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To cite this article: Hidetoshi Saitoh *et al* 2005 *Sci. Technol. Adv. Mater.* **6** 205

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Metal composition of $Y_2O_3:Eu$ powder evaluated using particle analyzer

Hidetoshi Saitoh^{a,*}, Ken-ichiro Kawahara^a, Shigeo Ohshio^a, Atsushi Nakamura^{a,b},
Nobuyoshi Nambu^{a,b}

^aDepartment of Chemistry, Nagaoka University of Technology, 1603-1 Kamitomioka, Nagaoka Niigata 940-2188, Japan

^bChubu Chelest Co. Ltd, 3-3 Hinagahigashi 3-chome, Yokkaichi, Mie 510-0886, Japan

Received 15 September 2004; revised 20 October 2004; accepted 24 November 2004

Abstract

$Y_2O_3:Eu$ red phosphor powder was synthesized with powders of metal–ethylenediaminetetraacetic acid (EDTA) complexes as a starting material. The compositional analysis of each metal–EDTA complexes particle and $Y_2O_3:Eu$ particle was performed using a particle analyzer. In this study, first, the particles of a mixture of Y– and Eu–EDTA complexes were obtained by a spray drying method from solution consisting of Y– and Eu–EDTA· nNH_4 . Then, the metal–EDTA complex powder was fired in obtaining the $Y_2O_3:Eu$ red phosphor. The metal composition of each particle was scattered for the powder of the metal–EDTA mixture, while it became narrow for the $Y_2O_3:Eu$ powder. The intensity of cathodoluminescence obtained from the $Y_2O_3:Eu$ powder increased with increasing the fired temperature. In addition, the maximum intensity was obtained from the sample with $x=0.12$ for $Y_{2-x}O_3:Eu_x$.
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Keywords: Metal–EDTA complex; Spray dry; Phosphor; $Y_2O_3:Eu$; Cathodoluminescence; Particle analyzer

1. Introduction

Synthesis of fine ceramics particles with a uniform metal composition attracts much attention widely. An example of the ceramic powder that needs uniform metal composition is RGB phosphors utilized in the color display, such as $Y_2O_3:Eu$, $ZnSi_2O_4:Mn$ and $BaMgAl_{10}O_{17}:Eu$. The ceramic phosphor powder possesses the complicated metal composition with a small quantity of the dopant introduced as a luminescence center.

The synthesis of the $Y_2O_3:Eu$ red phosphor is carried out through a direct solid-state reaction method. The powders of Y_2O_3 and Eu_2O_3 are first mixed mechanically, then these atoms diffuse each other at the temperatures over 1200 °C. As the red phosphor for the commercial use includes Eu with a desired concentration, the starting powders should be mixed uniformly with well-controlled atomic fraction. Therefore, much efforts are needed to manufacture well-designed ceramic phosphor industrially by the direct solid-phase reaction.

We have proposed a new concept of the synthetic method of ceramic particles that satisfy following two conditions: the particle size of several micrometers and uniform metal composition among the particles. This process uses the solution of metal–ethylenediaminetetraacetic acid (EDTA) as a starting material [1,2]. In this process, the particles of the mixture of metal–EDTA complexes are obtained by a spray drying method from solution consisting of M–EDTA· nNH_4 (M: metal), followed by a firing process of the metal–EDTA complex mixture. We believe that this process may have an ability to design uniform metal composition among the particles due to the uniform composition in solution of metal–EDTAs.

We have synthesized the metal–EDTA target that consists of (Sr, Ba, Ti)–EDTA or (Y, Ba, Cu)–EDTA for the ceramic film synthesis using laser ablation [3–5]. For the film synthesis of (Sr, Ba)TiO₃, the metal composition of the films indicated approximately 1.00 for the value of [Sr]/[Ti] without Ba presence in the target. In addition, the composition of Ba in the film was well-designed by variation of the Ba composition in the target.

In this study, the metal composition of each metal–EDTA particle and fired $Y_2O_3:Eu$ particle was evaluated using a particle analyzer. The particle analyzer uses

* Corresponding author. Tel.: +81 258 47 9316; fax: +81 258 47 9300.
E-mail address: hts@nagaokaut.ac.jp (H. Saitoh).

the microwave-induced He plasma to analyze the elemental composition and the particle size of each micro sized particle directly. The detection of halogens and light elements is also possible. This technique has been used for the analysis of presence of the particles inside the clean room and the analysis of the composition of the toner on the photo-sensitive drum equipped in the copy machine [6]. As the $Y_2O_3:Eu$ ceramic powder is useful for the electron-excited red phosphor, cathodoluminescence measurement was also performed.

