Photoluminescence properties of Pr doped and Tb-Mg codoped CaSnO₃ with Perovskite structure

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Title
Photoluminescence properties of Pr doped and Tb-Mg codoped CaSnO$_3$ with perovskite structure

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Abstract
In the survey of photoluminescence properties of rare-earth doped alkaline-earth stannates, CaSnO$_3$ was found to show intense white luminescence by Pr doping and green luminescence by Tb-Mg codoping. Pr-doped CaSnO$_3$ showed not only a red emission line originating from the f-f transition from $^1$D$_2$ to $^3$H$_4$ state, which is observed in Pr doped CaTiO$_3$ or SrTiO$_3$, but also an intense blue-green line assignable to the f-f transition from $^3$P$_0$ to $^3$H$_4$ state in Pr$^{3+}$ ions. Because of the mixture of the red and blue-green luminescence, the Pr-doped CaSnO$_3$ was seen in white under uv excitation. Tb-Mg codoped CaSnO$_3$ showed a sharp green emission line derived from the f-f transition of from $^5$D$_4$ to $^7$F$_{5}$ state in Tb$^{3+}$ ions along with other small emission lines. Tb-Mg codoping effectively enhanced the green luminescence of Tb$^{3+}$ ions probably due to the local lattice distortion around Tb ions induced by the small Mg ions at Ca sites. The photoluminescence properties of Pr doped and Tb-Mg codoped ASnO$_3$ (A = Sr, Ba) and CaMO$_3$ (M = Ti, Zr) with perovskite structures were also examined and compared to understand the luminescence mechanisms in these materials.

Keywords
luminescence, optical materials, oxides, ceramics
photoluminescence, stannates, perovskite structure, rare-earth ions

PACS codes
78.55.Hx, 81.05.Je
Introduction

It is known that Pr\(^{3+}\) doped CaTiO\(_3\) and SrTiO\(_3\) show intense red luminescence that is assigned to the f-f transition from \(^{1}D_2\) to \(^{3}H_4\) state in Pr\(^{3+}\) ions [1-3]. Tm\(^{3+}\) doped SrHfO\(_3\) and Tb\(^{3+}\) doped CaSnO\(_3\) were recently reported to show blue and green luminescence, respectively [4,5]. In addition, BaSnO\(_3\) was lately found to exhibit near-infrared luminescence probably due to the oxygen vacancies [6]. These findings of perovskite-type phosphors have reactivated the investigation and development of new luminescent rare-earth doped perovskite-type oxides along with the analysis of their luminescence mechanisms [7].

Several luminescence colors were found in the recent survey of photoluminescence (PL) properties of rare-earth doped alkaline-earth stannates with perovskite-related structures. In our previous paper [8], the PL properties of doped strontium stannates, Tb-Mg codoped SrSnO\(_3\), Ti doped or Eu-Ti codoped Sr\(_2\)SnO\(_4\) and Sm doped Sr\(_2\)Sn\(_2\)O\(_7\), were mainly reported among the alkaline-earth stannates and it was found that the layered structures and local structures at alkaline-earth ion sites significantly influence on the luminescence properties. Calcium stannates do not form the layered perovskite structures expressed by A\(_{n+1}\)Sn\(_n\)O\(_{3n+1}\) (A = alkaline earth ions, n = integer) except for the simple perovskite structure (n = ∞) in contrast to the strontium or barium stannates. The absence of the layered perovskite structures in the calcium stannates is due to the smaller ion radii of Ca ions (\(r_{(\text{Ia})}\) = 1.34 Å) than Sr ions (\(r_{(\text{II})}\) = 1.44 Å). This fact suggests that the distortion of the crystal structure, as well as local structures at alkaline-earth ion sites, in CaSnO\(_3\) perovskite is larger than in SrSnO\(_3\), anticipating that the larger structural distortion enhances the PL intensites in CaSnO\(_3\). Therefore, in this paper, the fundamental PL properties of Pr doped and Tb-Mg codoped CaSnO\(_3\) were examined. In addition, luminescence mechanisms and the influences of the structural distortion on the PL properties were discussed comparing the PL properties between analogous perovskites such as ASnO\(_3\) (A = Ca, Sr, Ba) and CaMO\(_3\) (M = Sn, Ti, Zr).

