Site dependence of Tb³⁺ Luminescence in Double Perovskite-Type Alkaline Earth Lanthanum Tantalates

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ABSTRACT

Tb³⁺ doped alkaline earth lanthanum tantalates with the B-site-ordered double perovskite-type structure (AA')[BB']O₆ (namely (CaLa_{1-x}Tb_x)[CaTa]O₆ (CLTO:Tb³⁺) and Ba₂[La_{1-x}Tb_xTa]O₆ (BLTO:Tb³⁺) with x =0.01, 0.10) were prepared and their Tb³⁺ photoluminescence (PL) properties were examined and explained based on the occupied crystal sites (A or B sites). The location of Tb³⁺ activators were elucidated by analyzing powder X-ray diffraction patterns and X-ray absorption near edge structure at the Tb L_{III} edge. Tb³⁺ ions are located at A sites in the CLTO:Tb³⁺ and at B sites in the BLTO:Tb³⁺ as indicated in the nominal compositions. Both CLTO:Tb³⁺ and BLTO:Tb³⁺ exhibited intense PL excitation (PLE) peaks in the UV region due to the 4f–5d excitation for Tb³⁺. The PLE peak of Tb³⁺ in BLTO:Tb³⁺ showed a marked red shift compared to that in CLTO:Tb³⁺ primarily because of the larger crystal field at the B sites than at the A sites. The main PL peaks associate with the 4f–4f transitions from ⁵D₄ to ⁷F₅ states are also influenced by the crystal field and the splitting of the PL peaks for Tb³⁺ at B sites in BLTO:Tb³⁺ is more pronounced than for Tb³⁺ at A sites in CLTO:Tb³⁺. In addition, owing to a downshift of the Tb 5d orbitals, the PL in the blue region derived from ⁵D₃–⁷F_J transitions are quenched for Tb³⁺ in BLTO:Tb³⁺.

1. INTRODUCTION

Green phosphors are of capital importance for white lightening sources where red, green and blue emissions are combined as primary colors of light. Many green luminescent materials exist and give rise to various applications; $\text{CeMgAl}_{10}\text{O}_{19}:\text{Tb}^{3+}$, $(\text{La,Ce})\text{PO}_4:\text{Tb}^{3+}$, $(\text{Gd,Ce})\text{MgB}_5\text{O}_{10}:\text{Tb}^{3+}$ for trichromatic fluorescent lamps, $\text{SrGa}_2\text{S}_4:\text{Eu}^{2+}$ and $\beta\text{-SiAlON}:\text{Eu}^{2+}$ for white light emitting diodes (LEDs), $\text{Zn}_2\text{SiO}_4:\text{Mn}^{2+}$, $\text{BaAl}_{12}\text{O}_{19}:\text{Mn}^{2+}$ and $(\text{Y,Gd})\text{BO}_3:\text{Tb}^{3+}$ for plasma display panels (PDPs), $\text{ZnS}:\text{Cu}^+-\text{Al}^{3+}$, $\text{Y}_2\text{SiO}_5:\text{Tb}^{3+}$, $\text{InBO}_3:\text{Tb}^{3+}$ for cathode-ray tubes (CRTs) and field-emission displays (FEDs).¹⁻³ Clearly, Tb^{3+} ions, which are widely used in the industry, stably show green luminescence irrespective of the host lattices (HLs) because the Tb^{3+} green luminescence originates from intraconfigurational 4f–4f transitions and the inner 4f orbitals are less sensitive to the surroundings than the outer 5d orbitals.^{4,5} Therefore, an intense photoluminescence (PL) peak at approximately 545 nm is usually observed for Tb^{3+} due to the radiative $^5\text{D}_4 - ^7\text{F}_5$ transitions. To obtain the Tb^{3+} green luminescence, Tb^{3+} is frequently excited through the 4f–5d transitions under UV irradiation. In contrast to the PL peak position for Tb^{3+} , the position of the PL excitation (PLE) peak for the Tb^{3+} 4f-5d transitions changes from one HL to another because the energy levels of the outer 5d orbitals is much influenced by the local structure that varies with metal – ligands distances, coordination numbers, etc.⁵

