Preparation and luminescent properties of Eu-doped BaTiO$_3$ thin films by sol–gel process

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Abstract

Eu-doped BaTiO$_3$ thin films with a pseudo-cubic perovskite structure were successfully fabricated on magnesia substrates at low temperature by using a high-concentration sol–gel process, in which the newly developed gel-aging process on substrate was employed. Film microstructure, crystallinity, sintering properties and photoluminescence (PL) were investigated. The xerogel thin films exhibited strong PL associated with Eu$^{3+}$ ions under ultraviolet excitation at room temperature; the PL was visible to naked eyes. The intensity maximum of PL was reached with doping concentration of about 8 mol%. Sintering above 600 °C caused reduction of europium, resulting in a rapid quenching of Eu$^{3+}$ emission and enhancement of Eu$^{2+}$ emission.

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1. Introduction

With increased demand for portable computers, communication equipment and consumer electronic products in recent years, flat panel displays (FPDs) have been marking dramatic growth and will soon become ubiquitous products in our homes, workplaces and a number of places in between [1,2]. The future proliferation of FPDs cannot be doubted for their advantages over cathode-ray tube, such as increase contrast, color purity, resolution, lifetime, and viewing angle while the cost, weight, volume, and power consumption are to be further reduced. As the key materials in FPDs, the researches and development of luminescent materials are attracted more and more attention. Since Destriau observed light emission from an oil suspension containing ZnS/Cu, sulfide phosphors have been extensively developed and many of them are now commercially available. But their inherent problems such as their chemical instability and sensitivity to moisture and operation environments have hindered them from full commercialization. In comparison with the traditional sulfide luminescent phosphors, oxide thin film phosphors offer potential advantages because of their acceptable atmospheric stability, high brightness, reduced degradation under applied voltages, and lack of hazardous constituents in field emission FPD applications [3,4]. Barium titanate ceramics have been found for extensive applications in a variety of devices due to their excellent optical and electrical properties [5,6]. Because of the intrinsic capability of the perovskite structure to host ions with different sizes, a large number of different dopants can be accommodated in the lattice. In the past few years, ABO$_3$-like compounds with the perovskite structure such as SrTiO$_3$ [7,8], BaTiO$_3$ [9], CaTiO$_3$ [10] doped with rare earth ions have also revealed to have very interesting luminescent properties.

The sol–gel processing is a relatively easy and economical way for making uniform large size, high quality stoichiometric thin film phosphors [11,12]. A new sol–gel process using high-concentration of alkoxide precursor solutions has proved to have a significant advantage in synthesizing BaTiO$_3$ gel and ceramic materials [13,14]. Transparent, crack-free BaTiO$_3$ monolithic gels and thin films have been successfully synthesized [15–17]. In the present study, the photoluminescent properties of Eu$^{3+}$-doped BaTiO$_3$ thin films prepared by the newly developed sol–gel method has been investigated.

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2. Experimental

2.1. Preparation of precursor solution

High purity barium diethoxide (Ba(OC₂H₅)₂, purity > 99%), dehydrated europium chloride (EuCl₃, purity > 99.99%) and titanium tetra-iso-propoxide (Ti(OiC₃H₇)₄, purity > 99%) were dissolved in a mixed solvent of dehydrated CH₃OH and CH₃OC₂H₄OH (purity > 99.8%) with a volume ratio of 3:2. As reported in a previous work on BaTiO₃ [18], using such mixed solvent it was possible to dissolve a large amount of alkoxides and produce high-concentration precursor solutions of 1.2 mol/l at room temperature. In the present work, the concentration of barium and europium in the precursor solution was about 1 mol/l and the doping concentration was varied from 0.1 to 10 mol%. The solution was then stirred for 24 h in a dry N₂ atmosphere at room temperature.

2.2. Film deposition, drying and thermal treatment

A newly developed method named gel-aging process on substrate (GAPS) was introduced to prepare thin films. The precursor solution was spin-coated on a magnesia substrate at a speed of 3000 rpm for 20 s in a sealed container which was filled with a saturated vapor of H₂O and CH₂OC₂H₄OH mixed solution of a volume ratio of 1:1 (Fig. 1). The formed liquid films were hydrolyzed and aged at 50 °C for 1 h and then dried at 150 °C for 1 h on a hot plate. The films doped with 5 mol% Eu were heat-treated in air from 300 to 850 °C for 3 h.

2.3. Characterization

Surface morphology and film thickness were evaluated by field emission scanning electron microscopy (FE-SEM, HITACHI, S5000). The crystallinity of obtained films was examined by X-ray diffractometry (XRD, Mac Science, M18XHF). Thermogravimetric and differential thermal (TG-DTA) analysis was performed in the range of 50–1000 °C to investigate the combustion behavior of organic compounds contained in the xerogel thin films with a Seiko TG/DTA6300 analyser.