Experiments

Pr doped and Tb-Mg codoped CaSnO\(_3\) samples were prepared by solid state reaction using the starting materials of CaCO\(_3\) (99.99%), MgCO\(_3\) (99.9%), SnO\(_2\) (99.9%), Pr\(_6\)O\(_{11}\) (99.9%) and Tb\(_4\)O\(_7\) (99.9%). Their nominal chemical compositions were (Ca\(_{1-x}\)Pr\(_x\))SnO\(_3\) and {(Ca\(_{1-z}\)Mg\(_z\))\(_{1-y}\)Tb\(_y\)}SnO\(_3\) (x, y, z=0.0 ~ 0.1). In addition to these doped CaSnO\(_3\), Pr doped and Tb-Mg codoped ASnO\(_3\) (A=Sr, Ba) and CaMO\(_3\) (M=Ti, Zr) were also prepared to analyze PL mechanisms in these samples, additionally using the starting materials of SrCO\(_3\) (99.9%), BaCO\(_3\) (99.9%), TiO\(_2\) (99.9%) and ZrO\(_2\) (98%). Appropriate amounts of these starting materials were thoroughly mixed in a mortar with ethanol and dried. The dried powders were pressed into disks and the disks were heated at 1000 ~ 1400°C for 6h in air.

X-ray diffraction (XRD) patterns were measured using a Rint 2500 diffractometer (Rigaku) with CuK\(_{\alpha}\) radiation. PL emission/excitation spectra were measured using an F-4500 fluorescence spectrometer (Hitachi) at room temperature. Diffuse reflection spectra were also measured at room temperature using a V-570 uv/vis/nir spectrometer (Jasco) with an integrating sphere. The diffuse reflectance spectra were converted to absorption spectra following the Kubelka-Munk theory.
Results and discussion

PL properties of Pr doped and Tb-Mg codoped CaSnO₃

The single phase of CaSnO₃ was obtained by heating the samples at 1200 °C although CaSnO₃ itself was already formed at 1000 °C with secondary phases. Each XRD peak becomes sharper indicating the improvement of crystallinity, as the heating temperature increases up to 1400 °C. For the doped CaSnO₃, the single phases of (Ca₁₋ₓPrₓ)SnO₃ and {(Ca₁₋ₓMgₓ)₁₋ₙTbₙ}SnO₃ were obtained at 1400 °C in the dopant concentration range of x=0.0~0.01, y=0.0~0.005, z=0.0~0.03. Peak shifts in the XRD patterns were not clearly observed between the nondoped and Pr/Tb-Mg doped samples, probable because of the small dopant concentration. All doped samples prepared above 1100 °C showed the PL, but the PL intensity markedly increased by preparing the samples above 1200 °C in agreement with the formation of the single phase. The maximum PL intensity was obtained for the samples with high crystallinity prepared at 1400°C.

Fig. 1 shows the emission spectra of (Ca₀.₉₉₈Pr₀.₀₀₂)SnO₃, (Ca₀.₉₉₅Tb₀.₀₀₅)SnO₃, {(Ca₀.₉₇Mg₀.₀₃)₀.₉₉₅Tb₀.₀₀₅}SnO₃ and (Ca₀.₉₉₅Tb₀.₀₀₅)(Sn₀.₉₇Mg₀.₀₃)O₃ under uv excitation of λ<sub>ex</sub> = 254 nm. Pr doped and Tb/Tb-Mg doped samples showed white and green luminescence, respectively. A series of sharp emission lines at 490, 530, 612 nm were observed in the Pr doped samples and these emission lines were assigned to the f-f transition of ²P₀₋³H₄, ³P₀₋³H₅, ¹D₂₋³H₄ in Pr<sup>3+</sup> ions. The white coloration of the Pr doped samples occurs due to the mixture of complementary colors of these emissions. The Tb/Tb-Mg doped samples showed sharp emission lines at 490, 543, 580, 620 nm and these emission lines were assigned to the f-f transition of ⁵D₄₋⁷Fₐ (J=6, 5, 4, 3) in Tb<sup>3+</sup> ions. Although the green emission of Tb doped CaSnO₃ was already reported [5], we found that Tb-Mg codoping significantly increases the PL intensity. The PL intensity of Tb-Mg co-doped CaSnO₃ is more than twice larger than that of Tb doped CaSnO₃.

