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Gel combustion synthesis of fine crystalline $(Y_{0.95}Eu_{0.05})_2O_3$ phosphor in presence of lithium flux

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Abstract

Gel combustion synthesis of $(Y_{0.95}Eu_{0.05})_2O_3$ phosphor was performed in presence of several kinds of lithium salt flux. Luminescence intensity of the products and the appearance of combustion reaction were different with the kind and the amount of Li salts added. There were two maxima in the intensity against the Li amount; one is due to Li doping into $(Y_{0.95}Eu_{0.05})_2O_3$ lattice and another is flux effect. The highest luminescence intensity was obtained for the product synthesized with adding 60 wt.% LiCl. It was about 2.5 times larger than that of $(Y_{0.95}Eu_{0.05})_2O_3$ synthesized without flux, and almost comparable to that of commercial sample.

Keywords: Y_2O_3:Eu; Luminescence; Combustion; Sol–gel synthesis; Flux

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1. Introduction

Fine particle is very important in many applications and also required in the area of phosphor. Fine particle phosphors result in high resolutions, high densities, and small consumption in displays, and may also exhibit unique physical properties [1]. Although fine particle phosphor has been synthesized in several methods [2,3], the luminescence intensity decreases compared with commercially available micron size phosphor. Imperfections in the surface region affect the luminescence properties. This effect is enhanced because the surface to volume ratio increases in fine particle phosphors. It is especially important for phosphors used in plasma display panels (PDP) and field emission display (FED), where the excitation energy is absorbed on the surface of the phosphor reflecting short wavelengths (147 nm) for PDP and low excitation voltages (0.5–10 kV) for FED [4]. It is necessary to improve the surface of fine particle phosphor.

We synthesized fine particle red-emitting Y_2O_3:Eu by gel combustion method [5]. A nitrate oxidant with a gelling agent such as glycine worked as a fuel in this method. Fine oxide particles, less than 100 nm particle size, was obtained because gases such as H_2O and CO_2 were generated from the mixture in only a few seconds during the exothermic reaction. The molar ratio of glycine to nitrate was important to control crystallinity, morphology and luminescence intensity of the products. The fine particles formed a porous agglomerate. The luminescence intensity was much lower than that of commercial sample as is the case with the fine particle phosphor synthesized in different synthesis methods. Crystallinity and dispersion of the fine particles would be important to improve the luminescence intensity. In conventional solid-state synthesis of phosphor, halide and carbonate have been used as fluxes to grow the crystals and to improve their crystallinity.

In the present study, fine crystalline $(Y_{0.95}Eu_{0.05})_2O_3$ phosphor was prepared by gel combustion in presence of various kinds of lithium flux. Luminescence property was studied with morphology by changing the kinds and the amount of Li salts as flux.

2. Experimental

$Y(NO_3)\cdot 6H_2O$ (Wako 99.9%) and $Eu(NO_3)\cdot 5H_2O$ (Aldrich 99.9%) were dissolved in a ratio of Y:Eu = 0.95:0.05

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in distilled water with the molar ratio of glycine (Wako GR) to nitrate of 1.5. LiCl (Kanto GR), LiF (Wako GR) or Li_2SO_4 (Wako GR) were used as Li fluxes. They were added to the nitrate solution with the ratio of 0.4–80 wt.% of the nitrate. This solution was heated in a crucible on a hot plate to obtain a viscous gel. When most of the water had evaporated, the crucible was put into a pre-heated muffle furnace at 300 °C for 30 min, where combustion occurred and fine particles were obtained. X-ray diffraction (XRD) patterns were recorded with a Philips X'pert diffractometer with monochromatized Cu Kα radiation. Photoluminescence (PL) spectra were measured with a spectrofluorometer (JASCO FP6300). The powder morphology was observed by transmission electron microscope (TEM) (JEOL JEM2000FX).