The excitation and emission spectra were recorded using a JASCO FP-750 spectrophotometer. All the measurements were carried out at room temperature. The bandwidth for emission and excitation were 10 nm and sensitivity was medium.

3. Results and discussion

Fig. 2 shows XRD patterns of the doped BaTiO₃ xerogel thin films dried at 150 °C in air for 1 h with the Eu concentration of 1, 2, 3, 5, 6 and 8 mol%, respectively. Besides the presence of the strong diffraction peaks from the magnesia substrate, the obtained thin films tended to crystallize a pseudo-cubic perovskite phase when the Eu concentration was below 6 mol%, and the intensity of the peaks belonging to BaTiO₃ phase decreased with increasing Eu concentration. When the Eu concentration was above 6 mol%, the thin film was amorphous and only the peaks of magnesia substrate were observed. The different valence and ion radius of Ba²⁺ and Eu³⁺ \((R_{\text{Ba}} = 1.27 \, \text{Å}, R_{\text{Eu}} = 0.95 \, \text{Å}) [19] \) may make it difficult to form crystalline thin films with high doping concentration.

The as-grown samples were transparent and crack-free. Fig. 3(a) and (b) show the top view and cross-sectional view of FE-SEM micrographs for crystalline BaTiO₃ xerogel thin films doped with 5 mol% Eu, respectively. The thin films possessed a porous morphology with small aggregates of particles of 10–30 nm in diameter. The thickness of the thin films by single spin-coating reached about 400 nm using this high-concentration sol–gel process.

BaTiO₃ has a wide band gap about 3.2 eV, which offers a large spectral area where the rare earth metal can emit light. Fig. 4 shows the room temperature emission spectra in the range of 570–670 nm of the 5 mol% Eu doped BaTiO₃ thin
film and excitation spectra in the range of 220–300 nm. Five sharp emission bands at 590, 612, 651, 694 and 708 nm were due to intra-4f-shell transitions from the excited level to lower levels: $^5\text{D}_0 \rightarrow ^7\text{F}_j$ ($j = 1, 2, 3, 4, 5$) for Eu$^{3+}$ ions. In our previous work [20], a small $^5\text{D}_0 \rightarrow ^7\text{F}_0$ emission peak was observed for Eu-doped BaTiO$_3$ dried gels prepared by the same high-concentration sol–gel process when excited with a pulsed Nd:YAG laser. In this study, since a JASCO FP-750 spectrophotometer with a weak excitation source and low resolution was used, the $^5\text{D}_0 \rightarrow ^7\text{F}_0$ emission peak was difficult to be detected. Among the measured emission transitions of Eu$^{3+}$, the transition $^5\text{D}_0 \rightarrow ^7\text{F}_2$ showed a prominent and bright red color fluorescent band, as was expected from Judd-Ofelt selection rules. As shown in Fig. 5, compared with the substrate, strong red emission from the samples doped with 5 mol% Eu could be seen by naked eyes when a 254 nm UV lamp impinged on the films. The photoluminescence (PL) excitation spectrum of the $^5\text{D}_0 \rightarrow ^7\text{F}_2$ emission band at 612 nm exhibited a broadband centered at around 270 nm, which was attributed to charge transfer (CT) between the Eu$^{3+}$ and the surrounding anions.

The relationship between emission intensity and the europium concentration of the Eu-doped BaTiO$_3$ thin films was plotted in Fig. 6 for the electric-dipole transition $^5\text{D}_0 \rightarrow ^7\text{F}_2$ at 612 nm and the magnetic transition $^5\text{D}_0 \rightarrow ^7\text{F}_1$ at 590 nm. The Eu$^{3+}$ emission intensity first increased with doping concentration and reached a maximum value at the doping concentration of Eu$^{3+}$ around 8 mol%. Then a slightly concentration quenching occurred when Eu concentration reached 10 mol%.

It is well known that if the concentration of an activator is higher than an appropriate value, the emission of the phosphor is usually lowered, which is called as concentration quenching. For europium doping, the luminescent properties of Eu$^{3+}$ have strong dependence on the doping concentration. As shown in Fig. 6, PL of thin films with higher doping concentration had a rapid increase compared with thin films with doping concentration lower than 2 mol%. This is because when Eu concentration increases from 2 mol% up to 8 mol%, concentration quenching occurs at the higher emitting levels, $^5\text{D}_1$ of Eu$^{3+}$; in other words, ions at such levels transfer their energies to neighboring Eu$^{3+}$ ions by the following cross-relaxations [21],

$$^5\text{D}_1(\text{Eu}^{3+}) + ^7\text{F}_0(\text{Eu}^{3+}) \rightarrow ^5\text{D}_0(\text{Eu}^{3+}) + ^7\text{F}_6(\text{Eu}^{3+})$$

So such energy transfers among activator ions efficiently improve the possibility of radiative relaxation from $^5\text{D}_0$ levels and thus increase the photoluminescent intensity of $^5\text{D}_0 \rightarrow ^7\text{F}_2$ and $^5\text{D}_0 \rightarrow ^7\text{F}_1$ transitions. Further increasing the doping concentration, because excitation migration due to the resonance between the activators increases with the concentration, the energy is trapped at remote killers or
the crystal surface acting as quenching centers and dissipated as heat, thus the emission is weakened.

