

Thermal stability of high-pressure phase of SrO:Ce phosphor

Keiji Komatsu¹, Atsushi Nakamaura^{2,1}, Hidetoshi Saitoh¹

¹ Nagaoka Univ.of Tech.

1603-1 Kamitomioka-Machi, Niigata, Japan

Phone: +81-258-9379 E-mail: kkomatsu@vos.nagaokaut.ac.jp

² Chubu Chelest Co.,Ltd.

3-3-3 Hinagahigashi, Yokkaichi, Mie 510-0886, Japan.

Abstract

Alkaline-earth metal oxide having 6-coordinated configuration easily reacts with water because of their deliquescent nature. In this study, high-pressure phase (8-coordinated) of cerium-doped strontium oxide (SrO:Ce) phosphors were synthesized by sintering at 1500°C in reduction atmosphere, and investigated its thermal stability. Obtained results indicated that the 8-coordinated SrO:Ce ultraviolet phosphor have high thermal stability.

1. Introduction

Phosphor materials with high thermal/chemical stability are suitable for commercial applications. Performance of the phosphors are degraded by environmental effects. For examples, host materials degradation and oxidation of emission center by heating were reported [1]. In addition, the degradation by reacts with absorbed water were also reported because of humidity [2]. For plasma display panel (PDP) application, the phosphor materials should be stable under the annealing process at 500°C, typically in the PDP manufacturing process. Thus, optical and structural degradation tests have been conducted to investigate for applications.

We developed a new blue europium-doped strontium oxide (SrO:Eu²⁺) phosphor with orthorhombic lattice[3][4]. Obtained blue emission is originated from f-d transition of Eu²⁺ ion. The SrO:Eu²⁺ phosphor was assigned to 8-coordinated structure of SrO by crystal structure analysis. Many compounds at high pressures indicate crystalline lattice which is different from that existing at normal pressure. The 8-coordinated SrO at over 36 GPa is known as high-pressure phase [5,6]. The crystal structure of the alkaline-earth metal oxides existing at the normal pressure belong to the cubic crystal with 6-coordinated structure, such as NaCl-type structure. On the other hand, the crystal structure of the compound exciting at high-pressure is the cubic crystal with 8-coordinated structure, such as the CsCl-type structure. Furthermore, the obtained SrO:Eu²⁺ phosphor have a high structural stability compared to 6-coordinated SrO. The SrO are reacted with water easily. In contrast, the obtained SrO:Eu²⁺ phosphor show strong emission peak after immersion in water. In this study, we attempted to synthesize SrO:Ce phosphor. It is well known that the emission color is attributed to the 5d–4f transition of Ce³⁺, which depends strongly on the crystal field [7]. Ion radius of Ce³⁺ ion is 1.14 Å with 8 coordination number of oxygen[8]. The radius of Sr²⁺ and Eu²⁺ ions are 1.26 Å and 1.25 Å. The radius of Ce³⁺ ion is smaller than the Sr²⁺ and Eu²⁺ ions. For an example, one Y³⁺ ion is surrounded by eight

O²⁻ ions in a distorted dodecahedron in cerium-doped YAG phosphor [9]. The coordination number around the Ce³⁺ ion changes with 5d orbital energy state positions, resulting that the emission color varies. Thus, the new phosphor material with high structural stability are expected by changing emission center to Ce³⁺ from Eu²⁺ ion. Crystal structure identification and PL measurement are conducted. Furthermore, the obtained SrO:Ce phosphor is expected to have a high structural stability as SrO:Eu²⁺ phosphor. Thermal stability of SrO:Ce phosphor was investigated.

