

Research on new precursor for nanosheets phosphors

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Photoluminescence properties of Rb(La_{0.90}Bi_{0.10})Ta₂O₇, Layered Perovskite compound, and its exfoliated form, (La_{0.90}Bi_{0.10})Ta₂O₇ nanosheet were characterized. The excitation and emission peaks of Rb(La_{0.90}Bi_{0.10})Ta₂O₇ were 305 nm and 553 nm, respectively. The emission peak of (La_{0.90}Bi_{0.10})Ta₂O₇ nanosheets solution was at 524 nm when the sample was excited at 281 nm. (La_{0.90}Bi_{0.10})Ta₂O₇ nanosheets are promising candidates for thin film inorganic EL or luminescence sheet to prevent counterfeiting currency.

Key words: Nanosheets, Bi³⁺, Phosphor, RbLaTa₂O₇, Layered Perovskite.

Introduction

In recent years, attractive functionalities of nanosheets have been paid attention because of their morphology. Nanosheets are prepared by exfoliation of layered oxide have been classified into the two-dimensional nanoscale materials have a thickness of nanoscale, infinite length in the plane. It is expected that nanosheets can apply to photocatalyst, catalyst, optical devices, dielectric materials [1-4]. Moreover transparent nanosheets phosphors are promising candidates for thin film inorganic EL or luminescence sheet to prevent counterfeiting currency. Nanosheets phosphors are prepared by exfoliating RbLa_{0.7}Tb_{0.3}Ta₂O₇ and K₂Gd_{1.6}Eu_{0.4}Ti₃O₁₀ [5], Li₂Eu_{0.56}Ta₂O₇ [6], KLa_{0.90}Eu_{0.05}Nb₂O₇ [7], KLa_{0.90}Sm_{0.05}Nb₂O₇ [8] have already been reported. In a lot of studies, Ida et al. have reported the blue photoluminescence of an oxide mono-nanosheet prepared by exfoliation of Layered Perovskite Bi₂SrTa₂O₉ which exhibited green emission [9]. Since the optical absorption of Bi³⁺ ion derived from allowed transition is strong, luminescence of Bi³⁺ ion is expected strong [10]. Therefore, We focused on Bi³⁺ ion as luminescence center.

In this study, we synthesized Layered Perovskite compound of Rb(La_{0.90}Bi_{0.10})Ta₂O₇ exhibited yellowish green emission and (La_{0.90}Bi_{0.10})Ta₂O₇ nanosheets solution exhibited green emission, and investigated its photoluminescence properties.

Experiments

Rb(La_{1-x}Bi_x)Ta₂O₇ (x = 0 - 0.2) were prepared by the reported method for the undoped phase RbLaTa₂O₇. The starting materials were Rb₂CO₃ (Wako Pure Chemical Industries, Ltd, 97.0 + %), La₂O₃ (Wako pure Chemical Industries, Ltd 99.99%), Bi₂O₃ (Kanto Chemical, Co., Inc 99.9%), and Ta₂O₅ (Kanto Chemical, Co., Inc 99.95%). An excess amount of Rb₂CO₃ (50 mol%) was added to compensate for the loss due to the volatilization of the rubidium component. The mixture was pressed into disk-shape pellets of 15 mm in diameter and 1 mm thick under a pressure 20 MPa, and then, the pellets were heated at 1373 K for 4 h in air using an electric-box furnace. Synthesized Rb(La_{0.90}Bi_{0.10})Ta₂O₇ was reacted with 1 M HNO₃ for 3 days at 353 K in order to exchange interlayer Rb⁺ with H⁺. The protonated sample was exfoliated with a 10-fold (TBA⁺/H⁺ = 10) excess of Tetra-n-butylammonium Hydroxide Solution (TBAOH) (Kanto Chemical, Co., Inc 0.4 mol / L) for 2 weeks at room temperature.

Powder XRD data were obtained using a diffractometer (MX-Labo; Mac Science Ltd.) with Cu K α radiation. Excitation and emission spectra of the samples were measured using a spectrofluorometer with Xe lamp light source (FP-6500/6600; Jasco Inc.). Transmission Electron Microscope (TEM) and SAED (selected-area electron diffraction) were carried out using a JEOL JEM-1200EX transmission electron microscope at an accelerating voltage of 60 kV.

