B-site-ordered Double-perovskite Oxide Up-conversion Phosphors Doped with Yb and Ho, Er, or Tm

Kohei Kasuya, Yasushi Sato, Makoto Kobayashi, Hideki Kato, Masato Kakihana, and Koji Tomita

1 Graduate School of Science and Technology, Tokai University, 4-1-1 Kitakaname, Hiratsuka, Kanagawa 259–1292, Japan
2 Department of Chemistry, Okayama University of Science, Ridaicho, Okayama Kita-ku, Okayama 700–0005, Japan
3 Institute of Materials and Systems for Sustainability, Nagoya University, Furocho, Nagoya Chikusa-ku, Aichi 464–8601, Japan
4 Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, 2-1-1 Katahira, Aoba-ku, Sendai 980–8577, Japan
*tomita@keyaki.cc.u-tokai.ac.jp

B-site-ordered double-perovskite oxide up-conversion phosphors La$_2$ZnTiO$_6$, La$_2$MgTiO$_6$, and Ba$_2$LaTaO$_6$ doped with Yb and Ho, Er, or Tm were synthesized by a citric acid complex gelation method and a polymerizable complex method. Under 980-nm excitation, the double-perovskite oxide phosphors doped with luminescent ions at the A-site (La$_2$ZnTiO$_6$ and La$_2$MgTiO$_6$) showed stronger up-conversion emission than the phosphor doped with luminescent ions at the B-site (Ba$_2$LaTaO$_6$). La$_2$ZnTiO$_6$ and La$_2$MgTiO$_6$, in which dopants occupied the A-site, showed different up-conversion emission behaviors because of structural distortion resulting from the substitution of B-site cations.

Keywords: Double-perovskite, Up-conversion, Phosphor, Lanthanide ion

1. Introduction

Up-conversion phosphors can convert several low-energy photons to a higher-energy photon through multistep excitation. Multistep excitation becomes possible by doping of two lanthanide ions as an emitting ion and a sensitizer. Ho$^{3+}$, Er$^{3+}$, or Tm$^{3+}$ is often used as the light-emitting ion, and Yb$^{3+}$ is often used as the sensitizer. These phosphors are expected to have applications in bioimaging, three-dimensional displays, security inks, and solar cells [1-6]. However, to enable their use in the aforementioned applications, the intensity of the up-conversion luminescence need to be enhanced.

In our previous work, we found a correlation between up-conversion emission and crystal structure [7]. Therefore, we focused on a double-perovskite structure that can be actively distorted compared with the common perovskite structure.

Oxide phosphors with a double-perovskite structure have been studied for downshifting phosphors doped with Eu and Mn [8-12]; however, in recent years, research into up-conversion phosphors co-doped with Er$^{3+}$–Yb$^{3+}$ or Ho$^{3+}$–Yb$^{3+}$ has been reported [13-16]. In addition, La$_2$MgTiO$_6$ has been reported to be prepared via a citric acid complex gelation method [17]. In this study, La$_2$ZnTiO$_6$, La$_2$MgTiO$_6$, and Ba$_2$LaTaO$_6$ double-perovskite up-conversion phosphors were prepared using a citric acid complex gelation method and a polymerizable complex method, and their up-conversion luminescence characteristics were investigated.

2. Experimental

La$_2$O$_3$ (99.9%, Nippon Yttrium Co.), Ho$_2$O$_3$ (99.9%, Nippon Yttrium Co.), Er$_2$O$_3$ (99.9%, Nippon Yttrium Co.), Tm$_2$O$_3$ (99.9%, Nippon Yttrium Co.), and Yb$_2$O$_3$ (99.9%, Nippon Yttrium Co.) were dissolved in nitric acid to form an aqueous nitrate solution. Zn(NO$_3$)$_2$·6H$_2$O (99.0%,...
La3+, Ba2+, Ta5+, Ho3+, Er3+, Tm3+, and/or Yb3+ was complex. Citric acid was added to this solution to an ice bath to form a peroxo–tantalum acid synthesized (Table 1). An aqueous solution of La3+, 60 °C [19]. ammonia were subsequently removed by heating at 120 °C until it gelled; the product was then calcined at 450 °C. The precursors were ground in an agate mortar, placed in a mullite crucible, and fired at 1200 °C for 5 h to obtain samples of Ba2LaTaO6.

Fifteen double-perovskite oxide samples were synthesized (Table 1). An aqueous solution of La3+, Zn2+, Mg2+, Ti4+, Ho3+, Er3+, Tm3+, and/or Yb3+ was prepared with a total cation concentration of 2 mmol according to the stoichiometric ratio of the target; 3.3 mL of 3 M citric acid solution and 40 mmol of propylene glycol were then added, and the resultant mixture was stirred. The solution was then concentrated by being heated at 120 °C until it gelled; the product was then calcined at 450 °C. The precursor was ground in an agate mortar, placed in a mullite crucible, and fired at 1200 °C for 5 h to obtain samples of Ba2LaTaO6.

