2WO_6:Eu^{3+}$ were prepared using the solid state reaction at 1000°C for 10 h. Powder X-ray diffraction patterns were obtained for the arc-melted samples ground in an alumina mortar. For phase identification in this study, X-ray diffractometer (MX-Labo; Mac Science Ltd., Tokyo, Japan) CuK*a* radiation, which had been monochromatized using a curved graphite, was used. For photoluminescence measurements of the powder samples, a spectrofluorometer (FP-6500; Jasco Inc.) equipped with a Xe lamp was used at room temperature.

Results and discussion

The $La_2WO_6:Eu^{3+}$ phosphors with $0<x<0.33$ in $(La_{1-x} Eu_x)_2WO_6$ were synthesized using melt technique within a short period of 5–60 s in a single step from a mixed oxide powder. The melt synthesis is a high-temperature approach for inorganic materials synthesis, whereas solid-state synthesis is a low-temperature approach. The melt synthesis might produce metastable or high-temperature phases from a molten state, which might not be formed by solid-state reactions, even after a prolonged heating process. Doped activator Eu^{3+} is replaced homogeneously by the La site, which is a rare-earth element. Homogeneous distribution of small amounts of activator ions in the host materials is quite important for synthesis of a phosphor. In this sense, the melt-synthesis is advantageous. The sample prepared using melt synthesis was of globular shape with about 5 mm diameter (Fig. 2). Figure 3 depicts X-ray diffraction patterns of the synthesized $La_2WO_6:Eu^{3+}$ phosphor samples. The samples were doped with low concentrations of Eu^{3+} crystallize in a γ-type phase, although the samples with high concentrations crystallize in a β-phase. In the La_2O_3-WO_3 binary system, no detailed information exists for crystallographic data based on single crystal structure determination. According to reference [12], there are three morphologies of α-, β-, and γ-phases for La_2WO_6 deduced from the phase diagram. The phase transition between the α-phase and β-phase occurs reversibly at 1440±30°C. Both the α-phase and β-phase are high-temperature forms that are not stable at room temperature. In addition, the γ-phase is reportedly obtained by annealing treatment [12]. In fact, we obtained La_2WO_6 as a γ-phase by the solid-state reaction at 1400ºC for 12 h or 1500°C for 12 h. In other words, the γ-phase seems to be a stable phase at room temperature for La_2WO_6. As depicted in Fig. 3, although the diffraction intensities of the γ-phase are small, the La_2WO_6 samples doped with 1% and 5% Eu consist mainly of γ-phase (γ-La_2WO_6). The La_2WO_6 samples doped with 25% Eu and 33% Eu consist mainly of high-temperature β-phase (β-La_2WO_6). Because the melt synthesis has a high cooling rate of more than 100°C/s, it is possible to obtain a phase that is stable just below the melting temperature. Furthermore, the large difference in ionic radius between La^{3+} and Eu^{3+} is one factor for β-phase stabilization. These results lead to the conclusion that the melt synthesis was able to yield a high-temperature phase easily.

Figure 4 presents emission and excitation spectra of the La_2WO_6:Eu^{3+} samples. The CIE chromaticity value of La_2WO_6:Eu^{3+} is $(x, y) = (0.648, 0.338)$. In La_2WO_6:Eu^{3+} samples, the red emission spectral intensity of $^5D_0 \rightarrow {}^7F_2$ (613 nm) increased with Eu^{3+} contents up to x=0.25. In most Eu^{3+}-activated red phosphors, the luminescence intensity usually decreases when the Eu^{3+} concentration is greater than several mol% because of concentration quenching [13]. Regarding research of red phosphors showing less concentration quenching, several research groups have recently reported some molybdate and tungstate phosphors with sheelite-type structures that performed strong f–f excitations of Eu^{3+} around 395 nm [14–16]. The compound of La_2WO_6 is composed of a large anionic radius, which is, respectively, 1.03 and 0.60 for La^{3+} and W^{6+}. It is assumed that, for large anion, long distance between emission ions saves migration of the excitation energy between emission ions. All excitation spectra monitored at 618 nm consist of two interwoven broad excitation bands (215–350 nm), belonging to a strong charge-transfer band (CTB) of W^{6+}-O^{2-} at the UV region (215–280 nm) and another weak CTB of Eu^{3+}-O^{2-} (λ_{max} -285 nm) at the near-UV region (250–350 nm), and several sharp excitation lines of Eu^{3+} 4f levels between 350–500 nm. When the CTB is excited, the energy absorbed from the charge-transfer state is transferred efficiently to the Eu^{3+} ion by a nonradiative mechanism. It generates red-light emission of the $^5D_0 \rightarrow {}^7F_J$ transition of Eu^{3+} [17]. Figure 5 portrays a comparison of emission spectra. The melted sample shows the emission, which is twice the intensity to that of the solid-state reacted samples, because the single β-phase was not obtained using a conventional solid-state reaction at 1000°C, 6 h. In addition, the commercial red phosphor, Y_2O_3:Eu (Tokyo Kagaku Kenkyusho Co. Ltd.), shows about half the emission intensity of the La_2WO_6 melted sample. The internal efficiency of 25% doped La_2WO_6:Eu^{3+} sample was 22% at room temperature (λ_{ex}=395 nm). It is higher than $Y_{1.98}Eu_{0.02}WO_6$ [18].

