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

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B-site-ordered double-perovskite oxide up-conversion phosphors $\text{La}_2\text{ZnTiO}_6$, $\text{La}_2\text{MgTiO}_6$, and $\text{Ba}_2\text{LaTaO}_6$ 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 ($\text{La}_2\text{ZnTiO}_6$ and $\text{La}_2\text{MgTiO}_6$) showed stronger up-conversion emission than the phosphor doped with luminescent ions at the B-site ($\text{Ba}_2\text{LaTaO}_6$). $\text{La}_2\text{ZnTiO}_6$ and $\text{La}_2\text{MgTiO}_6$, 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 $\text{Er}^{3+}\text{-Yb}^{3+}$ or $\text{Ho}^{3+}\text{-Yb}^{3+}$ has been reported [13-16]. In addition, $\text{La}_2\text{MgTiO}_6$ has been reported to be prepared via a citric acid complex gelation method [17].

In this study, $\text{La}_2\text{ZnTiO}_6$, $\text{La}_2\text{MgTiO}_6$, and $\text{Ba}_2\text{LaTaO}_6$ 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_2O_3 (99.9%, Nippon Yttrium Co.), Ho_2O_3 (99.9%, Nippon Yttrium Co.), Er_2O_3 (99.9%, Nippon Yttrium Co.), Tm_2O_3 (99.9%, Nippon Yttrium Co.), and Yb_2O_3 (99.9%, Nippon Yttrium Co.) were dissolved in nitric acid to form an aqueous nitrate solution. $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (99.0%,

Wako) and $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ (98.0%, Wako) were dissolved in water to form an aqueous solution. Titanium metal powder (99.9%, Furuuchi Chemical Co.) was dissolved in an ice-cooled solution of 30% H_2O_2 (Wako) and 28% NH_3 (Wako). Citric acid (98%, Wako) was then added into solution of the Ti-peroxo complex and kept for 1 day at 80 °C until an orange gel formed. The obtained gel was dissolved in water to form an aqueous solution [18]. BaCO_3 (99.0%, Kanto Chemical Co.) was dissolved with lactic acid aqueous solution to make a lactic acid–Ba complex. TaCl_5 was dissolved in 30% H_2O_2 and 28% NH_3 in an ice bath to form a peroxo–tantalum acid complex. Citric acid was added to this solution to stabilize the Ta complex. Excess H_2O_2 and ammonia were subsequently removed by heating at 60 °C [19].

Fifteen double-perovskite oxide samples were synthesized (Table 1). An aqueous solution of La^{3+} , Zn^{2+} , Mg^{2+} , Ti^{4+} , Ho^{3+} , Er^{3+} , Tm^{3+} , and/or Yb^{3+} 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 was then added, and the resultant solution was mixed with stirring. The solution was concentrated by being heated at 120 °C until it gelled; the product was subsequently 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 $\text{La}_2\text{ZnTiO}_6$ and $\text{La}_2\text{MgTiO}_6$.

Five samples containing Ba were synthesized by the polymerizable complex method to avoid precipitation of $\text{Ba}(\text{NO}_3)_2$. An aqueous solution of La^{3+} , Ba^{2+} , Ta^{5+} , Ho^{3+} , Er^{3+} , Tm^{3+} , and/or Yb^{3+} 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 precursors were ground in an agate mortar, placed in a mullite crucible, and fired at 1200 °C for 5 h to obtain samples of $\text{Ba}_2\text{LaTaO}_6$.

The phases of all products were characterized by powder X-ray diffraction (XRD, D8 ADVANCE, Bruker) carried out with Cu-K α radiation ($\lambda = 0.1540596$ 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 $\text{LaZn}_{0.5}\text{Ti}_{0.5}\text{O}_3$ (ICSD No.172755), monoclinic $\text{LaMg}_{0.5}\text{Ti}_{0.5}\text{O}_3$ (ICSD No.95992), and monoclinic $\text{Ba}_2\text{LaTaO}_6$ (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, Er^{3+} (0.89 Å) and Yb^{3+} (0.87 Å), were doped at the La^{3+} (1.03 Å) site; the La^{3+} ion has a larger ionic radius than the dopant ions and the same valence in the respective host materials [20,21].

Table 1. Chemical compositions of the target materials.