2. Experimental

The following materials were used: $EDTA \cdot 2NH_4$ (99.9%) is from Chubu Chelest Co.; $Y_2(CO_3)_3 \cdot 3H_2O$ (99.99%) and Eu_2O_3 (99.95%) were supplied by Kanto Chemical Co. The chelating procedure is explained using an example of $EDTA \cdot Y \cdot NH_4$ synthesis. First, 0.6 M $EDTA \cdot 2NH_4$ was solved into deionized water followed by gentle stirred for 0.5 h at a temperature of 60 °C. Next, the mixture of $Y_2(CO_3)_3 \cdot 3H_2O$ and $EDTA \cdot 2NH_4$ solution was stirred for 2 h at a temperature of 100 °C. Furthermore, the solution was concentrated using an evaporator to form solution slurry. The slurry was cooled at the ambient temperature and stirred for 12 h. Finally, the crystal form of $EDTA \cdot Y \cdot NH_4$ was obtained from the slurry using a centrifuge. Other crystalline chelate, $EDTA \cdot Eu \cdot NH_4$ was also synthesized same procedure.

In this experiment, a detailed comparative evaluation was carried of two types of the chelate mixture. One was produced by the conventional route of mixing, milling of crystalline chelate in an agate mortar, the other was made using spray-drying of chelate solution. A spray dryer with a double-fluid nozzle was employed in this experiment. A solution tank has a charging capacity of 3 l. The metal-EDTA solution is sprayed with a rate of 300 ml/h, that produces metal-EDTA powder with a manufacturing speed of 50 g/h. To synthesize $Y_2O_3:Eu$ powder, optimum quantities of $EDTA \cdot Y \cdot NH_4$ and $EDTA \cdot Eu \cdot NH_4$ crystalline powders were mixed. For mechanical mixing, the sample was milled in the agate mortar for 1 h. On the other hand, to prepare chelate solution for the spray-dry method, $EDTA \cdot Y \cdot NH_4$ and $EDTA \cdot Eu \cdot NH_4$ crystalline powders were solved into deionized water followed by gentle stirred for 0.5 h at pH 5–6. The mixture of solution was dried using the spray-dryer at a drying temperature of 160 °C. Both samples are fired to obtain $Y_2O_3:Eu$ powder using an air-opened electric furnace.

The metal composition of each particle was determined using the particle analyzer DP-1000 manufactured by Horiba Co. In addition, the metal composition of the powders was evaluated by inductive coupled plasma-atomic emission spectroscopy (ICP-AES) with a Seiko Instruments, SPS-400. A scanning electron microscope (SEM; JSM T-300, JEOL) was used to detect the cathodoluminescence of

the phosphor. The particle analyzer is employed for the evaluation of the metal composition of each micro-particle. First, micro-particles are gathered on the filter using a sampler. Then, the particles are carried into the microwave discharge room by He gas flow. The particles are introduced into the discharge room by a supplying rate of 1000 particles each minute. The luminescence from the Y and Eu atoms is detected by a photomultiplier from the direction of opposite side of the He-gas carrier flow. Although the luminescence intensity obtained from the atoms is strongly dependent on the particle size, the relationship between the intensity of the atoms and the particle size follows the linear function basically.

3. Results and discussion

3.1. Metal composition of each particle

3.1.1. EDTA powder

The metal composition of Y-EDTA, (Y, 5% Eu)-EDTA and (Y, 10% Eu)-EDTA powders was evaluated by a synchronized distribution technique using the particle analyzer. The synchronized distribution technique adopts data when the emissions from two elements are detected at a moment. It guarantees that the equipment detects the emission from one specific particle. Fig. 1 shows the synchronized distribution obtained from the Y-EDTA particles. The longitudinal and horizontal axes are the cube root of the intensities emitted from Eu and Y atoms, respectively. The cube root axes rearrange the relationship between the intensity and particle size to be linear function. The distribution is divided two regions. The first region identified by the capital letter A is attributed to the optical emission from the Y atom. If only the Y atoms exist in the particle, data should be plotted on the horizontal axes. However, the distribution denoted as capital letter A separated from the X axis due to the strong interference on the signal position of Eu from the strong signal of the Y atom. Unfortunately, this analytical system cannot avoid such