Two types of Tb-Mg codoping expressed by the nominal chemical compositions of {(Ca₀.₉₇Mg₀.₀₃)₀.₉₉₅Tb₀.₀₀₅}SnO₃ and (Ca₀.₉₉₅Tb₀.₀₀₅)(Sn₀.₉₇Mg₀.₀₃)O₃ were investigated to examine the effect of Mg ions. In the former case, Mg (r<sub>i</sub>(XII) = 1.20 Å) ions are considered to substitute for Ca (r<sub>i</sub>(XII) = 1.34 Å) ions increasing the the local lattice distortion around Ca or Tb ions. In the latter, Mg (r<sub>i</sub>(VI) = 0.72 Å) ions are supposed to replace Sn (r<sub>i</sub>(VI) = 0.69 Å) ions compensating the excess charge of Tb ions at Ca sites. The result of this investigation was that the PL intensity of the former {(Ca₀.₉₇Mg₀.₀₃)₀.₉₉₅Tb₀.₀₀₅}SnO₃ remarkably increased, while that of the latter (Ca₀.₉₉₅Tb₀.₀₀₅)(Sn₀.₉₇Mg₀.₀₃)O₃ definitely decreased as shown in Fig. 1. It is, therefore, suggested that Mg ions substituted for Ca ions promote the radiative transition in Tb ions by decreasing the site symmetry of the Tb ions.

The dopant concentration dependence of PL intensity in (Ca₁₋ₓPrₓ)SnO₃ and {(Ca₁₋ₓMgₓ)₁₋ₙTbₙ}SnO₃ is shown in Fig. 2. The PL intensity shows sharp concentration quenching against Pr or Tb concentration as frequently observed in other rare earth doped phosphors [9, 10] due to the resonance and/or cross-relaxation between Pr or Tb ions. On the other hand, the PL intensity of {(Ca₁₋ₓMgₓ)₁₋ₙTbₙ}SnO₃ moderately depends on Mg concentration. As a consequence, maximum PL
intensity was obtained at the concentration of $x = 0.002$ for $(\text{Ca}_{1-x}\text{Pr}_x)\text{SnO}_3$ and $y = 0.005, z = 0.03$ for $(\text{Ca}_{1-z}\text{Mg}_z)_{1-y}\text{Tb}_y\text{SnO}_3$.

The excitation spectra of $(\text{Ca}_{0.998}\text{Pr}_{0.002})\text{SnO}_3$ and $(\text{Ca}_{0.97}\text{Mg}_{0.03})_{0.995}\text{Tb}_{0.005}\text{SnO}_3$ were shown in Fig. 3 along with the absorption spectra of these samples and nondoped CaSnO$_3$. The excitation spectra were measured by monitoring the emission at 490nm for Pr doped sample and 543nm for Tb-Mg codoped sample. In the absorption spectra, intense absorption appears in the wavelength range shorter than approximately 280 nm for all samples, indicating the fundamental absorption of CaSnO$_3$. Pr doping or Tb-Mg codoping does not seem to influence the absorption spectra probably due to the small dopant concentration. In the excitation spectra, the excitation bands at 260 nm were observed in both Pr doped and Tb-Mg codoped samples and the long-wavelength side edges of these bands almost agreed with the absorption edge of CaSnO$_3$. This agreement implies that the excitation energy from a uv light is first absorbed by the host lattice through the interband transition, and then the absorbed energy sequentially transfers from the host lattice to Pr or Tb ions.

The influence of crystal structures on the PL spectra

The influence of crystal structural distortion on the PL intensity was investigated by substituting alkaline-earth ions at A sites in ASnO$_3$. The fundamental structural data for ASnO$_3$ ($A=$Ca, Sr, Ba) are summarized in Table 1. Although all ASnO$_3$ samples have perovskite-type crystal structure, the Ca and Sr samples have the distorted perovskite-type structures in contrast to the Ba sample with the ideal perovskite structure. The deviation from the ideal values in the $\angle$O-A-O angles ($\angle$O-A-O$_\text{ideal} = 90^\circ$) and tolerance factors ($t_{\text{ideal}} = 1.0$) clarifies the degree of the distortion, indicating the Ca samples have the most distorted structure among ASnO$_3$ ($A=$Ca, Sr, Ba). Fig. 4 shows the emission spectra of $(A_{0.998}\text{Pr}_{0.002})\text{SnO}_3$ and $(A_{0.97}\text{Mg}_{0.03})_{0.995}\text{Tb}_{0.005}\text{SnO}_3$ ($A=$Ca, Sr, Ba) under the uv excitation of $\lambda_{\text{ex}} = 254$ nm. Although the Ba samples do not show any PL at all, the Ca and Sr samples exhibit the PL by Pr doping or Tb-Mg codoping. In addition, the most intense emission from Pr or Tb ions was obtained in the Ca samples. These observations lead to the tendency that the PL intensity increases as the local distortion of Pr or Tb ions increases, which is consistent with the increase of the PL intensity by Tb-Mg codoping discussed above. This tendency is reasonable because the f-f transition is originally prohibited under high spherical symmetry.

The influence of electronic structures on the PL spectra and luminescence mechanisms

The modulation of electronic structures in stannate perovskites and the comparison of electronic structures between calcium perovskites were carried out to understand luminescence mechanisms in Pr doped and Tb-Mg codoped CaSnO$_3$.