Nondoped	$\text{La}_2\text{ZnTiO}_6$	$\text{La}_2\text{MgTiO}_6$	$\text{Ba}_2\text{LaTaO}_6$
Er 1%, Yb 2%	$\text{La}_{1.94}\text{Er}_{0.02}\text{Yb}_{0.04}\text{ZnTiO}_6$	$\text{La}_{1.94}\text{Er}_{0.02}\text{Yb}_{0.04}\text{MgTiO}_6$	$\text{Ba}_2\text{La}_{0.97}\text{Er}_{0.01}\text{Yb}_{0.02}\text{TaO}_6$
Er 5%, Yb 10%	$\text{La}_{1.7}\text{Er}_{0.1}\text{Yb}_{0.2}\text{ZnTiO}_6$	$\text{La}_{1.7}\text{Er}_{0.1}\text{Yb}_{0.2}\text{MgTiO}_6$	$\text{Ba}_2\text{La}_{0.85}\text{Er}_{0.05}\text{Yb}_{0.1}\text{TaO}_6$
Ho 0.1%, Yb 3%	$\text{La}_{1.938}\text{Ho}_{0.002}\text{Yb}_{0.06}\text{ZnTiO}_6$	$\text{La}_{1.938}\text{Ho}_{0.002}\text{Yb}_{0.06}\text{MgTiO}_6$	$\text{Ba}_2\text{La}_{0.969}\text{Ho}_{0.001}\text{Yb}_{0.03}\text{TaO}_6$
Tm 0.1%, Yb 3%	$\text{La}_{1.938}\text{Tm}_{0.002}\text{Yb}_{0.06}\text{ZnTiO}_6$	$\text{La}_{1.938}\text{Tm}_{0.002}\text{Yb}_{0.06}\text{MgTiO}_6$	$\text{Ba}_2\text{La}_{0.969}\text{Tm}_{0.001}\text{Yb}_{0.03}\text{TaO}_6$

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. (▼: $\text{Ba}_3\text{Ta}_2\text{O}_8$).

Figure 2 shows the up-conversion luminescence intensity of the obtained samples. The luminescence intensities of the $\text{Ba}_2\text{LaTaO}_6$ phosphors were extremely weak, whereas those of the $\text{La}_2\text{ZnTiO}_6$ and $\text{La}_2\text{MgTiO}_6$ 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 $\text{La}_2\text{ZnTiO}_6$, $\text{La}_2\text{MgTiO}_6$, and $\text{Ba}_2\text{LaTaO}_6$. In the $\text{La}_2\text{ZnTiO}_6$ and $\text{La}_2\text{MgTiO}_6$, which showed strong up-conversion emission, the La occupies the A-site in the perovskite structure. By contrast, in $\text{Ba}_2\text{LaTaO}_6$, 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, $\text{Ba}_2\text{LaTaO}_6$, in which dopants are substituted at the B site, exhibited extremely weak emission intensity, and $\text{La}_2\text{ZnTiO}_6$ and $\text{La}_2\text{MgTiO}_6$, 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 $\text{La}_2\text{ZnTiO}_6$, a higher Er concentration resulted in stronger emission; in addition, Ho doping resulted

Fig. 2. Up-conversion luminescence intensities of the samples. ($\lambda_{\text{ex}} = 980$ nm, laser power: Er, Yb, and Ho–Yb = 72.5 mW; Tm–Yb = 228 mW).

Fig. 3. Crystal structures of double-perovskite oxides: (a) $\text{La}_2\text{Zn}_{0.5}\text{Ti}_{0.5}\text{O}_3$ (ICSD No. 172755), (b) $\text{LaMg}_{0.5}\text{Ti}_{0.5}\text{O}_3$ (ICSD No. 95992), and (c) $\text{Ba}_2\text{LaTaO}_6$ (ICSD No. 190845).

in stronger emission than Tm doping. In the $\text{La}_2\text{MgTiO}_6$, 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 from the A sites in the two host crystals originates from the different distortions of the A sites of the two double-perovskite host crystals by the B cations.