Recently, site-sensitive luminescence properties of Tb^{3+} were reported in some distorted simple perovskite-type oxides (ABO_3), namely LaScO_3 and LaLuO_3 .^{6,7} Even though Tb^{3+} at both A and B sites led to a similar green luminescence ($^5\text{D}_4 - ^7\text{F}_J$ transitions) under UV excitation, Tb^{3+} at B site gave larger splitting of the main PL peak at 545 nm ($^5\text{D}_4 - ^7\text{F}_5$ transitions) than Tb^{3+} at A site. In addition, Tb^{3+} at A site gave rise to not only the green luminescence but also a weak blue luminescence ($^5\text{D}_3 - ^7\text{F}_J$ transitions), while the blue luminescence quenched for Tb^{3+}

at B site. Moreover, an intense PLE peak derived from Tb^{3+} 4f-5d excitation was found at much longer wavelength for Tb^{3+} at B site than Tb^{3+} at A site. These observations suggest that new phosphors with targeted optical properties could benefit from this site-selective doping concept not only in perovskite-type materials but also in other crystalline materials. The site-selective doping accompanying the changes of Tb^{3+} 4f and 5d energy levels may enable some adjustments of excitation wavelengths, defect energy levels for electron trapping, etc. In the specific case of the simple perovskite-type structure, only few candidates for HL oxides are accessible to the large Tb^{3+} ionic sizes according to Goldschmidt tolerance factor.⁸⁻¹⁰ In contrast, double perovskite-type oxides $((\text{AA}')[\text{BB}']\text{O}_6)$ appear suitable HLs to probe for further examination of the site-sensitive Tb^{3+} luminescence because they are highly capable to accommodate various lanthanide (Ln) ions at A and B sites.

Among double perovskite-type oxides,^{11,12} alkaline earth lanthanum tantalates were selected to control Tb^{3+} -doping site. The crystal structures of the $\text{Ca}_2\text{LaTaO}_6$ (CLTO) and $\text{Ba}_2\text{LaTaO}_6$ (BLTO) are illustrated in Figure 1. Both materials are reported to crystallize in monoclinic phase with the space group of P21/n (No. 14), although the space group of I2/m (No. 12) has been

Figure 1. Crystal structures of double perovskite-type (a) $\text{Ca}_2\text{LaTaO}_6$ and (b) $\text{Ba}_2\text{LaTaO}_6$. La ions are located at A sites in $(\text{CaLa})[\text{CaTa}]\text{O}_6$ and at B sites in $(\text{Ba}_2)[\text{LaTa}]\text{O}_6$.

considered recently for the Ba material.¹³⁻¹⁵ In the Ca material, the coordination number for B-site ions is six, whereas that for A-site ions is regarded to be eight rather than twelve because of the large distortion from the ideal cubic structure. The important structural difference between the Ca and Ba materials lies in the atomic position of the La ions; namely, La^{3+} ions occupy A sites (eight-folded coordination with site symmetry of 1) in the Ca material, while they occupy B sites (six-folded coordination with site symmetry of $\bar{1}$) in the Ba material. Therefore, the accurate chemical formula for CLTO and BLTO should be written as $(\text{CaLa})[\text{CaTa}]\text{O}_6$ and $(\text{Ba}_2)[\text{LaTa}]\text{O}_6$, respectively. Because both materials are B-site ordered double perovskite-types, Ca^{2+} and Ta^{5+} in CLTO and La^{3+} and Ta^{5+} in BLTO alternately occupy B sites. On the contrary, Ca^{2+} and La^{3+} are randomly distributed at A sites in CLTO. Therefore, it can be easily anticipated that Tb^{3+} should be located at the A sites in CLTO and at the B site in BLTO when Tb^{3+} are substituted for La^{3+} .

In this study, Tb^{3+} doped alkaline earth lanthanum tantalates, i.e. CLTO: Tb^{3+} and BLTO: Tb^{3+} , were synthesized via a conventional ceramic route. The location of Tb^{3+} activators was determined by X-ray diffraction (XRD) and X-ray absorption near edge structures (XANES) measurements. Tb^{3+} luminescence properties were investigated and related to the position of the emission center in the double perovskite-type structure. Obtained results were compared to the previous ones examined on the $\text{LaScO}_3\text{:Tb}^{3+}$ and $\text{LaLuO}_3\text{:Tb}^{3+}$ simple perovskite-type oxides.