Conclusions

- Oxide phosphors were synthesized using a rapid reaction via a melt-solidification technique with an arc-imaging furnace.
- A single high-temperature β-phase, and stable γ-phase of the phosphor La_2WO_6:Eu^{3+} were synthesized
- These PL measurement results show that the intensity ratio of $^5D_0 \rightarrow {}^7F_2$ differed according to the Eu^{3+} concentration.
- Because La_2WO_6 was composed of large anion, the Eu^{3+} concentration quenching slightly decreased in this

compound.

Acknowledgements

The authors are thankful to Dr. A. K. Subramani of the Tokyo Institute of Technology for meaningful discussions. This work was supported by the project of Center for Transdisciplinary Research, Niigata University and The MEXT project G-COE Young Researchers grant, Tokyo Institute of Technology.

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Figure 1

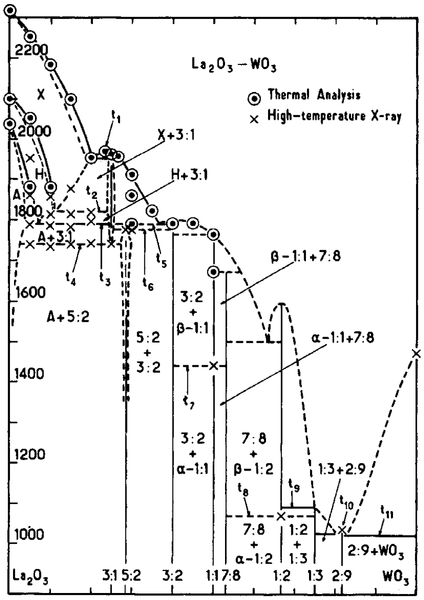
$La_2O_3 - WO_3$
⊙ Thermal Analysis
× High-temperature X-ray
2200
2000
1800
1600
1400
1200
1000
X
H
A
A+3:1
A+5:2
X+3:1
H+3:1
t1
t2
t3
t4
t5
t6
t7
t8
t9
t10
t11
5:2 + 3:2
3:2 + β-1:1
3:2 + α-1:1
β-1:1+7:8
α-1:1+7:8
7:8 + β-1:2
7:8 + α-1:2
1:2 + 1:3
1:3+2:9
2:9+WO_3
La_2O_3
3:1
5:2
3:2
1:1
7:8
1:2
1:3
2:9
WO_3