Since the crystal structure of CaSnO$_3$ is basically the same with that of SrSnO$_3$, a complete solid solution can be formed between CaSnO$_3$ and SrSnO$_3$, which enable us modulating its bandgap continuously. The excitation and absorption spectra of $\{(\text{Ca}_{1-\alpha}\text{Sr}_\alpha)_{0.998}\text{Pr}_{0.002}\}\text{SnO}_3$ and $\{(\text{Ca}_{1-\alpha}\text{Sr}_\alpha)_{0.97}\text{Mg}_{0.03}\}_{0.995}\text{Tb}_{0.005}\text{SnO}_3$ ($\alpha=0.0~0.60$) are shown in Fig. 5. In the absorption spectra, the red shift of the fundamental absorption edges was observed in both Pr-doped and Tb-Mg codoped
samples as the Sr concentration increases; from $\lambda_{\text{edge}} = 280$ nm for CaSnO$_3$ to $\lambda_{\text{edge}} = 300$ nm for Ca$_{0.4}$Sr$_{0.6}$SnO$_3$. In the excitation spectra, similar single broad excitation bands were observed irrespective of the rare-earth ions and the maxima of the bands, which are close to the corresponding absorption edges, were shifted to the long wavelength side with an increase in the Sr concentration. These simultaneous red shifts in the absorption and excitation spectra clarify the luminescence mechanism in the doped CaSnO$_3$ that the interband transitions from the O 2p band to Sn 5s band first occur in the host lattices under uv excitation and then the excited energy transfers to the Pr or Tb ions. Accordingly, the electronic structures of these materials can be schematically illustrated as shown in the inset of Fig. 5.

To examine the luminescence mechanisms further, Ti or Zr ions were substituted for Sn ions in Ca samples, CaMO$_3$ (M=Sn, Ti, Zr), and their PL properties were compared. The emission spectra of (Ca$_{0.998}$Pr$_{0.002}$)MO$_3$ and {(Ca$_{0.97}$Mg$_{0.03}$)$_{0.995}$Tb$_{0.005}$}MO$_3$ (M=Sn, Ti, Zr) under uv excitation of $\lambda_{\text{ex}} = 254$ nm are shown in Fig. 6. Pr doped zirconate showed a PL spectrum very similar to those of the Pr doped stannates and the observed emission lines are also assigned in the same manner for the stannates. A sharp single emission line at 612 nm was observed in Pr doped titanate and the emission was assigned to the f-f transition of $^1D_2-^3H_4$ in Pr$^{3+}$ ions as previously reported [1-3]. Therefore, the Pr doped stannate or zirconate exhibited white or blue-green luminescence, while the Pr doped titanate did red luminescence. In the case of Tb-Mg codoping, codoped titanate showed no PL but co-doped zirconate exhibited several emission lines which are partly different from those for the stannates. The observed blue luminescence for the zirconate consists of sharp emission lines at 380, 415, 435, 460, 472, 490, 543, 580, 620nm which were assignable to the f-f transition of $^5D_2-^7F_J$ (J=6, 5, 4, 3, 2) and $^5D_4-^7F_J'$ ((J'=6, 5, 4, 3) in Tb$^{3+}$ ions. The basic structural data of CaMO$_3$ (M=Sn, Ti, Zr) are listed in Table 2. Because these materials are all distorted perovskites, the differences of their luminescence properties are not simply attributed to the local distortion at alkaline-earth ion sites as in ASnO$_3$ (A=Ca, Sr, Ba).

The excitation and absorption spectra of the Pr doped or Tb-Mg codoped CaMO$_3$ (M=Sn, Ti, Zr) are shown in Fig. 7 (a) and (b). In the absorption spectra of the Pr doped samples, the absorption edges of the Pr doped samples were seen at almost the same wavelengths with the nondoped samples indicating that the absorption edges were derived from the interband transition of each host material. However, the wavelengths of the absorption edges are significantly dependent on the M ions revealing the differences of their bandgaps; approximately 350 nm for Ti samples, 280nm for Sn samples and 230 nm for Zr samples. Therefore, in spite of similar distorted perovskite structures, the electronic structures of these materials are largely different from each other and responsible for the differences in the PL spectra in Fig. 6. In the excitation spectra, broad single bands were observed in the titanate and stannate, while two bands, band I at 220 nm and band II at 250 nm, were observed in the zirconate. Since the excitation bands in the titanate and stannate and the excitation band I in the zirconate were observed near the absorption edges of the host materials, the excitation at these bands are considered to cause the interband transition followed by the sequential energy transfer to the Pr ions. On the other hand, the excitation band II in the zirconate is assigned to the f-d transition band in Pr ions. In the case
of Tb-Mg codoped samples, the obtained results were very similar to those of the Pr doped samples except that the Tb-Mg codoped titanate shows no PL and no excitation band. The absorption spectra were almost the same irrespective of Pr doping or Tb-Mg co-doping but different in terms of M ions, showing the variation of the bandgap of the host materials. In the excitation spectra, the stannate shows a single excitation band near the absorption edge and the zirconate exhibits two excitation bands; one is near the absorption edge and the other is below the absorption edge. The bands near the absorption edges in the stannate and zirconate originate from the interband transition and the band below the absorption edge in the zirconate is attributed to the f-d transition in Tb ions.