3. Results and discussion

In gel combustion, an explosive reaction vigorously occurred with fire and sound at an appropriate mixing ratio of glycine to nitrate. The combusted product was dispersed thoroughly inside the muffle furnace. The appropriate glycine to nitrate ratio is around 1.5 [5] and this ratio was kept in this experiment. The appearance of reaction changed with the amount of Li salt added. The above-mentioned vigorous reaction was observed below 20 wt.% of the added Li salt. Above 30 wt.%, the product was a dome shaped lump. No dispersion of product and sound were observed. Heat produced in the combustion reaction got smaller with the amount of Li salts.

Fig. 1 shows XRD patterns of $(Y_{0.95}Eu_{0.05})_2O_3$ prepared by gel combustion with 30 or 40 wt.% Li salt and without Li salt. $(Y_{0.95}Eu_{0.05})_2O_3$ phase was observed in all patterns. Li_2SO_4 and LiF were recognized on the products combusted in presence of Li_2SO_4 and LiF, respectively. There were no peaks of LiCl in the product combusted in presence of LiCl. LiCl may be present as amorphous phase in the product because of its high hygroscopic character. The peak intensity was a little weaker for combusted sample with Li salt than the combusted sample without the salt. This is due to a decrease in relative amount of $(Y_{0.95}Eu_{0.05})_2O_3$ in the product.

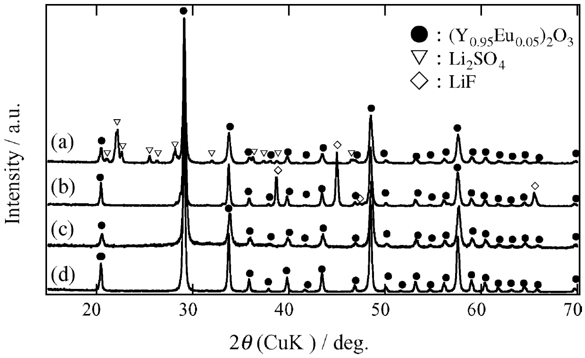

Fig. 1. XRD patterns of gel combusted $(Y_{0.95}Eu_{0.05})_2O_3$ with different kinds of Li salts and without Li salt: (a) 40 wt.% Li_2SO_4, (b) 40 wt.% LiF, (c) 30 wt.% LiCl and (d) without Li salt.

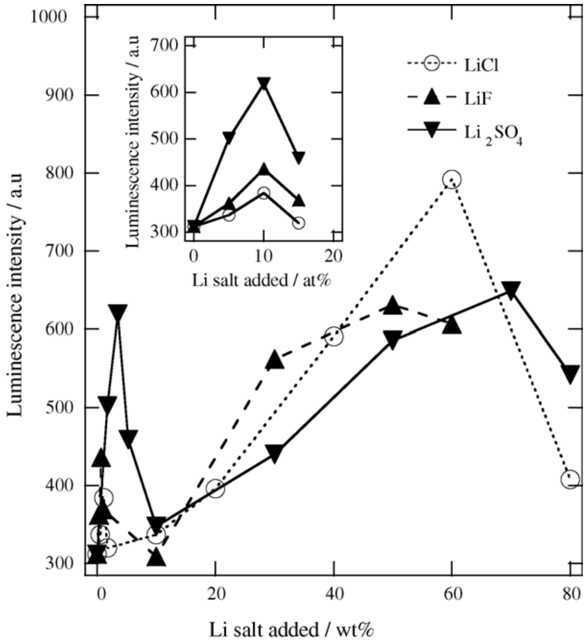

Fig. 2. Luminescence intensity against Li salts added as fluxes in their concentrations ~80 wt.% and ~20 at.%.

All products showed the main peak at 612 nm of the $^5D_0$–$^7F_2$ transition of Eu^{3+} in their emission spectra. The luminescence intensity excited by 280 nm light changed with the amount of Li salt as shown in Fig. 2. There were two compositional regions where luminescence intensity was enhanced. At low Li concentration range, the luminescence intensity enhanced rapidly. It had maximal values at 10 at.% independently on the kind of Li salts as shown in an inset of