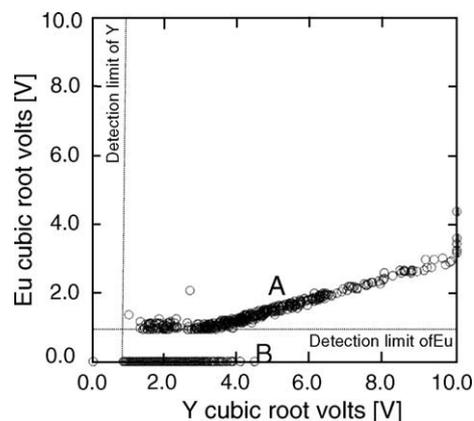


Fig. 1. Synchronized distribution obtained from the Y-EDTA particles.

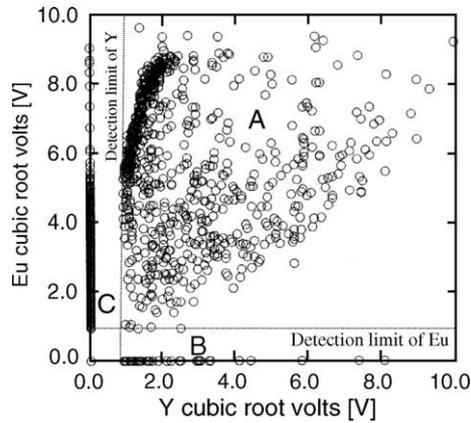


Fig. 2. Synchronized distribution obtained from the (Y, 5% Eu)-EDTA particles.

problem. The second region identified by the capital letter B is attributed to the Y signal. In this region, the interference on the signal portion of Eu is below the detection limit of the Eu signal. If the system has no detection limit, region B would be on the extension of the region A.

Fig. 2 shows the synchronized distribution obtained from the (Y, 5% Eu)-EDTA particles. Three regions are obtained in the distribution. The wide scattered region identified by the capital letter A is attributed to the region in which luminescence from Y and Eu atoms are detected at a moment. Two regions B and C are attributed to the Y and Eu signals with the relatively low intensity that is below the detection limit, respectively. If the system has no detection limit, the regions B and C would be in the extension of the region A. Fig. 3 also indicates the synchronized distribution obtained from the (Y, 10% Eu)-EDTA particles. The result implies that the Eu composition is higher than that obtained in Fig. 2.

As a comparative experiment, the mixture of Y-EDTA and 5% Eu-EDTA formed using the mortar was also evaluated by the synchronized distribution as shown in Fig. 4. In this result, four regions are obtained in the distribution. The region A is attributable to the existence of

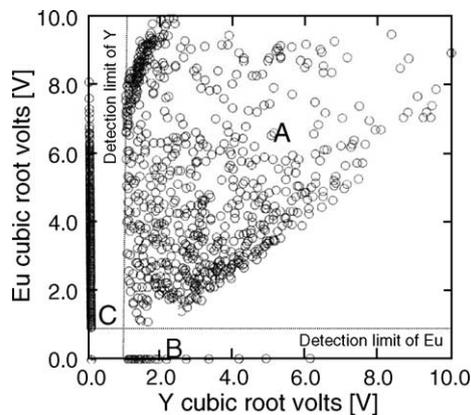


Fig. 3. Synchronized distribution obtained from the (Y, 10% Eu)-EDTA particles.

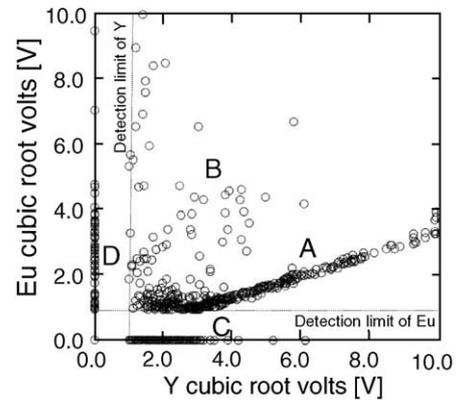


Fig. 4. Synchronized distribution obtained from the mixture of Y-EDTA and 5% Eu-EDTA formed using the mortar.