2. Experimental methods

Sr- and Ce-EDTA (metal-ethylenediamine tetraacetic acid) complexes were used for the synthesis of Ce-doped SrO phosphors. Ce-EDTA was mixed with Sr-EDTA at 0.02 at.%. Mixed (Sr,Ce)-EDTA complexes were dried in a spray-dry apparatus (SD-1000 Tokai Rika-KiKai Co.). Then, to obtain the homogenous SrO:Ce oxide particles, thermal treatment was performed at 800°C for 3h in the air. During experiment, the SrO:Ce oxide particles mounted on a single crystalline magnesia substrate. To synthesize the SrO:Ce phosphor, the sample were sintered in a tube furnace under reduction condition with 3 vol.%H₂+Ar gas. Sintering was performed a temperature of 1500°C. In addition, the SrO:Ce phosphor was annealed at 500,1000°C in Ar atmosphere. The emission properties of the sample were characterized using a photoluminescence (PL) spectrometer (JASCO FP-6500). An X-ray diffractometer (XRD, Mac Science M03XHF MXP3) was used to investigate their structural changes by annealing. The surface morphology, emission distribution and elemental distribution changes after the annealing were investigated using a cathodoluminescence (CL) microscope (Gatan MonoCL3), energy-dispersive X-ray (EDX) spectrometer (JEOL JED-2201F) equipped with a scanning electron microscope (FE-SEM; JEOL JSM6700F). Then, the accelerating voltage were 20 kV.

3. Results and Discussion

Figure 1 show XRD profiles for obtained sample. The XRD profiles were not assigned to reported 6-coordinated SrO and related materials such as SrCO₃. So, we conducted the crystal structure identification from the arrangements with the calculated XRD pattern using various traditional crystal structure. We reported 8-coordinated SrO:Eu²⁺ with orthorhombic lattice. The obtained XRD profiles were similar to that of the SrO:Eu²⁺ phosphor. The obtained XRD profiles were indexed as 8-coordinated SrO with orthorhombic lattice. The obtained

lattice parameter were $a=3.9060\text{ \AA}$, $b=3.8908\text{ \AA}$, $c=3.9109\text{ \AA}$. Figure 2 show PL spectrum of obtained phosphor synthesized on single crystalline magnesia. Photograph of the obtained phosphor emitting ultraviolet light were also show in Fig.2. Excitation wavelength was 325 nm. The obtained samples show a strong ultraviolet emission peak at 393 nm. These results indicated that the 8-coordinated SrO:Ce ultraviolet phosphor was synthesized on single crystalline magnesia.

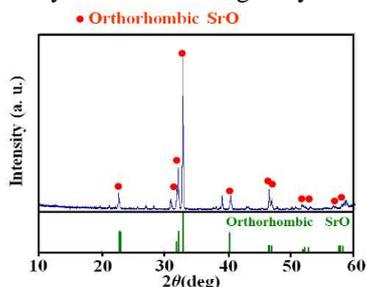


Fig. 1 XRD profile for obtained sample compared with calculated diffraction pattern of 8-coordinated SrO structure with orthorhombic lattice.

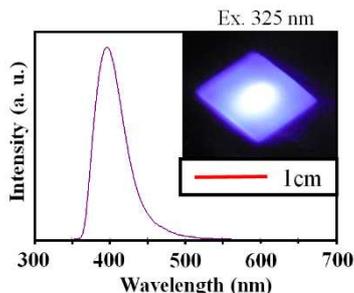


Fig. 2 PL spectrum for obtained sample. Photograph of the sample excited by 325 nm He-Cd laser was also shown.

To investigate thermal stability of the obtained SrO:Ce phosphor, annealing treatments were conducted. Figure 3 show PL spectra of obtained phosphor. After annealing at 500,1000°C under Ar atmosphere, the ultraviolet emission peak at 393 nm was remained with weak emission intensities. Emission peak positions of SrO:Ce were constant at 393 nm by the annealing. Existence of high pressure phase of SrO with orthorhombic lattice were confirmed from XRD analysis These results indicated that the 8-coordinated SrO:Ce ultraviolet phosphor have a high thermal stability.