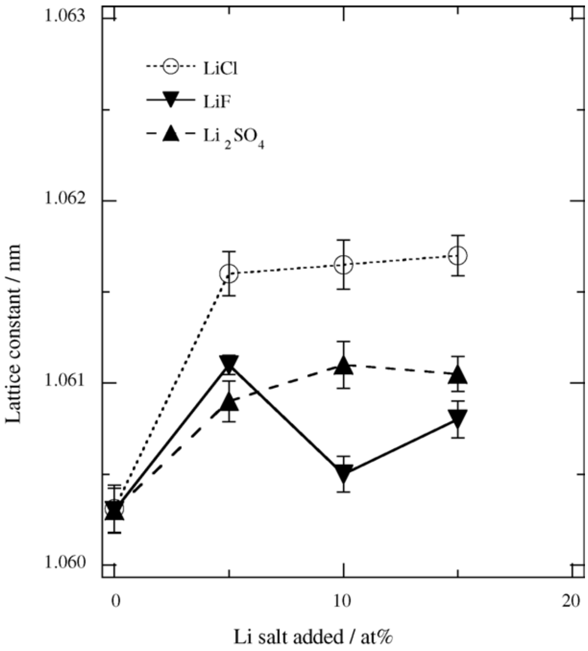

Fig. 3. Lattice constant of $(Y_{0.95}Eu_{0.05})_2O_3$ against the Li salt amount added in the preparation.

expanded compositional range, where wt.% is converted to at.%. The largest intensity was obtained for the combusted sample with Li_2SO_4. In higher Li salt concentration range, the luminescence intensity increased gradually and showed maximal value at 50–70 wt.% although the volume fraction of $(Y_{0.95}Eu_{0.05})_2O_3$ was small in the product. The highest luminescence intensity was observed for combusted product with 60 wt.% of LiCl. The intensity was about 2.5 times larger than that of $(Y_{0.95}Eu_{0.05})_2O_3$ synthesized without flux and almost as same as those of commercial samples.

Lattice parameter of $(Y_{0.95}Eu_{0.05})_2O_3$ changed against the Li salt amount in the lower concentration region as shown in Fig. 3. The value of 1.0603 nm obtained from the product synthesized without Li salt was nearly the same as a reference value of 1.0604 nm (JCPDS 25–1011). The lattice parameter expanded with the amount of Li salt. This lattice expansion indicates that Li is incorporated into $(Y_{0.95}Eu_{0.05})_2O_3$ lattice as well as its flux effect. When Li^+ replaces the Y^{3+} site in Y_2O_3 structure, oxygen vacancy is generated according to the formula $(Y_{0.95}Eu_{0.05})_{2-x}Li_xO_{3-x}$. The lattice might expand because of a repulsive interaction between cations having oxide anion vacancy. Reducing the site symmetry in Eu^{3+} site by Li^+ doping may increase transition probability of electron and enhance the luminescence intensity. Higher Li doping into $(Y_{0.95}Eu_{0.05})_2O_3$ lattice decreased the luminescence intensity as shown in Fig. 2. Too much deficiency in crystal quench the luminescence. Similar Li effect on luminescence has been reported in a glycine gel combustion of Y–Eu–Li nitrates mixture [6].

Fig. 4 shows TEM photographs of $(Y_{0.95}Eu_{0.05})_2O_3$ prepared by gel combustion with 10 at.% Li salt and without Li salt. The crystal size of $(Y_{0.95}Eu_{0.05})_2O_3$ prepared by gel combustion with 10 at.% Li salt was almost the same as the product prepared without Li salt. The surface crystallinity seemed to be a little improved by Li salts worked as fluxes. Li salts have two kinds of roles in its low concentration; predominant one was the Li source for doping into Y_2O_3:Eu lattice and another was flux. Lithium doping into Y_2O_3:Eu

