

Photoluminescence from epitaxial films of perovskite-type alkaline-earth stannates

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Abstract

The epitaxial films of the recently developed calcium and strontium stannates phosphors with perovskite or its related structure were fabricated by the pulsed-laser deposition method. The films were all highly transparent in the visible region, and showed intense luminescence of several colors under ultraviolet excitation. Light scattering at the substrates' surfaces varied the appearance of photoluminescence. In combination with epitaxial-film-growth technologies for many perovskite functional materials, the obtained results provide a promise for future developments of multifunctional optoelectronic devices.

Text

Many oxides with perovskite structure show a range of physical properties such as semiconducting, superconducting, ferroelectric, or ferromagnetic properties.¹ Desirable features of these functional materials that are not displayed by the powdered materials are frequently displayed by epitaxial films grown on single crystal substrates as a result of their crystal structure. Therefore, the film-growth technique plays an important role in making maximum use of these desirable properties in various devices. Despite the diverse functions of perovskite oxides, luminescent materials, particularly in the form of films with a high crystal quality, have not been extensively studied, probably because intense luminescence has not previously been observed in perovskite oxides. In this Letter, we investigate the fabrication of doped epitaxial films of the recently developed calcium and strontium stannates with perovskite or its related structure.^{2,3} The basic photoluminescence (PL) properties of the films are examined and their color variations or PL intensities are compared with previously reported thin-film phosphors, such as Pr-doped $\text{Ca}_{0.6}\text{Sr}_{0.4}\text{TiO}_3$ (red), Ar^+ -irradiated SrTiO_3 (blue) and Tm-doped $(\text{Ca},\text{Sr})\text{HfO}_3$ (blue).⁴⁻⁶

The film samples were grown on SrTiO_3 substrates by pulsed-laser deposition (PLD) using polycrystalline targets of $\text{Sr}_2(\text{Sn}_{0.95}\text{Ti}_{0.05})\text{O}_4$, $(\text{Sr}_{0.98}\text{Eu}_{0.02})_2(\text{Sn}_{0.9}\text{Ti}_{0.1})\text{O}_4$, $(\text{Sr}_{0.995}\text{Sm}_{0.005})_3\text{Sn}_2\text{O}_7$, $\{(\text{Ca}_{0.97}\text{Mg}_{0.03})_{0.98}\text{Tb}_{0.02}\}\text{SnO}_3$, or $(\text{Ca}_{0.98}\text{Pr}_{0.02})\text{SnO}_3$. These single-phase powders and polycrystalline targets were prepared by the conventional solid-state reaction method described in our previous paper.^{2,3} SrTiO_3 (100) single-crystal substrates polished on one or both sides were used for the growth of the films. During the film growth, the substrates were heated to 600 °C or 800 °C, and the oxygen partial pressure was controlled between 10 and 100 Pa. An ArF excimer laser was used for PLD and was operated with a repetition rate of 4 Hz and a fluence of $\sim 1.2 \text{ J cm}^{-2} \text{ pulse}^{-1}$ at the surface of the target. All the films in this study were

approximately 300-nm thick. X-ray fluorescence analysis confirmed that the chemical composition of the films was almost the same as that of the bulk targets. Post-annealing treatments were performed at 1000, 1100, or 1200 °C in air. As-deposited films were quickly placed in the heated furnace, kept there for 1 h, and then promptly removed. The crystalline phase and crystallinity of the films were examined by x-ray diffraction (XRD) and reflection high-energy electron diffraction (RHEED). To evaluate the basic PL properties of the films, PL emission and excitation spectra were measured by using a conventional fluorescence spectrophotometer with a xenon lamp at room temperature.

Thin films prepared on SrTiO₃ (100) substrates by PLD gave the XRD patterns shown in Figures 1a and 1b. These XRD patterns of as-grown films show the exclusive presence of (*hh*0) or (*00l*) planes in both the calcium and strontium stannates. Although these stannates are classified into the orthorhombic system,⁷ the reduced lattice parameters (*a_p*) as the cubic system are *a_p* = 3.95 Å for Ca stannates and *a_p* = 4.03 Å for Sr stannates. These values are slightly larger than the lattice parameter (*a* = 3.91 Å) of SrTiO₃ substrates, and the lattice mismatch is less than 3%. As shown in the inset to Figure 1a, the diffraction intensities from these planes were enhanced after post-annealing treatments, indicating that annealing improves the crystallinity and maintains the strong orientation of the films. In-plane XRD measurements also showed diffraction from the (220) planes, and a four-fold symmetry was distinctly observed by the ϕ scan, as shown in the inset to Figure 1b. In addition, RHEED from the films showed streaky patterns. The XRD patterns and the RHEED patterns taken together confirmed that the films were grown epitaxially on the SrTiO₃ (100) substrates and have a high crystal quality.