The phases of all products were characterized by powder X-ray diffraction (XRD, D8 ADVANCE, Bruker) carried out with Cu-Kα radiation (λ = 0.1540596 nm). The up-conversion luminescence spectra were recorded at room temperature using a multichannel photodetector (MCPD-7700:311C, Otsuka Electronics Co., Ltd.) with a 980-nm near-infrared laser diode (L980P300J, THORLABS) as the excitation source. Samples co-doped with Er and Yb or Ho and Yb were measured at a laser power of 72.5 mW; samples co-doped with Tm and Yb were measured at 228 mW.

### 3. Results and discussion

Figure 1 shows XRD patterns of nondoped samples and the samples doped with 5% Er and 10% Yb. The main phases of the obtained nondoped samples were confirmed to be monoclinic LaZn0.5Ti0.5O3 (ICSD No.172755), monoclinic LaMg0.5Ti0.5O3 (ICSD No.95992), and monoclinic Ba2LaTaO6 (ICSD No.190845). The XRD peaks of the samples doped with Er and Yb were slightly shifted to higher angles. This shift suggests that the dopant ions, Er3+ (0.89 Å) and Yb3+ (0.87 Å), were doped at the La3+ (1.03 Å) site; the La3+ ion has a larger ionic radius than the dopant ions and the same valence in the respective host materials [20,21].
Figure 2 shows the up-conversion luminescence intensity of the obtained samples. The luminescence intensities of the Ba2LaTaO6 phosphors were extremely weak, whereas those of the La2ZnTiO6 and La2MgTiO6 phosphors were stronger. This difference in luminescence intensity is attributed to the site occupancy of the La ions in the double-perovskite structure. Figure 3 shows crystal structures of La2ZnTiO6, La2MgTiO6, and Ba2LaTaO6. In the La2ZnTiO6 and La2MgTiO6, which showed strong up-conversion emission, the La occupies the A-site in the perovskite structure. By contrast, in Ba2LaTaO6, which showed weak up-conversion emission, La occupies the B-site.

Up-conversion emission based on an f–f transition is strongly affected by the crystal field of lanthanide ions. If the lanthanide ions occupy a symmetry inversion center, electric-dipole f–f transitions are forbidden, resulting in very low up-conversion emission intensities [22]. In the double-perovskite oxide, the B-site is an inversion symmetry center, whereas the A-site is not. Therefore, Ba2LaTaO6, in which dopants are substituted at the B site, exhibited extremely weak emission intensity, and La2ZnTiO6 and La2MgTiO6, in which dopants are substituted at the A site, showed strong emission intensity. Moreover, the difference in up-conversion emission from A-site ions in the two host crystals is also due to differences in the f–f transition probabilities. In the La2ZnTiO6, a higher Er concentration resulted in stronger emission; in addition, Ho doping resulted in stronger emission intensity of the Ba2LaTaO6 samples. The calculated patterns are included for comparison. (▼: Ba3Ta2O8).

Fig. 1. XRD patterns of the nondoped samples and the samples co-doped with 5% Er and 10% Yb; the calculated patterns are included for comparison. (▼: Ba3Ta2O8).

Fig. 2. Up-conversion luminescence intensities of the samples. (λex = 980 nm, laser power: Er, Yb, and Ho–Yb = 72.5 mW; Tm–Yb = 228 mW).

Fig. 3. Crystal structures of double-perovskite oxides: (a) LaZn0.5Ti0.5O3 (ICSD No. 172755), (b) LaMg0.5Ti0.5O3 (ICSD No. 95992), and (c) Ba2LaTaO6 (ICSD No. 190845).
in stronger emission than Tm doping. In the La$_2$MgTiO$_6$, a lower Er concentration resulted in stronger emission and Tm doping resulted in stronger emission than Ho doping. The A site of the double-perovskite structure can be distorted by the BO$_6$ polyhedra, and such distortions will affect the electric-dipole f–f transition probability. The difference in up-conversion emission intensities was attributed to differences in the symmetry of the dopant sites. The A-site of the double-perovskite structure is not a symmetry inversion center; in this case, electric-dipole f–f transitions are forbidden, resulting in very weak up-conversion emissions. The A-site of the double-perovskite structure is not a symmetry inversion center; therefore, electric-dipole f–f transitions are allowed, resulting in strong emissions.

By contrast, the B-site of the double-perovskite structure is a symmetry inversion center; in this case, electric-dipole f–f transitions are forbidden, resulting in very weak up-conversion emissions. The up-conversion emission behaviors of La$_2$ZnTiO$_6$ and La$_2$MgTiO$_6$ doped with Ho, Er, or Tm as the emission ion differed. These differences are explained by the different f–f transition probability of dopants at the A-sites as a result of distortions originating from ZnO$_6$ and MgO$_6$ polyhedra.

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