Figure 2

Figure 3

Figure 3

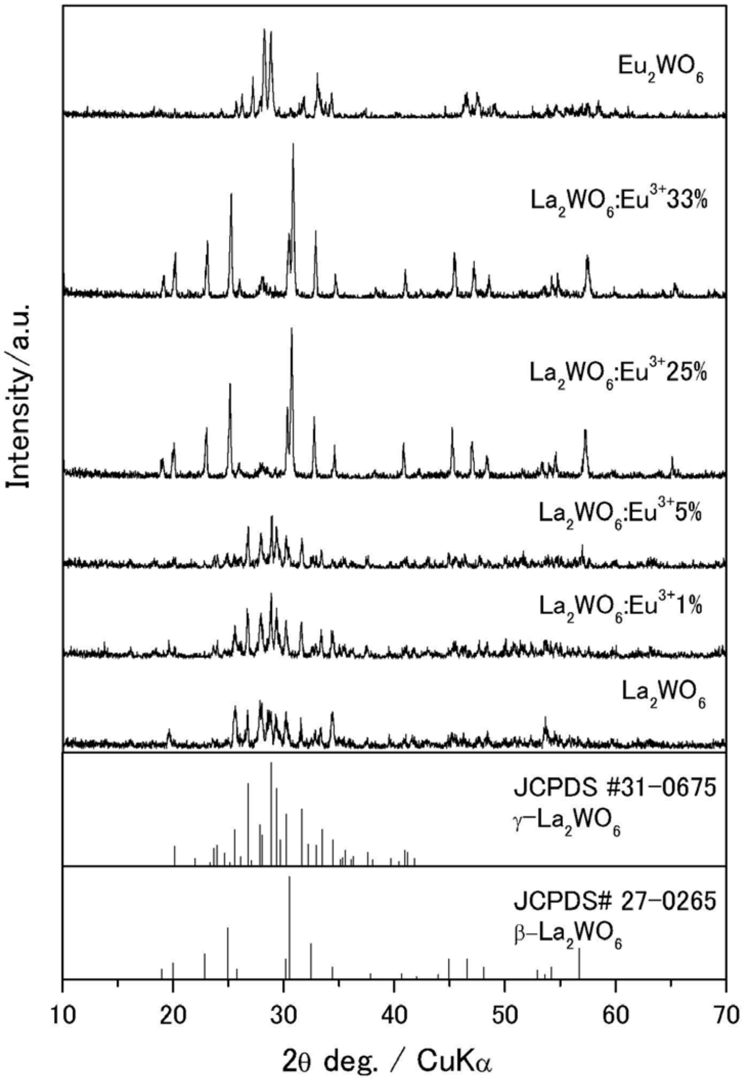

Figure 4

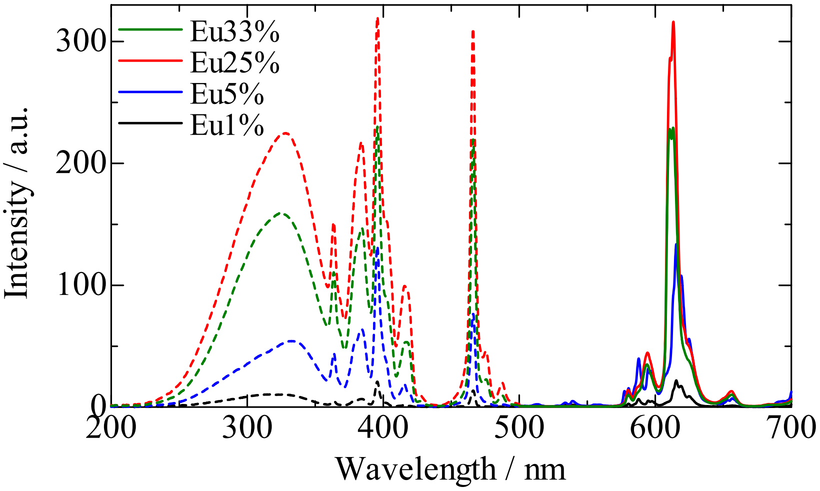
Eu33%
Eu25%
Eu5%
Eu1%
Intensity / a.u.
0
100
200
300
200
300
400
500
600
700
Wavelength / nm

Figure 5

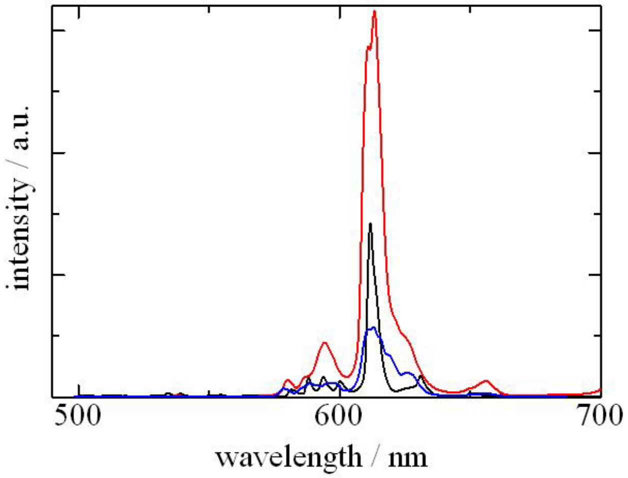

Figure 1

Phase diagram of the system La_2O_3-WO_3. Refer to [2].

[t_n°C] : t_1=1960±30, t_2=1820±30, t_3=1790±30, t_4=1740±30, t_5=1790±30, t_6=1770±30, t_7=1440±30, t_8=1067±10, t_9=1068±10, t_{10}=1030±10, t_{11}=1020±10.

Figure 2

Schematic illustration of melted sample La_2WO_6:Eu^{3+}.

Figure 3

XRD patterns of the sample La_2WO_6:Eu^{3+}; depend on Eu^{3+} concentration, comparison with JCPDS #31-0675(γ-La_2WO_6) and #27-0265(β-La_2WO_6).

Figure 4

Emission and excitation spectra of La_2WO_6:Eu^{3+} phosphor samples showing $(La_{1-x}Eu_x)_2WO_6$: $0.01<x<0.33$.

Dotted lines are excitation spectra (λ_{em}=613 nm); solid lines are emission spectra (λ_{ex}= 395 nm).

Figure 5

Emission spectra comparison of synthesis, melt, solid-state reaction, and commercial sample (λ_{ex}= 395 nm).

Red, melted sample $(La_{1-x}Eu_x)_2WO_6$ (x=0.25); Blue, solid state reaction $(La_{1-x}Eu_x)_2WO_6$ (x=0.25); Black, commercial Y_2O_3:Eu.