2. EXPERIMENTS

Non-doped and Tb^{3+} doped CLTO and BLTO samples were prepared by solid state reaction with the nominal compositions of $(\text{CaLa}_{1-x}\text{Tb}_x)[\text{CaTa}]\text{O}_6$ and $\text{Ba}_2[\text{La}_{1-x}\text{Tb}_x\text{Ta}]\text{O}_6$ ($x = 0.00, 0.01,$

0.10) , respectively. The starting materials, CaCO_3 or BaCO_3 , La_2O_3 , Ta_2O_5 and Tb_4O_7 (Kojundo Chemical Laboratory Co.,Ltd., 99.9%) were weighed in stoichiometric amounts. They were thoroughly mixed with ethanol in an agate mortar and dried. Powders were then pressed into disks and the disks were heated at 1300 °C for 6 h in Ar atmosphere. Disks were ground and refired at 1400 °C for 6 h in Ar atmosphere to obtain pure materials.

The phase analyses of the obtained samples were carried out by XRD measurements using an X-ray diffractometer (Rigaku, RINT-2500) with a rotational Cu target. The powder XRD patterns for the non-doped samples were calculated from reported crystal structural data using the RIETAN code.¹⁶ The crystal structures of the double perovskites were visualized using the VESTA code.¹⁷ The XANES spectra for the Tb L_{III} edges were measured at the BL14B2 beamline of the SPring-8 synchrotron radiation facility. The XANES measurements by a transmission method were carried out on the samples with $x = 0.10$ to increase the signal/noise ratio along with reference samples. Conventional spectrofluorometers (JASCO FP-6500 and Horiba Fluorolog-3) were used to examine the PL and PLE spectra at room temperature (RT) and liquid nitrogen temperature (LNT). The decay curves of Tb^{3+} PL were measured to estimate the lifetimes of radiative transitions at RT and LNT. Diffuse reflectance spectra were measured at RT using a conventional UV-VIS-NIR spectrometer (JASCO V-570) and converted to absorption spectra via a Kubelka-Munk treatment.

3. RESULTS AND DISCUSSION

The XRD patterns of $(\text{CaLa}_{1-x}\text{Tb}_x)[\text{CaTa}]\text{O}_6$ and $\text{Ba}_2[\text{La}_{1-x}\text{Tb}_x\text{Ta}]\text{O}_6$ ($x = 0.00, 0.01, 0.10$) samples are shown in Figure 2. No impurity phases were detected for all six samples. In insets,

diffraction patterns in the 2θ range of 72–75 degree for CLTO and that of 59–62 degree for BLTO were magnified to highlight peak shifts consecutive to the Tb^{3+} substitution for La^{3+} . The peak shifts were observed and conspicuous for $x = 0.10$ in both the $\text{CLTO}:\text{Tb}^{3+}$ and $\text{BLTO}:\text{Tb}^{3+}$. The peak shifts to higher angles indicate a shrinking of the lattice spacing, and the results fully agree with the fact that ionic radii for La^{3+} ions are larger than those for Tb^{3+} ions; 1.300 Å and 1.172 Å for La^{3+} vs. 1.180 Å and 1.063 Å for Tb^{3+} at eight (A) and six (B) coordinated sites, respectively.⁸ Accordingly, the peak shifts evidence the insertion of Tb^{3+} into the HLs; Tb^{3+} at A site in CLTO and at B site in BLTO.

Figure 2. XRD patterns of (top) $(\text{CaLa}_{1-x}\text{Tb}_x)[\text{CaTa}]\text{O}_6$ and (bottom) $\text{Ba}_2[\text{La}_{1-x}\text{Tb}_x\text{Ta}]\text{O}_6$ ($x=0.00, 0.01, 0.10$) along with patterns calculated from the structural data. Insets show magnification of some diffraction peaks at high 2θ angles.