In the present paper, the microstructure and PL properties of the sintered samples were also investigated. The crystallization process of Eu-doped BaTiO₃ thin films was studied by TG-DTA, XRD and FE-SEM. The TG-DTA curve for thin films with 5 mol% Eu showed a remarkable exothermic reaction in temperature range 200–400 °C was shown in Fig. 7, indicating the evaporation and oxidation of OH and organic groups, and a significant weight loss about 13% was observed around 600 °C. As seen from the XRD patterns of Fig. 8 for the thin films with 5 mol% Eu sintered at different temperatures, the crystallinity was considerably enhanced with increased intensity of the peaks belonging to BaTiO₃ phase and decreased the value of full width at the half-maximum (FWHM) when the sintering temperature increased. In agreement, an obvious grain growth was observed in the FE-SEM micrographs of Eu-doped BaTiO₃ thin film sintered at 850 °C, as seen in Fig. 9.

The relationship between room temperature PL and sintering temperature was shown in Fig. 10 at identical excitation conditions. No change in the peak positions of the Eu³⁺ emissions from the samples with various annealing temperatures was observed. It is because such emissions are due to the 4f–4f transitions, and the 4f-orbital electrons are well shielded by the outer 5s²5p⁶ orbital electrons. Thus, the emission positions originated from 4f–4f transitions are hardly affected by external factors such as temperature, structure and crystal field. When increasing sintering temperature up to 600 °C, the intensity of ⁵D₀ → ⁷F₂ transition of Eu³⁺ increased due to the improvement of the crystallinity. However, further increasing sintering temperature from 600 to 700 °C the intensity decreased significantly. On the other hand, a broad band emission centered at about 440 nm was observed and its increasing photoluminescent intensity gradually dominated the ⁵D₀ → ⁷F₂ transition of Eu³⁺ ions. Europium is known to have valence states both ²⁺ and ³⁺, and many Eu-doped phosphor materials, such as europium silicate [22,23], Eu-doped BaMgAl₁₀O₁₇ [24,25], barium aluminum oxynitride [26], have been reported to experience a reduction of europium from trivalent state to divalent state during sintering. Different from the luminescence spectrum of Eu³⁺ ion, luminescence of Eu²⁺ ion involves an electric-dipole allowed transition ⁴f⁶5d¹ → ⁴f⁷. The emission peaks of Eu²⁺, lying in the green-blue region of spectrum depending on the host materials, are much wider than those of Eu³⁺ ion due to the overlap of ⁴f⁶5d¹ levels. In previous researches on crystal and defect chemistry of rare earth cations in BaTiO₃, Takeda [27] detected Eu²⁺ on the A-site in BaTiO₃ and Tsur et al. [28] also reported from room temperature XRD measurements Eu is ²⁺ on A-site in the doped BaTiO₃ sintered at 1400 °C in reducing atmosphere. So it is possible during sintering above 600 °C,
Europium ions were reduced from trivalent state to divalent state, accompanying rapid quenching of Eu\(^{3+}\) emission and enhancement of Eu\(^{2+}\) emission.

4. Conclusions

In present work, preparation and characterization of the novel luminescent system based on barium titanate thin films doped with Eu\(^{3+}\) on MgO substrate were investigated. Crack-free and polycrystalline Eu-doped BaTiO\(_3\) xerogel thin films were successfully prepared by high-concentration sol–gel process and GAPS at low temperature. Strong red emission can be seen by naked eyes under UV excitation. The PL of thin films heat-treated below 600 °C was related to the \(^{5}D_0 \rightarrow ^{7}F_j\) (j = 1, 2, 3, 4, 5) Eu\(^{3+}\) electronic transition, with the \(^{5}D_0 \rightarrow ^{7}F_2\) red emission being the most prominent. Maximum PL intensity occurred when the Eu\(^{3+}\) doping concentration in the xerogel thin films was around 8 mol%. With increasing sintering temperature above 600 °C, reduction of europium ions from trivalent state to divalent state resulted in a change of emission spectrum. A broad band emission center at about 440 nm associated with the \(4f^65d^1 \rightarrow 4f^7\) transition of the Eu\(^{2+}\) ions occurred and dominated the \(^{5}D_0 \rightarrow ^{7}F_j\) (j = 1, 2, 3, 4, 5) transition of Eu\(^{3+}\) ions.

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