4. Conclusion

B-site-ordered double-perovskite oxides $\text{La}_2\text{ZnTiO}_6$, $\text{La}_2\text{MgTiO}_6$, and $\text{Ba}_2\text{LaTaO}_6$ doped with Yb and Ho, Er, or Tm were synthesized, and their up-conversion luminescence characteristics were investigated. Dopants occupied the A-site of the perovskite structure of $\text{La}_2\text{ZnTiO}_6$ and $\text{La}_2\text{MgTaO}_6$, which showed strong up-conversion emission under 980-nm excitation. By contrast, $\text{Ba}_2\text{LaTaO}_6$, in which dopants occupied the B-site of the perovskite structure, showed very weak up-conversion emission. The difference in the 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; 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 $\text{La}_2\text{ZnTiO}_6$ and $\text{La}_2\text{MgTiO}_6$ 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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References

1. W. Yin, L. Zhou, Z. Gu, G. Tian, S. Jin, L. Yan, X. Liu, G. Xing, W. Ren, F. Liu, Z. Pan, and Y. Zhao, *J. Mater. Chem.*, **22** (2012) 6974.
2. L. Zhou, B. He, J. Huang, Z. Cheng, X. Xu, and C. Wei, *ACS Appl. Mater. Interfaces*, **6** (2014) 7719.
3. F. He, L. Feng, P. Yang, B. Liu, S. Gai, G. Yang, Y. Dai, and J. Lin, *Biomaterials*, **105** (2016) 77.
4. R. Deng, F. Qin, R. Chen, W. Huang, M. Hong, and X. Liu, *Nat. Nanotechnol.*, **10** (2015) 237.
5. J. M. Meruga, A. Baride, W. Cross, J. J. Kellar, and P. S. May, *J. Mater. Chem. C*, **2** (2014) 2221.
6. A. Shalav, B. S. Richards, and M. A. Green, *Sol. Energy Mater. Sol. Cells*, **91** (2007) 829.
7. S. Tamura, M. Iwaoka, Y. Sato, M. Kobayashi, M. Kakihana, and K. Tomita, *Chem. Lett.*, **47** (2018) 1282.
8. H. Chen, Q. Huang, J. Xu, B. Wang, Z. Lin, J. Zhou, and Y. Wang, *J. Mater. Chem. C*, **4** (2016) 2374.
9. Q. Liu, X. Li, B. Zhang, L. Wang, Q. Zhang, and L. Zhang, *Ceram. Int.*, **42** (2016) 15294.
10. L. Zhang, Q. Liu, N. Ding, H. Yang, L. Wang, and Q. Zhang, *J. Alloys Compd.*, **642** (2015) 45.
11. X. Yin, J. Yao, Y. Wang, C. Zhao, and F. Huang, *J. Lumin.*, **132** (2012) 1701.
12. A. Fu, C. Zhou, Q. Chen, Z. Lu, T. Huang, H. Wang, and L. Zhou, *Ceram. Int.*, **43** (2017) 6353.
13. D. R. Kim, S. W. Park, B. K. Moon, S. H. Park, J. H. Jeong, H. Choib, and J. H. Kim, *RSC Adv.*, **7** (2017) 1464.
14. P. Rawat, S. K. Saroj, M. Gupta, G. V. Prakash, and R. Nagarajan, *J. Fluorine Chem.*, **200** (2017) 1.
15. X. Gao, D. Xu, J. Du, J. Li, and J. Sun, *J. Mater. Sci.: Mater. Electron.*, **29** (2018) 1146.
16. K. N. Kumar, L. Vijayalakshmi, and J. Choi, *Inorg. Chem.*, **58** (2019) 2001.
17. Y. Xu, P. Lu, G. Huang, and C. Zeng, *Mater. Chem. Phys.*, **92** (2005) 220.
18. M. Kakihana, K. Tomita, V. Petrykin, M. Tada, S. Sasaki, and Y. Nakamura, *Inorg. Chem.*, **43** (2004) 4546.
19. S. Tamura, M. Iwaoka, Y. Sato, M. Kobayashi, M. Kakihana, and K. Tomita, *J. Photopolym. Sci. Technol.*, **30** (2017) 507.
20. R. D. Shannon, *Acta Cryst.*, **A32** (1976) 751.
21. Y. Q. Jia, *J. Solid State Chem.*, **95** (1991) 184.
22. S. Tanabe, *Kidorui*, **23** (2014) 67 (in Japanese).