CL analysis were conducted on the obtained SrO:Ce phosphors. Before annealing, the SrO:Ce phosphor shows strong CL peaks at around 360 nm and 380 nm. In contrast, annealed (in Ar atmosphere) SrO:Ce phosphor shows weak CL peaks at around 360 nm and 380 nm. In particular, the 380 nm CL peak was decreased by annealing. The cross-sectional CL images of SrO:Ce phosphors indicated that emission distribution was homogenous and not changed by annealing. Oxidation or reduction of Ce^{3+} ion in the 8-coordinated SrO:Ce phosphor would be happened by annealing.

To investigate chemical bond distribution in SrO:Ce phosphor, XPS analysis was conducted. The chemical shift information is very powerful tool for function group, chemical en-

vironment, oxidation state. Figure 4 show narrow-scan spectra for the SrO:Ce phosphors. The $\text{Sr}3d^{5/2}$ and $\text{O}1s$ peaks were not shifted by annealing. In contrast, the $\text{Ce}4d^{5/2}$ peak was shifted slightly to higher binding energy by annealing. The chemical shift of $\text{Ce}4d^{5/2}$ peak suggested that oxidation process of Ce^{3+} ion in the 8-coordinated SrO:Ce by annealing. Peaks analysis for the spectra would be discussed in detail.

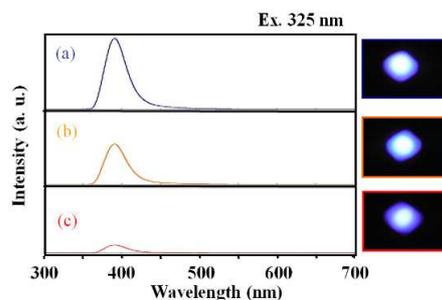


Fig. 3 PL spectra for obtained samples, (a)as-synthesized (before annealing), (b) annealed at 500°C, (c)annealed at 1000°C. Photographs of the sample excited by 325 nm He-Cd laser were shown.

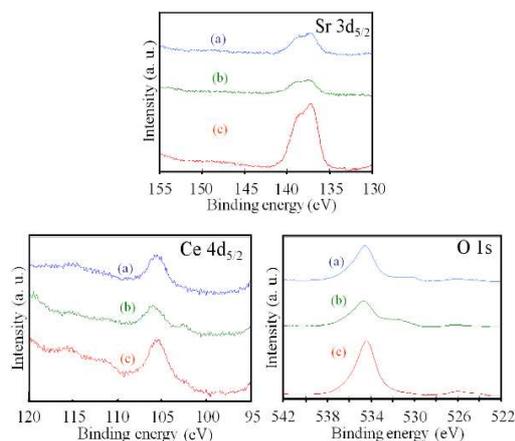


Fig. 4 XPS spectra for obtained samples, (a)as-synthesized (before annealing), (b) annealed at 500°C, (d)annealed at 1000°C.

3. Conclusions

High-pressure phase of SrO:Ce phosphor with high thermal stability was synthesized from SrO:Ce powder on the single crystalline MgO substrate by sintering under reduction condition. To investigate thermal stability, XRD, PL, SEM/CL, and XPS analysis for the SrO:Ce phosphor were conducted.

References

- [1] C.-C. Tsai *et al*, IEEE TRANS. DEVICE MATER. RELIAB. **9**, (2009) 367-371.
- [2] C. M. Tan *et al*, Microelectron Rel. **49** (2009) 1226-1230.
- [3] K. Komatsu *et al*, Ceram. Inter. **39** (2013) 7115-7118.
- [4] K. Komatsu *et al*, J. Solid State Chem. **204** (2013) 186-189.
- [5] Y.Sato *et al*, J. Geophys. Res. **86** (1981) 11773-11778.
- [6] L.-G. Liu *et al*, J.Geophys. Res. **78** (1973) 8470-8473.
- [7] P. Dorenbos, J. Lumin. **91** (2000) 155-176.
- [8] R.D. Shannon, Acta Cryst. **A32** (1976) 751.
- [9] M. Nazarov, Moldavian J. Phys. Sci. **4** (2005) 347-356.