These epitaxial films, however, showed no PL or only slight PL in as-grown states, even though they were grown at 600 °C or 800 °C. After post-annealing in air for 1 h, the PL intensity of the films increased markedly, as shown in Figures 2a and 2b. The optimal annealing

temperatures to give maximal PL intensities were 1100 °C for Tb–Mg-codoped or Pr-doped CaSnO_3 and 1000 °C for Ti-doped or Eu–Ti-codoped Sr_2SnO_4 . The film-growth temperature (substrate temperature) also affected the PL intensity of the films. In both CaSnO_3 and Sr_2SnO_4 , films grown at 600 °C showed more-intense luminescence after the post-annealing treatment than those grown at 800 °C. These characteristics are very similar to those of red-luminescent $\text{Ca}_{0.6}\text{Sr}_{0.4}\text{TiO}_3\text{:Pr}$ epitaxial films.⁴

There are two major causes of the increase in PL intensity after post-annealing: a decrease in the concentration of defects, such as oxygen vacancies, and an improvement in crystallinity. Because they are prepared at low partial pressures of oxygen, the as-grown films usually contain some defects, such as oxygen vacancies, that induce nonradiative decay processes. We consider that post-annealing in air considerably reduces the number of oxygen vacancies, leading to an enhancement in the radiative decay processes. The increase in XRD peak intensities after the post-annealing confirmed that an improvement of crystallinity had occurred. The crystallinity of the as-grown films also affects their PL intensity after post annealing. We believe that the lower film-growth temperature results in easier incorporation of dopants into the crystal lattices because of the low crystallinity; this subsequently leads to a higher luminescence when the crystallinity is improved by post-annealing.

The PL and PL excitation (PLE) spectra for the optimized films are shown in Figure 3, along with a photograph of the films under UV excitation ($\lambda_{\text{ex}} = 254 \text{ nm}$) at room temperature. The general features of the spectra are similar to those for bulk samples.^{2,3} The CaSnO_3 films showed sharp emission lines at 490, 543, 582, and 620 nm when codoped with Tb and Mg, and at 490, 530, and 612 nm when doped with Pr. These emission lines are assigned to the f–f emissions from $^5\text{D}_4 - ^7\text{F}_j$ ($J = 6, 5, 4, 3$) transitions in Tb ions or from $^3\text{P}_0$ or $^1\text{D}_2 - ^3\text{H}_j$ ($J = 4, 5$) transitions in Pr ions. The Sm-doped $\text{Sr}_3\text{Sn}_2\text{O}_7$ exhibited sharp pairs of emission lines at (570,

580) and (609, 621) nm ascribed to the f–f emissions from ${}^4G_{5/2} - {}^6H_J$ ($J = 5/2, 7/2$) transitions in Sm ions. The PLE bands of these samples are very close to the fundamental absorption edge of CaSnO_3 and $\text{Sr}_3\text{Sn}_2\text{O}_7$ ($\lambda \approx 280$ nm).^{2,3} It is therefore most likely that excitation energy is first absorbed by the host lattices and then this energy is transferred to the rare-earth ions.

In contrast to the rare-earth doped samples, Ti-doped Sr_2SnO_4 showed a broad emission band centered at 410 nm that we attribute to luminescence from Ti-related complexes.^{8,9} In addition, the codoping of Sr_2SnO_4 with Eu and Ti leads to sharp emission lines at 577, (592, 598), and (611, 616) nm assigned to the f–f emissions from ${}^5D_0 - {}^7F_J$ ($J = 0, 1, 2$) transitions in Eu ions along with a broad emission band arising from the Ti-related complexes. The PLE bands of both Ti-doped and Eu–Ti-codoped Sr_2SnO_4 appear at wavelengths that are slightly longer than the fundamental absorption edge of the host lattices ($\lambda \approx 270$ nm).^{2,10} This observation implies that the Ti-related complexes, rather than the host lattices, are excited first: the excited Ti-related complexes then emit blue luminescence in Ti-doped Sr_2SnO_4 whereas, in Eu–Ti codoped Sr_2SnO_4 , the energy is transferred from the excited Ti complexes to Eu ions.