Y-EDTA, suggesting that Y-EDTA and Eu-EDTA are not mixed completely. The region B implies that a few particles of the Y-EDTA crystals associate with the Eu-EDTA crystal by the result of mixing. Two regions C and D are attributed to the Y and Eu signals, which are below the detection limit, respectively. If the system has no detection limit, the regions C and D would be in the extension of the regions A and B.

3.1.2. Phosphor powder

The ceramic powders obtained by firing of Y-EDTA, (Y, 5% Eu)-EDTA and (Y, 10% Eu)-EDTA were also measured by a synchronized distribution technique using the particle analyzer.

Fig. 5 shows the synchronized distribution obtained from the Y_2O_3 powder formed from Y-EDTA particles, indicating the similar distribution with that obtained in Fig. 1. However, the distribution obtained from $Y_2O_3:Eu$ powder is different from the results of the EDTA mixture, as shown in Figs. 6 and 7. The synchronized distribution obtained from the $Y_2O_3:Eu$ particles formed by (Y, Eu)-EDTA is divided into three regions. Relatively narrow scattered region identified by the capital letter A is attributed to the region in which luminescence of Y and Eu atoms are detected at a moment. Two regions B and C are attributed to the Y and Eu signals,

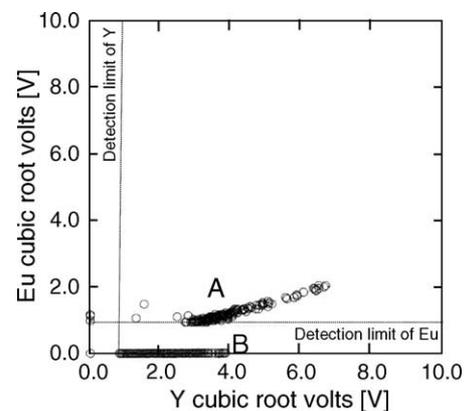


Fig. 5. Synchronized distribution obtained from the Y_2O_3 powders formed from Y-EDTA particles.

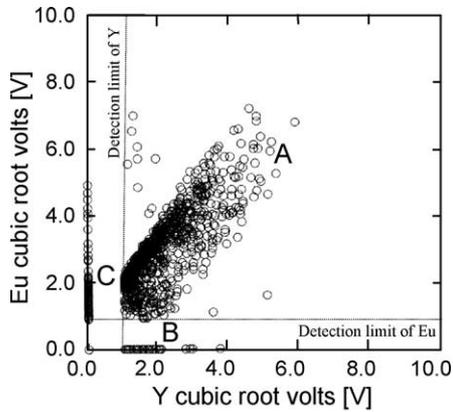


Fig. 6. Synchronized distribution obtained from the $Y_2O_3:Eu$ particles formed with the (Y, 5% Eu)–EDTA particles.

which are below the detection limit, respectively. Note that the degree of scatter at the region A is narrower than that observed in Figs. 2 and 3. This phenomenon might come from biased distribution of the composition in each particle. During the spray dry procedure, Y– and Eu–EDTAs might be separated in the particle due to the difference of solubilities between two EDTAs. Therefore, preferential separation of Eu–EDTA in the particle is expected. In the He plasma discharge room, two typical cases may occur: (1) the part of preferential separation appears on the surface of the particle; (2) it appears inside of the particle. Although the former case indicates strong luminescence, the latter case generates relatively weak luminescence by He plasma excitation. The biased distribution of the composition may result the wide scatter on the synchronized distribution. Once the mixture of (Y, Eu)–EDTA is fired, the Y and Eu atoms diffuse each other during sintering. Therefore preferential separation of Eu atoms may disappear, resulting narrow distribution as indicated in Figs. 6 and 7.

As a comparative experiment, ceramic powder sintered with the mixture of Y–EDTA and 5% Eu–EDTA using the mortar was also evaluated by the synchronized distribution as shown in Fig. 8. In this result, four regions are

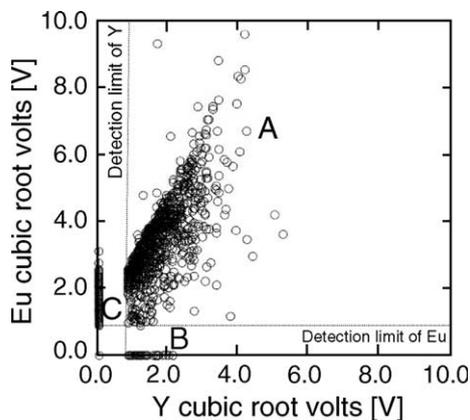


Fig. 7. Synchronized distribution obtained from the $Y_2O_3:Eu$ particles formed with the (Y, 10% Eu)–EDTA particles.

