

Photoluminescence in epitaxially grown BaTiO₃: Eu³⁺ films on SrTiO₃ (100) substrates by a solution based-route

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Epitaxially-grown europium-doped BaTiO₃ thin films have been prepared on single crystal SrTiO₃ (100) substrates by a wet solution process using metal carboxylate complexes. Thin films were fabricated by spin coating and the precursor films were pre-fired in argon at 500 °C for 10 min to decompose the organics. After multiple coating and pre-firing, the resultant films were annealed at 850 °C for 30 min in argon, followed by cooling to room temperature. The BaTiO₃: Eu³⁺ films after annealing were preferentially oriented with {100}- and/or {001} axis perpendicular to the substrate surface. Epitaxial growth to the substrate surface was confirmed by pole-figure analysis. The photoluminescence spectrum of epitaxial films under UV excitation showed clear red emission at 615 nm.

Key words: BaTiO₃, Epitaxial growth, Photoluminescence.

Introduction

Perovskite-structure materials are attractive as host materials for rare-earth doping because they present promising properties in integrated light emitting diodes, field emission displays and all-solid compact laser devices [1, 2]. Recently, visible photoluminescence (PL) at room temperature in disordered structurally perovskite titanates and highly emissive red-emitting phosphors have been reported in the literature [3, 4].

Thin films of oxide phosphors have attracted considerable attention for their application to flat-panel displays, not only because oxide phosphors have the potential advantage of chemical stability against high vacuum and electron bombardment but also thin-film phosphors offer a high image resolution and a strong adhesion to substrates.

Thin film phosphors have previously been prepared by different methods such as metal organic chemical vapor deposition (MOCVD), pulsed laser deposition (PLD) and sol-gel process [5-7]. Among these methods, chemical solution based route such as sol-gel and dipping-pyrolysis [8] have been intensively studied, because this process has many advantages such as low processing cost, precise controllability of chemical composition of films, and easy application to substrates of larger size.

However, the emission efficiencies of thin-film phosphors

are intrinsically low because their crystallinities are much lower than those of powders. To overcome this problem, epitaxially-grown phosphor films on single crystal were prepared for the case of Mn-doped ZnGa₂O₄ thin-film phosphors [9]. Enhanced PL intensity in the epitaxial films compared to randomly oriented polycrystalline films on glass was observed, revealing an important role of grain boundaries in limiting the performance of thin-film phosphors. Although many works have been done to improve the PL intensity of polycrystalline phosphor materials, as far as we know, there have been few works involving epitaxial luminescent thin films [10].

In present paper, we study the deposition in thin films of 3 mol% Eu-doped BaTiO₃ (BTO: Eu³⁺) by a wet solution route using metal carboxylate complexes. Epitaxial BaTiO₃ (BTO) thin films have been grown on single crystal substrates, such as SrTiO₃ (STO) and LaAlO₃ (LAO), by chemical solution process [11]. STO is a cubic perovskite with lattice parameter $a = 0.3905$ nm at room temperature. There is a 2.2% lattice mismatch for tetragonal BTO ($a = 0.3992$ nm, $c = 0.4036$ nm) on a (001) STO surface with (001)[100] BTO || (001) [100] STO, i.e., a c -axis-oriented epitaxial BTO film. We therefore expected that thin films of these perovskite-related oxide phosphors, BTO: Eu³⁺ on single crystal, could be grown with a high crystal quality.

Experimental Procedure

The starting solution was prepared by using barium naphthenate, titanium naphthenate and europium-2-ethylhexanoate [Eu(C₈H₁₅O₂)₃]. Starting materials with

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a stoichiometric molar ratio were dissolved with toluene. After mixing at 60°C for 60 min in air, stable 3 mol% Eu-doped BTO sol was formed. The precursor solution was diluted by a certain amount of toluene to adjust the viscosity for coating.

Prior to the coating process, STO (100) substrates were cleaned in deionized water, immersed in a H_2O_2 solution, and finally rinsed in acetone. Thin films were fabricated by spin coating onto STO (100) substrates at the rotation speed of 3000 rpm for 10 sec. After each deposition, the coating film was pyrolyzed in argon at 500°C for 10 min to decompose the organic species. For multiple coatings, the above-mentioned processes were repeated five times. The resultant films were directly annealed in a preheated furnace at 850°C for 30 min in argon, followed by cooling to room temperature.