Conclusion

Intense white and green PL were observed in (Ca$_{0.998}$Pr$_{0.002}$)SnO$_3$ and {(Ca$_{0.97}$Mg$_{0.03}$)$_{0.995}$Tb$_{0.005}$}SnO$_3$, respectively, and their emission lines were assigned to the f-f transition of each rare-earth ions. In the green luminescence of Tb ions, Mg ions substituted at Ca sites effectively increase the luminescence intensity probably due to the local lattice distortion around Tb ions caused by small Mg ions. Irrespective of doped rare-earth ions, the PL of CaSnO$_3$ showed the largest intensity among ASnO$_3$ (A = Ca, Sr, Ba), suggesting that the smallest Ca ions increase the radiative transition probability of rare-earth ions by increasing the distortion at A sites. Pr-doped and Tb-Mg codoped CaMO$_3$ (M =Sn, Ti, Zr) showed various luminescence color and luminescence mechanisms because of the large difference in the energy gaps. From the comparison of the PL properties between ASnO$_3$ (A = Ca, Sr, Ba) and CaMO$_3$ (M =Sn, Ti, Zr), the luminescence mechanism in the rare-earth doped CaSnO$_3$ was understood that the energy transfer from the host lattices to rare-earth ions occurs primarily after the energy absorption by the host materials.

References

### Table 1  Crystal structural data of ASnO₃ (A = Ca, Sr, Ba)

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### Table 2  Crystal structural data of CaMO₃ (M =Sn, Ti, Zr)

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Figure Captions

Figure 1
PL spectra of \((\text{Ca}_{0.998}\text{Pr}_{0.002})\text{SnO}_3, (\text{Ca}_{0.995}\text{Tb}_{0.005})\text{SnO}_3, (\text{Ca}_{0.97}\text{Mg}_{0.03})_{0.995}\text{Tb}_{0.005}\text{SnO}_3\) and \((\text{Ca}_{0.995}\text{Tb}_{0.005})(\text{Sn}_{0.97}\text{Mg}_{0.03})\text{O}_3\) under uv excitation of \(\lambda_{\text{ex}} = 254\) nm.

Figure 2
PL intensity of \((\text{Ca}_{1-x}\text{Pr}_x)\text{SnO}_3\) and \((\text{Ca}_{1-z}\text{Mg}_z)_{1-y}\text{Tb}_y\)\text{SnO}_3\) as a function of the dopant concentration.

Figure 3
Excitation and absorption spectra of \((\text{Ca}_{0.998}\text{Pr}_{0.002})\text{SnO}_3\) and \((\text{Ca}_{0.97}\text{Mg}_{0.03})_{0.995}\text{Tb}_{0.005}\text{SnO}_3\). Absorption spectra were measured with (solid lines) or without (dashed lines) visible-cut filters.

Figure 4
PL spectra of Pr doped and Tb-Mg codoped ASnO\(_3\) (A=Ca, Sr, Ba) under uv excitation of \(\lambda_{\text{ex}} = 254\) nm.

Figure 5
Excitation and absorption spectra of (a) Pr doped and (b) Tb-Mg codoped \((\text{Ca}_{1-\alpha}\text{Sr}_\alpha)\text{SnO}_3\) \((0 \leq \alpha \leq 0.6)\) solid solution. Inset shows schematic energy band/level diagram of the Pr doped materials; the bandgap becomes smaller as Sr concentration increases.

Figure 6
PL spectra of Pr doped and Tb-Mg codoped CaMO\(_3\) (M=Sn, Zr, Ti) under uv excitation of \(\lambda_{\text{ex}} = 254\) nm.

Figure 7
Excitation and absorption spectra of (a) Pr doped and (b) Tb-Mg codoped CaMO\(_3\) (M=Sn, Zr, Ti).
Fig. 3
Fig. 4
Fig. 5a
Fig. 5b
Fig. 7a
Fig. 7b