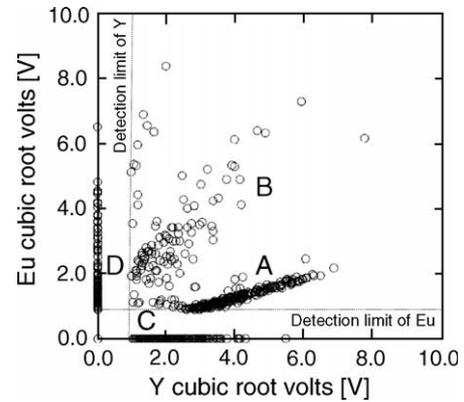


Fig. 8. Synchronized distribution obtained from the $Y_2O_3:Eu$ particles formed with the mixture of Y–EDTA and 5% Eu–EDTA formed using the mortar.

recognized. The region A is attributable to the existence of non-doped Y_2O_3 , suggesting that no uniform composition of Y and Eu is obtained. These results strongly support that the (Y, Eu)–EDTA particles are optimum for the starting material in obtaining $Y_2O_3:Eu$ ceramic phosphor with the uniform composition.

3.2. Cathodoluminescence

Fig. 9 demonstrates the cathodoluminescence spectra and their intensity obtained from the $Y_{1.94}O_3:Eu_{0.06}$ particles fired under various temperatures. Fig. 10 also shows

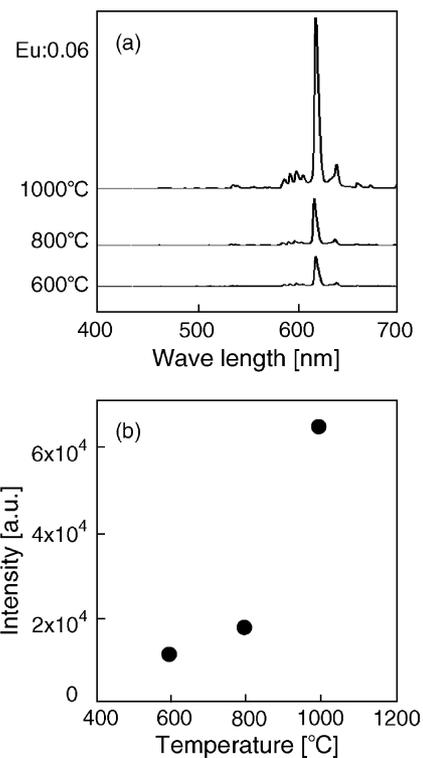


Fig. 9. (a) Cathodoluminescence of $Y_{1.94}O_3:Eu_{0.06}$ sample fired at various temperatures and (b) intensity of the peak at 611 nm.

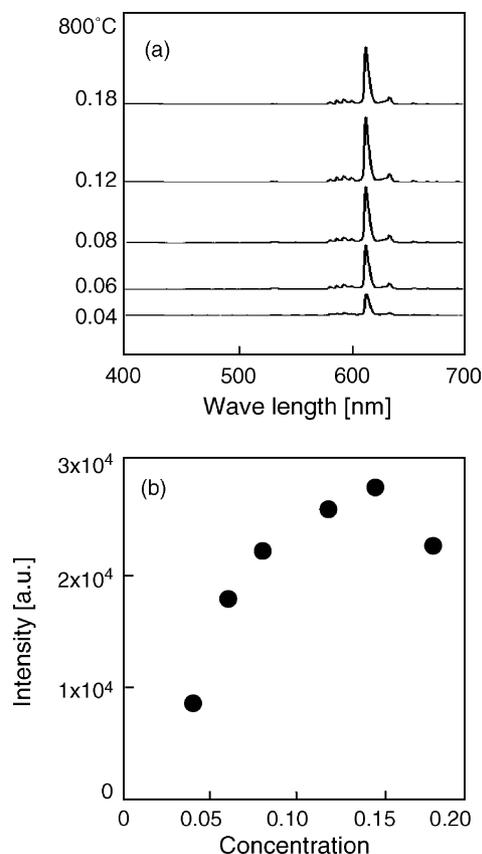


Fig. 10. (a) Cathodoluminescence of $Y_{2-x}O_3:Eu_x$ sample fired at various Eu concentrations (x) and (b) intensity of the peak at 611 nm.