To elucidate the Tb^{3+} sites in the HLs more accurately, the XANES spectra of Tb L_{III} edges for the $\text{CLTO}:\text{Tb}^{3+}$ and $\text{BLTO}:\text{Tb}^{3+}$ were measured. They are shown in Figure 3 with those of perovskite-type TbAlO_3 and double perovskite-type $\text{Ba}_2\text{TbTaO}_6$ as references for Tb^{3+} at the A and B sites, respectively.^{14,18} Electronic transitions from the 2p core states to the 5d empty states

primarily occur at the L_{III} edges.^{19,20} The peak shapes provide the information not only on the valence states of Tb ions but also on the occupied crystal sites.^{7,21,22}

$TbAlO_3$ shows a main single peak at 7516 eV and two additional broad peaks at 7528 and 7548 eV, while Ba_2TbTaO_6 exhibits a main peak at 7517 eV with a shoulder at 7514 eV and two broad peaks at 7533 and 7555 eV. The appearance of the shoulder indicates the splitting of the main peak derived from Tb 5d orbitals in Ba_2TbTaO_6 . The shoulder is regarded as an indicator of a large splitting (approximately 3 eV) of the empty d states under the action of a crystal field.^{23,24} The large splitting is attributed to the strong crystal field around Tb^{3+} in Ba_2TbTaO_6 because the average Tb–O bond length at the B site in this host, $d_{Tb-O} = 2.25 \text{ \AA}$, is much shorter than that at A sites in $TbAlO_3$ ($d_{Tb-O} = 2.46 \text{ \AA}$).

The XANES spectra of $CLTO:Tb^{3+}$ and $BLTO:Tb^{3+}$ show features very similar to those of $TbAlO_3$ and Ba_2TbTaO_6 , respectively. $CLTO:Tb^{3+}$ displays a unique and well defined peak at 7516 eV, which is characteristic of Tb^{3+} at A site. In contrast, $BLTO:Tb^{3+}$ exhibited a double

Figure 3. XANES spectra of Tb L_{III} edges for $(CaLa_{0.90}Tb_{0.10})[CaTa]O_6$ and $Ba_2[La_{0.90}Tb_{0.10}Ta]O_6$ samples along with those for $TbAlO_3$ and Ba_2TbTaO_6 reference samples.

peak with maxima at 7517 and 7514 eV, which become a fingerprint of Tb^{3+} at B site, accompanying two broad peaks at 7533 and 7555 eV. The local structural analysis of Tb^{3+} by the XANES measurements led to the reasonable results that are consistent with those by the XRD measurements.

PL and PLE spectra of CLTO:Tb^{3+} and BLTO:Tb^{3+} with the Tb concentration of $x = 0.01$ are depicted in Figure 4 along with the absorption (Abs) spectra of non-doped HLs. Similar spectra for the Tb concentration of $x = 0.10$ are given in Figure S1. Although peak intensities depend on the Tb concentration and the concentration dependence in CLTO is larger than in BLTO, the fundamental spectral features are the same for $x = 0.01$ and $x = 0.10$.

Based on the non-doped CLTO absorption spectrum, the fundamental absorption is found at the wavelengths below 240 nm. The PLE spectrum of CLTO:Tb^{3+} , which monitored the PL peak at 550 nm, exhibits an intense peak at 247 nm, just below the absorption edge of the HL. This

Figure 4. PL and PLE spectra of $(\text{CaLa}_{0.99}\text{Tb}_{0.01})[\text{CaTa}]\text{O}_6$ (red lines) and those of $\text{Ba}_2[\text{La}_{0.99}\text{Tb}_{0.01}\text{Ta}]\text{O}_6$ (blue lines) along with absorption spectra of non-doped samples. PL, PLE, and absorption spectra are drawn with thin lines, thick lines and dashed lines, respectively.

intense peak is assigned to the allowed 4f – 5d transition and matches with Tb³⁺ at A sites because Tb³⁺ at A sites in several Tb³⁺ doped perovskite-type oxides usually give the 4f – 5d excitation peaks in the range from 220 to 250 nm.^{5-7,25-29} The crystal site of Tb³⁺ in this assignment is consistent with the results obtained by XRD and XANES measurements. In the PL spectra measured under UV excitation at 247 nm, the Tb³⁺ luminescence is composed with two series of transitions from ⁵D₃ to ⁷F_J (J = 6, 5, 4, 3) and from ⁵D₄ to ⁷F_J states. Because the luminescence derived from ⁵D₃ – ⁷F_J transitions shows large concentration quenching, the emission in the blue region decreases considerably at the Tb concentration of x = 0.10 as shown in Figure S1.