The crystallinity and in-plane alignment of the film were investigated by using a high resolution X-ray diffraction (HRXRD, X'pert-PRO, Philips, Netherlands) θ - 2θ scan and pole-figure analysis. The thickness of the film was measured by observations of fractured cross-section using a field emission-scanning electron microscope (FE-SEM, S-4700, Hitachi, Japan). The microstructure of the films after annealing was examined using a FE-SEM. The excitation and emission spectra of the films were recorded at room temperature using a fluorescent spectrophotometer (F4500, Hitachi, Japan) equipped with a Xenon lamp source.

Results and Discussion

Figure 1 shows XRD θ - 2θ scan of $\text{BTO} : \text{Eu}^{3+}$ films on STO (100) substrate after pre-fired at 500°C , and subsequent annealing at 850°C . Film pyrolyzed at 500°C exhibited amorphous structure, not shown here. In contrast, distinct $(h00)/(00l)$ peaks of $\text{BTO} : \text{Eu}^{3+}$ film after annealing at 850°C were recognized while other peaks of BTO were faint, showing that the $\text{BTO} : \text{Eu}^{3+}$ film was preferentially oriented with $\{100\}$ - and/or $\{001\}$ -axis perpendicular to the substrate surface. The doped Eu ion has little influence on the host structure. This result indicates that highly oriented $\text{BTO} : \text{Eu}^{3+}$ film could be obtained by a wet chemical

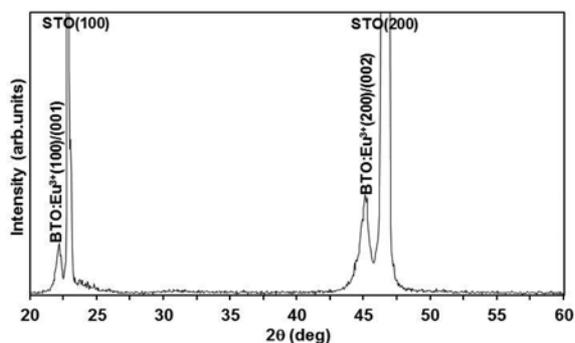


Fig. 1. XRD θ - 2θ scans of $\text{BTO} : \text{Eu}^{3+}$ films prepared on STO (100) substrates.

solution route after pyrolysis and final annealing. Using the substrate STO (200) peak as an internal calibration standard, the lattice parameter (d_{\perp}) of epitaxial $\text{BTO} : \text{Eu}^{3+}$ film along the direction perpendicular to the substrate surface was determined to be 0.3991 nm. This value is close to the a -axis lattice parameter ($a_0 = 0.3994$ nm) rather than c -axis one ($c_0 = 0.4038$ nm) of tetragonal BTO. It is difficult to determine the type of crystal structure and the plane of preferred orientation of the films because the d_{\parallel} value, the lattice constant parallel to the substrate surface, of $\text{BTO} : \text{Eu}^{3+}$ is still unknown. But the reflection of $\text{BTO} : \text{Eu}^{3+}$ is indexed as regarded as pseudo-cubic in this paper. From the XRD results, the lattice parameter a_0 of $\text{BTO} : \text{Eu}^{3+}$ is found to decrease with Eu doping. Such a contraction of the lattice parameter is due to the inter-atomic spacing reduction resulted from the substitution of 0.142 nm sized Ba^{2+} ions with 0.097 nm sized Eu^{3+} ions.