the cathodoluminescence spectra and their intensity obtained from the $Y_{2-x}O_3:Eu_x$ ($x=0.02 \sim 0.18$) particles. These spectra obtained at an acceleration voltage for the electrons of 30 kV. All spectra indicated the peaks at 593, 599 nm as well as the most intense peak at 611 nm assigned to $^5D_0 \rightarrow ^7F_2$ transition [7,8]. The intensity of luminescence increased with increasing the fired temperature. In addition, the maximum intensity was obtained from the sample with $x=0.12$ for $Y_{2-x}O_3:Eu_x$.

In previous our investigation [9], the crystallite size of the $Y_2O_3:Eu$ red phosphor increased with increasing the firing temperature and firing duration. The peak intensity of the photoluminescence excited by 254 nm ultraviolet ray was also increased with the firing temperature and firing duration. Thus, the photoluminescence is strongly dependent upon the crystallite size of the phosphor. As compared with the results obtained in this study, the intensity of photo- and cathodoluminescence of the phosphor might be the function of the crystallite size. The luminescence of the phosphor obtained under the firing conditions of 1000 °C

and 3 h reached 81% of intensity obtained from the commercial red phosphor.

4. Conclusion

The mixture of (Y,Eu)–EDTA complexes was synthesized using the spray dry method. Although the wide distribution of the metal composition of each particle was observed from the mixture of (Y,Eu)–EDTA complexes, the distribution became narrow after firing of the sample formed by the spray dry method. The intensity of cathodoluminescence of the $Y_2O_3:Eu$ phosphor was increased with increasing the metal composition, suggesting that well-controlled doping of Eu was achieved.

Acknowledgements

This work was partially supported by the Futaba Memorial Foundation and 21st century COE program at Nagaoka University of Technology. We also thank to Horiba Co. for operation of the particle analyzer.

References

- [1] H. Saitoh, R. Satoh, A. Nakamura, N. Nambu, S. Ohshio, Metal oxide powder synthesized with amorphous metal chelates, *J. Mater. Sci.* 37 (2002) 4315–4320.
- [2] H. Saitoh, K. Kawahara, S. Ohshio, A. Nakamura, N. Nambu, Synthesis of blue phosphor by decomposition of metal complex powder, *J. Ceram. Soc. Jpn* 110 (2002) 874–876.
- [3] N. Tanaka, H. Wakabayashi, S. Mochizuki, S. Ohshio, H. Saitoh, Synthesis of Y–B–C–O films with EDTA complexes assisted by eximer laser ablation, *J. Mater. Res.* 13 (1998) 2775–2778.
- [4] N. Tanaka, S. Ohshio, H. Saitoh, K. Uematsu, Crystal growth of highly oriented zinc oxide by laser deposition technique with metal–EDTA complexes, *Jpn. J. Appl. Phys.* 37 (1998) L1165–L1168.
- [5] N. Tanaka, H. Wakabayashi, Y. Tanaka, S. Ohshio, H. Saitoh, K. Uematsu, Complex beam epitaxy of metal oxide films, *Mat. Res. Innovat.* 2 (1998) 39–44.
- [6] H. Takahara, M. Iwasaki, Y. Tanibata, Particle analyzer system based on microwave-induced plasma technology, *IEEE Trans. IE* 44 (1995) 819–823.
- [7] O.A. Serra, S.A. Cicillini, R. Ishiki, Photophysical properties of $Ce^{3+}:Tb^{3+}$ supported on silicas and zeolites, *J. Alloys Comp.* 225 (1995) 63–65.
- [8] K.L. Choy, J.P. Feist, A.L. Heyes, B. Su, Eu-doped Y_2O_3 phosphor films produced by electrostatic assisted chemical vapor deposition, *J. Mater. Res.* 14 (1999) 3111–3114.
- [9] A. Nakamura, N. Nambu, K. Kawahara, S. Ohshio, H. Saitoh, $Y_2O_3:Eu$ red phosphor powder synthesized with EDTA complexes, *J. Ceram. Soc. Jpn* 111 (2003) 142–146 (in Japanese).