Non-doped BLTO is found to show the fundamental absorption below 250 nm. The PLE spectrum of BLTO:Tb³⁺, which monitored the PL peak at 552 nm, exhibits two intense peaks at 242 and 308 nm. Naturally, the former can be associated to the HL excitation for Tb³⁺ luminescence, and the latter is to the 4f – 5d excitation. Both the HL and 4f – 5d excitations result in almost the same PL spectral shapes as shown in Figure S1. In comparison between CLTO:Tb³⁺ and BLTO:Tb³⁺, the red shift of the PLE peak for the 4f – 5d on-site transition in BLTO:Tb³⁺ is evident. The 5d energy levels of Ln ions, as well as the red shifts, are generally analyzed in terms of the shift of the centroid energy and the crystal field splitting of the degenerate levels.³⁰⁻³⁴ However, the experimental separation of the two factors is not simple in the present materials because all 4f – 5d transitions cannot be observed in the optical absorption or excitation spectra due to the HL absorption. The centroid shifts for oxides (approximately 1 to 2 eV) are usually smaller than those for other compounds such as nitrides and sulfides (approximately 2 to 3 eV) because of the smaller polarizability of oxide ions.³⁴ On the other hand, the XANES spectra in Figure 2 revealed that the crystal field splitting for Tb 5d orbitals in

BLTO is as large as 3 eV, which would be larger than the centroid shift. Accordingly, the red shift of the 4f-5d excitation peak in BLTO:Tb³⁺ is primarily attributed to the larger crystal field at B sites than that at A sites, which is also observed in some perovskite-type oxides such as LaScO₃ and LaLuO₃.^{6,7} The preference of B-site occupation by Tb³⁺ in BLTO:Tb³⁺ observed in the PLE examination is consistent with the results of the XRD and XANES analyses. It is also worth noticing in the PL spectra that only the Tb³⁺ luminescence derived from the ⁵D₄ – ⁷F_J transitions is observed for BLTO:Tb³⁺. The absence of the luminescence from the ⁵D₃ – ⁷F_J transitions for BLTO:Tb³⁺ provides a marked contrast to the PL spectrum for CLTO:Tb³⁺. These features are also almost the same with those found in Tb³⁺ doped LaScO₃ and LaLuO₃ and implying that the 5d levels of Tb³⁺ at B sites lie more downside in energy than those at A sites.^{6,7}

Figure 5. Magnified PL spectra of (CaLa_{0.90}Tb_{0.10})[CaTa]O₆ (red lines) and those of Ba₂[La_{0.90}Tb_{0.10}Ta]O₆ (blue lines) measured at room temperature (thin lines) and liquid nitrogen temperature (thick lines).

Figure 5 shows magnified PL peaks derived from the $^5D_4 - ^7F_J$ transitions in CLTO:Tb³⁺ and BLTO:Tb³⁺ observed at RT and LNT. The excitation wavelengths (λ_{ex}) were slightly changed at LNT according to the wavelength shifts of the PLE peak maxima. Although the $^5D_4 - ^7F_J$ transitions are f – f intraconfigurational ones, the peak shapes are influenced by the crystal field at each crystal sites. Because the average La–O distance in CLTO and BLTO are $d_{\text{La-O}} = 2.61 \text{ \AA}$ and $2.43 \text{ \AA}$, respectively, the crystal field at B site in BLTO is considered to be larger than that at A site in CLTO. Although the main PL peaks derived from the $^5D_4 - ^7F_5$ transitions show the crystal field splitting at RT in both CLTO and BLTO, the splitting in BLTO is larger and more complicated than that in CLTO. The distinctive peak splitting for Tb³⁺ at B sites is seen in not only the $^5D_4 - ^7F_5$ transition but also $^5D_4 - ^7F_6$ and $^5D_4 - ^7F_4$ transitions. These features become more distinguishable at LNT and the main peaks for the $^5D_4 - ^7F_5$ transitions clearly split into three or more in BLTO:Tb³⁺.

Figure 6. Decay curves of PL peak intensities for (CaLa_{0.90}Tb_{0.10})[CaTa]O₆ (red symbols) and those of Ba₂[La_{0.90}Tb_{0.10}Ta]O₆ (blue symbols) observed under 4f-5d excitation at room temperature (filled symbols) and liquid nitrogen temperature (open symbols). Each symbol corresponds to the wavelength of each PL peak.