In-plane alignment of the $\text{BTO} : \text{Eu}^{3+}$ (00 l) / ($h00$) texture on STO (100) was investigated by X-ray pole-figure analysis. We used $\text{BTO} : \text{Eu}^{3+}$ (110) / (101) and STO (110) reflections for this analysis since they are strong enough and there are no other interfering peaks around them. Figure 2 shows the line profiles of β scans for which the α angle was fixed at 45° . As clearly seen in Fig. 2, the β scan of the pre-fired film gave only traces of the peaks beyond the noise level. In contrast, highly oriented $\text{BTO} : \text{Eu}^{3+}$ film annealed at 850°C gave four sharp peaks and each peak for the (110) / (101) reflection of $\text{BTO} : \text{Eu}^{3+}$ occurred exactly at the same β angle for the (110) / (101) reflection of STO substrate. This means that $\text{BTO} : \text{Eu}^{3+}$ films have grown epitaxially, *i.e.*, cube on cube, to the substrates surface. The orientation relationship between the $\text{BTO} : \text{Eu}^{3+}$ film and STO substrate was $\text{BTO} : \text{Eu}^{3+}$ (001) // STO (100) and $\text{BTO} : \text{Eu}^{3+}$ [100], [010] // STO [001]; or $\text{BTO} : \text{Eu}^{3+}$ (100) // STO (100) and $\text{BTO} : \text{Eu}^{3+}$ [010], [001] // STO [001]. It is interesting that temperature required for the epitaxial growth of $\text{BTO} : \text{Eu}^{3+}$ films is much higher than that of $\text{Pb}(\text{Zr,Ti})\text{O}_3$

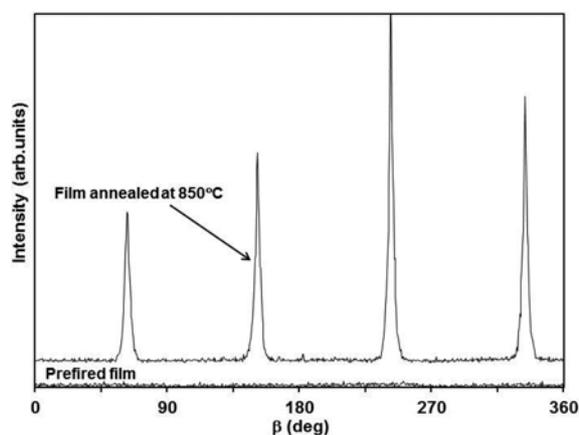


Fig. 2. Line profiles of β scans of $\text{BTO} (110) / (101)$ reflection for $\text{BTO} : \text{Eu}^{3+}$ films on STO (100).

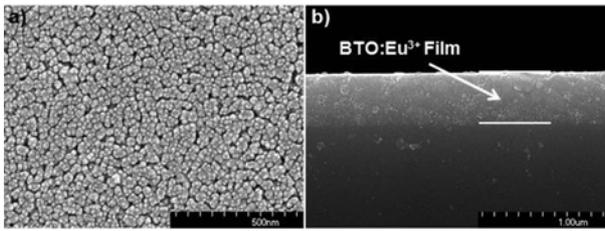


Fig. 3. FE-SEM photographs of a free surface (a) and a fracture cross-section (b) of a film on STO (100).

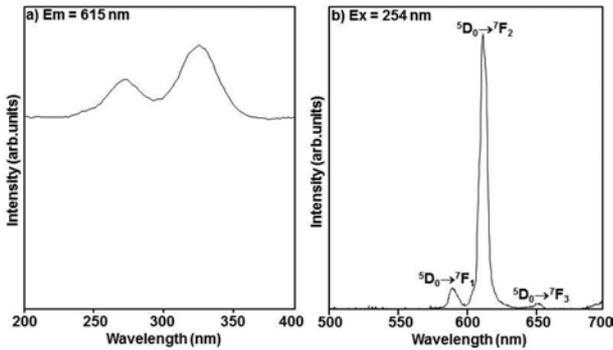


Fig. 4. Typical excitation (a) and emission (b) spectra of epitaxial BTO : Eu³⁺ films on STO.

films prepared by similar procedure on STO (100) substrates, *i.e.*, 600 °C [12]. This temperature difference may be due to differences between the mixing states of the pyrolyzed metal oxide components; the oxide mixture in the Pb-Zr-Ti system is presumably more reactive than the BaCO₃-TiO₂ mixture.

Figure 3 shows FE-SEM photographs of the free surfaces and the fractured cross section of the BTO : Eu³⁺ films after annealing at 850 °C. Particulate structure is indistinct. Crack-like texture and pores were unable to see on the surface of the film and there is no evidence on aggregation of particles. In chemical solution based-process, as the pre-firing temperature decreases to below 300 °C, the amount of organics in the pre-fired film increases, and therefore the decomposition and the crystallization may occur almost simultaneously. Since the structural relaxation of the pyrolyzed film induced by the decomposition can take place only before crystallization, the simultaneous decomposition and crystallization may give the film less chance to structurally relaxed, resulting in a micro-porous structure [13]. BTO : Eu³⁺ films, in this work, would obtain enough energy to vaporize organic species in the as-deposited films by pyrolyzed at 500 °C, resulting in a dense surface structure. The fractured cross-section of the BTO : Eu³⁺ film with an approximately 0.6 μm-thickness appears dense and uniform. This suggests that the bonding strength between the substrates and the film is sufficiently strong.