The photograph of the disks and films reproduced in Figure 3 shows the intense PL from the series of doped alkaline-earth stannates. As shown by the PL spectra, the PL intensities of these films are as high as that of Pr-doped $\text{Ca}_{0.6}\text{Sr}_{0.4}\text{TiO}_3$ films.⁴ Films on the substrates polished on both sides showed a high transparency without clouding and their luminescence was emitted mainly from the edge of the films and substrates, indicating that the films and substrates operate as slab waveguides for the PL. On the other hand, films polished on one side showed PL vertical to the film surfaces as a result of light scattering from the rough back surfaces of the substrates. The uniform luminescence seen in the photograph indicates that the dopant ions are homogeneously distributed within the epitaxial films from the microscopic and macroscopic viewpoints.

For perovskite-type materials, it is unusual for an intense luminescence of several colors to be obtained solely from the alkaline-earth stannate host lattice. Our demonstration of luminescent epitaxial films present a contrast to the limited range of luminescent colors available from titanate or hafnate perovskites. Because various devices based on perovskite-type oxides on single-crystal substrates have been actively developed,¹¹ these highly luminescent thin-film oxide phosphors are promising materials for the future development of not only light-emitting devices, but also multifunctional optoelectronic devices.

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Figure Captions

Figure 1 (color online)

XRD patterns of Pr-doped CaSnO_3 (a) and Eu-Ti-codoped Sr_2SnO_4 (b) thin films epitaxially grown on SrTiO_3 (100) substrates.

Figure 2 (color online)

Influences of post-annealing temperature (T_a) or film-growth temperature (T_g) on the PL intensities of Tb-Mg-codoped CaSnO_3 (a) and Ti-doped Sr_2SnO_4 (b) thin films. Solid and dashed lines express T_g of 800 and 600 °C, respectively.

Figure 3 (color online)

PL and PLE spectra of doped alkaline-earth stannate films and Pr-doped $\text{Ca}_{0.6}\text{Sr}_{0.4}\text{TiO}_3$ (CSTO) film, and the photograph of stannate samples under UV excitation ($\lambda_{\text{ex}} = 254$ nm). The photograph shows each sample in disk (top), film on the substrate polished on one side (middle) and film polished on both sides (bottom).

Figure 1

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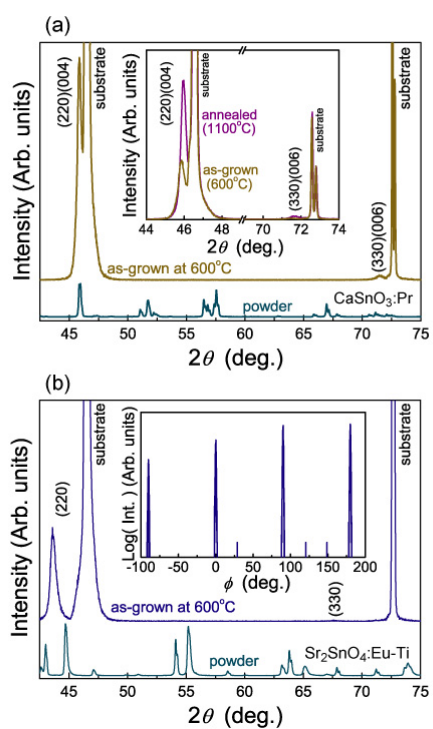


Figure 2

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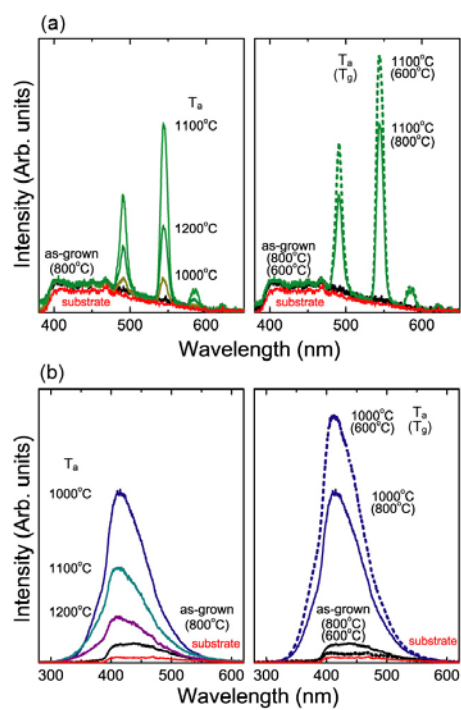


Figure 3

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