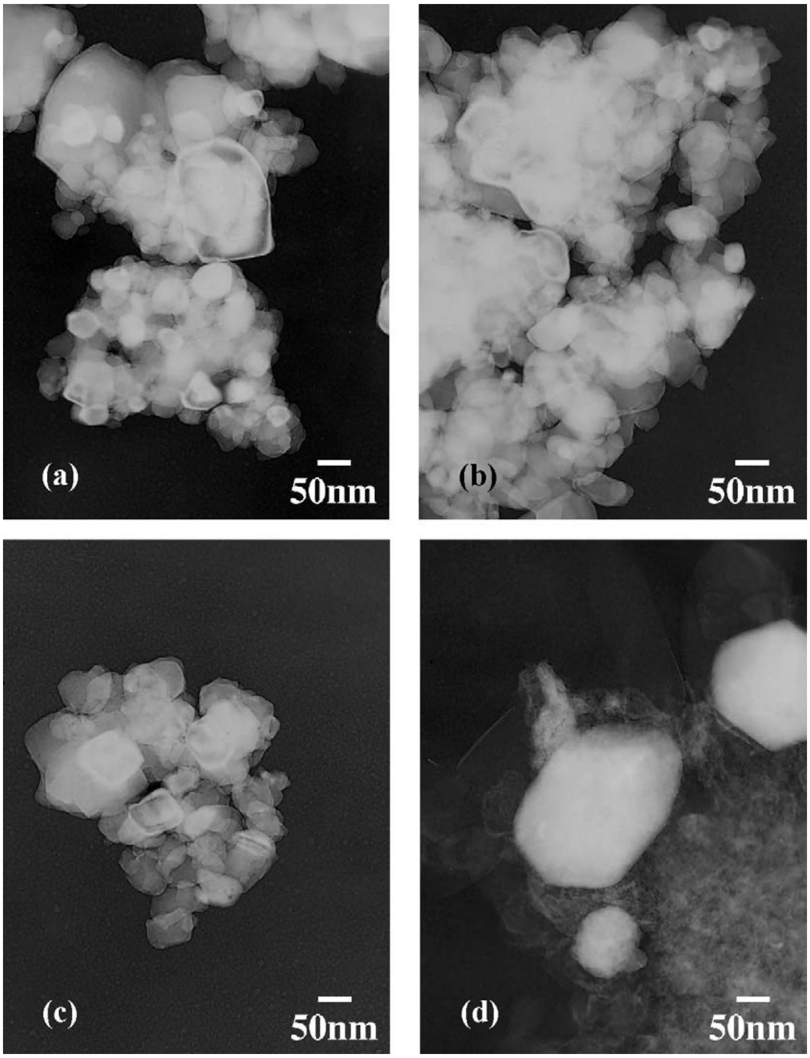

Fig. 4. TEM photographs of $(Y_{0.95}Eu_{0.05})_2O_3$ prepared by gel combustion: (a) with 10 at.% LiF, (b) 10 at.% LiCl, (c) without Li salt and (d) with 60 wt.% LiF.

lattice have been reported in several papers [6–8]. Li doping and improvements of morphology and dispersion have been described as the cause of the luminescent enhancement. It is necessary to carry out chemical analysis in detail to elucidate the Li doping into Y_2O_3:Eu lattice.

In higher Li salt concentration, the lattice constant of $(Y_{0.95}Eu_{0.05})_2O_3$ was nearly the same as the value obtained in 15 at.% Li salt addition. Solid solution limit of Li incorporation may have passed in this concentration. The luminescence intensity increased gradually with its maxima at 50–70 wt.% as mentioned above. Fig. 4(d) shows TEM photograph of $(Y_{0.95}Eu_{0.05})_2O_3$ prepared by gel combustion with 60 wt.% LiF. Large crystals of ca. 200 nm in diameter were dispersed in a matrix. The matrix may be LiF remained in the product because it moved around in TEM observation by electron beam radiation. The improvement of surface crystallinity was not apparent in this observation because the crystal surface was covered by LiF. Flux effect was predominant in the higher Li salt concentration. It is necessary to observe TEM in detail to study the improvement of surface crystallinity.

In conclusions, gel combustion synthesis of $(Y_{0.95}Eu_{0.05})_2O_3$ phosphor was performed in presence of several kinds of lithium salt flux. Luminescence enhancement was observed in both lower and higher concentration of Li salts addition. The Li doping into $(Y_{0.95}Eu_{0.05})_2O_3$ lattice and the crystal growth by using Li salt flux contributed to the respective luminescence enhancements in lower and higher concentration Li salts addition.

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