The luminescence properties were investigated by measuring the PL spectra of BTO : Eu³⁺ films at room temperature in the range of 500 ~ 700 nm and excited at 254 nm wavelength, as shown in Figs. 4 (a) & (b).

The excitation spectra were measured by monitoring the peak intensity at 615 nm. The excitation spectra of epitaxially grown BTO : Eu³⁺ films, as shown in Fig. 4 (a), consist of two broad band. Among them, the broad excitation band in the UV region centered at around 250 ~ 270 nm is a charge transfer band (CTB), corresponding to an electron transfer from an oxygen 2*p* orbital to an empty 4*f* orbital of Eu. The other peak at 300 ~ 350 nm is assigned to the intra-4*f*⁶ transition of Eu³⁺ ions.

The room temperature PL spectrum of epitaxially grown BTO : Eu³⁺ films of STO under UV excitation ($\lambda_{ex} = 254$ nm) is shown in Fig. 4 (b). The film exhibited clear red emission. Peaks centered at 595, 615, and 650 nm are assigned to ${}^5D_0 \rightarrow {}^7F_1$, ${}^5D_0 \rightarrow {}^7F_2$ and ${}^5D_0 \rightarrow {}^7F_3$, respectively, arising from the lowest excited 5D_0 level into the split by the crystal field 7F_J ($J = 0, 1, 2, 3, 4, 5, 6$) as observed by results reported for Eu³⁺ doped oxide phosphor [14, 15]. It is difficult to detect transitions to the higher lying levels 7F_5 and 7F_6 due to their low intensities.

Among the ${}^5D_0 \rightarrow {}^7F_J$ transitions of Eu³⁺ ions, the ${}^5D_0 \rightarrow {}^7F_1$ is a magnetic dipole induced transition and scarcely changes with the crystal field strength around the Eu³⁺ ions. On the contrary, the ${}^5D_0 \rightarrow {}^7F_{2,4}$ transitions are of electric dipole nature and dependent on the local electric field and hypersensitive to the local symmetry around the Eu³⁺ ions. When the Eu³⁺ ions locate at sites with inversion symmetry, the ${}^5D_0 \rightarrow {}^7F_1$ transition dominates the emission spectrum [16]. Otherwise, when the Eu³⁺ ions locate at sites without inversion symmetry, the ${}^5D_0 \rightarrow {}^7F_2$ transition dominates the emission spectrum and its intensity increases distortion of the local field around the Eu³⁺ [16]. Spectrum is dominated by the ${}^5D_0 \rightarrow {}^7F_2$ electron transition, called the hypersensitive forced electric dipole emission, which is much stronger than ${}^5D_0 \rightarrow {}^7F_1$ magnetic-dipole emission.

We observed intense red PL under UV excitation in epitaxial Eu-doped BTO thin films prepared on STO (100) substrates by chemical solution process. The observed sharp PL peak centered at 615 nm was assigned to the transition of Eu³⁺ ions from the 5D_0 state to the 7F_2 state. It was suggested that the UV energy absorbed by the host lattice was transferred to the Eu ions, leading to the red luminescence.

Conclusions

In this work, we prepared epitaxially grown BTO : Eu³⁺ thin films on STO(100) substrates by a chemical solution route using metal carboxylate complexes for red-emitting application. After spin coating and pyrolyzing at 500 °C for 10 min, the precursor films were heat treated at 850 °C for 30 min in argon, followed by cooling at room temperature. Their crystallinities, microstructures and PL properties were investigated. BTO : Eu³⁺ films after annealing have grown epitaxially, *i.e.*, cube on cube,

to the substrates surface. The fabrication of epitaxially grown film phosphors showing intense red emission at 615 nm under UV excitation may open a path to their application in display devices and light-emitting or laser devices in future.

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