The decay curves of the PL peaks for the $^5D_4 - ^7F_5$ transitions measured at RT and LNT are shown in Figure 6. The main two peaks split by the crystal field in CLTO:Tb³⁺ and those three peaks in BLTO:Tb³⁺, which are indicated in Figure 5, were examined at RT and LNT. It was clearly found that the luminescence of Tb³⁺ at A site in CLTO:Tb³⁺ shows much faster decay than that at B site in BLTO:Tb³⁺. The decay curves are almost the same between the two split peaks in CLTO:Tb³⁺ and between the three split peaks in BLTO:Tb³⁺. These results indicate that the $^5D_4 - ^7F_5$ transitions for Tb³⁺ only at A sites are responsible for the two peaks in CLTO:Tb³⁺ and those only at B sites are responsible for the three peaks in BLTO:Tb³⁺. The decay curves are not largely dependent on temperature between at RT and LNT, but the intensities of the PL for Tb³⁺ in BLTO:Tb³⁺ are found to decay slightly slower at LNT than at RT. This may suggest that lattice vibrations affect the Tb³⁺ luminescence more largely at B sites than at A sites because B–O bonds generally have more covalent character than A–O bonds in perovskite-type oxides.³⁵ The lifetimes (τ) for the luminescence derived from the $^5D_4 - ^7F_5$ transitions are evaluated from the $\ln(I/I_0)-t$ plots shown in the inset presuming that the decay curves follow a single-exponential function. The slopes in the inset give the lifetimes $\tau = 0.91$ ms for CLTO:Tb³⁺ both at RT and LNT and $\tau = 3.3$ ms for BLTO:Tb³⁺ at RT and $\tau = 3.8$ ms at LNT.

Although the lifetimes of Ln³⁺ in the double perovskite-type oxides have been reported in some literature, there are few reports on that for Tb³⁺.³⁶⁻³⁸ The lifetimes of the luminescence for Tb³⁺ at B sites in BLTO:Tb³⁺ were found to be approximately three times longer than those for Tb³⁺ at A sites in CLTO:Tb³⁺. This feature is the same with that observed for Tb³⁺ at A or B sites in orthorhombic perovskite-type LaScO₃ and LaLuO₃, where only B sites have an inversion center. Because f-f transitions are originally forbidden at the site with a center of symmetry, the

site symmetry at B sites with an inversion center is responsible for the longer lifetimes in these orthorhombic perovskite-type and monoclinic double perovskite-type oxides.

4. CONCLUSION

The Tb³⁺ luminescence of B-site-ordered double perovskite-type (CaLa_{1-x}Tb_x)[CaTa]O₆ and Ba₂[La_{1-x}Tb_xTa]O₆:Tb³⁺ (x = 0.01, 0.10) were investigated clarifying Tb³⁺ doping sites and its site dependence. XRD patterns and XANES spectra confirmed that Tb³⁺ are located at A sites in CLTO:Tb³⁺ and at B sites in BLTO:Tb³⁺ in accordance with the nominal compositions. In the PLE spectra, 4f–5d excitation peaks were observed in both CLTO:Tb³⁺ and BLTO:Tb³⁺ and the 4f–5d excitation peak for Tb³⁺ in BLTO:Tb³⁺ showed a marked red shift mainly because of the large crystal field at B sites. In the PL spectra, the splitting of the PL peaks induced by the crystal field was observed even though the PL peaks are derived from inner f-f transitions. The splitting in BLTO:Tb³⁺ was larger and more complicated than that in CLTO:Tb³⁺. Two series of the Tb³⁺ luminescence derived from ⁵D₃ – ⁷F_J and ⁵D₄ – ⁷F_J (J = 6, 5, 4, 3) transitions were observed in CLTO:Tb³⁺, while only the Tb³⁺ luminescence from ⁵D₄ – ⁷F_J transitions were observed in BLTO:Tb³⁺. In addition, the lifetime of Tb³⁺ luminescence in BLTO:Tb³⁺ was noticeably longer than that in CLTO:Tb³⁺. These luminescence properties of Tb³⁺ at A and B sites in the monoclinic double perovskite-type oxides are basically consistent with those observed in simple perovskite-type oxides with orthorhombic distortion such as LaScO₃ and LaLuO₃.

ASSOCIATED CONTENT

Supporting Information.

PL spectra of the CLTO:Tb³⁺ and BLTO:Tb³⁺ samples with Tb concentration of $x = 0.10$.

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Notes

The authors declare no competing financial interest.

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