Results and Discussion

Figure 1 shows the crystal structure of RbLaTa₂O₇

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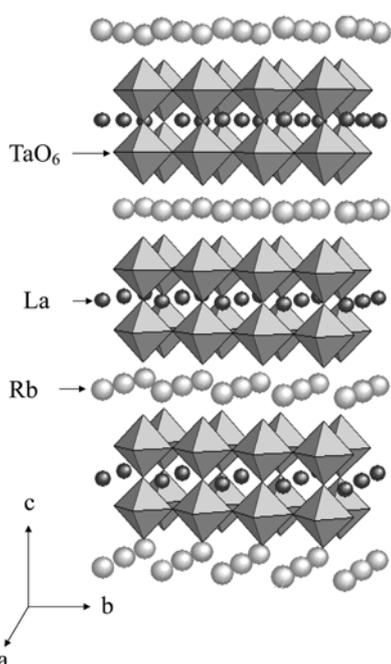


Fig. 1. Crystal structure of $\text{RbLaTa}_2\text{O}_7$. Rb (white ball), La (gray ball), TaO_6 (black octahedron).

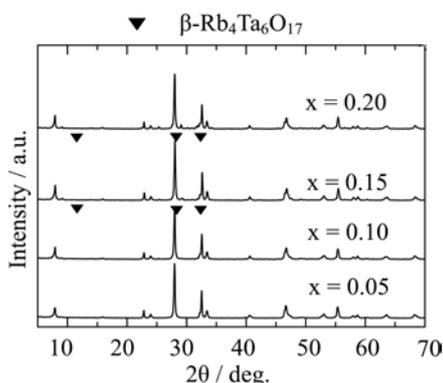


Fig. 2. XRD patterns of $\text{Rb}(\text{La}_{1-x}\text{Bi}_x)\text{Ta}_2\text{O}_7$. Samples were obtained in single phase, $x = 0 - 0.1$. When Bi^{3+} ion was doped more than $x = 0.1$, impurity $\beta - \text{Rb}_4\text{Ta}_6\text{O}_{17}$ phase observed.

[11]. This compound has a tetragonal structure ($a = 0.38820 \text{ nm}$, $c = 1.11053 \text{ nm}$) with an $\text{P4}/\text{mmm}$ space group, and is member of the Dion-Jacobson series of compound with the general formula $\text{A}[\text{M}_{n-1}\text{B}_n\text{O}_{3n+1}]$ ($\text{A} = \text{alkali metal}$) with $n = 2$. Layered Perovskite compound of $\text{RbLaTa}_2\text{O}_7$ exhibits a variety of chemical properties such as ion-exchange, intercalation, exfoliation reactions. We obtained $(\text{La}_{0.90}\text{Bi}_{0.10})\text{Ta}_2\text{O}_7$ nanosheets solution by ion-exchange, intercalation, exfoliation reactions [12-14].

XRD patterns of $\text{Rb}(\text{La}_{1-x}\text{Bi}_x)\text{Ta}_2\text{O}_7$ were shown in Figure 2. The Samples were obtained in the single phase, $x = 0 - 0.1$. When Bi^{3+} ion was doped more than $x = 0.1$, the impurity phase was observed, $\beta - \text{Rb}_4\text{Ta}_6\text{O}_{17}$.

Figure 3 shows the excitation and emission spectra of $\text{Rb}(\text{La}_{0.90}\text{Bi}_{0.10})\text{Ta}_2\text{O}_7$. The excitation and emission peaks of $\text{Rb}(\text{La}_{0.90}\text{Bi}_{0.10})\text{Ta}_2\text{O}_7$ were 305 nm and 553 nm, respectively. Since $6s^2 \rightarrow 6s6p$ transition of Bi^{3+} ion is

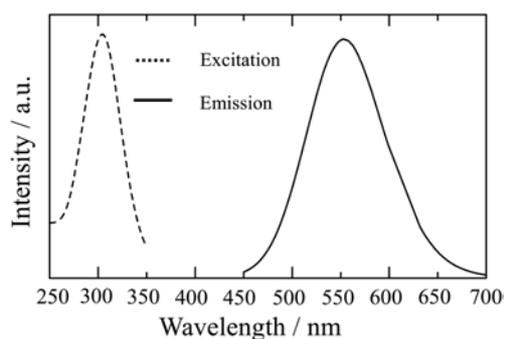


Fig. 3. Excitation and emission spectra of $\text{Rb}(\text{La}_{0.90}\text{Bi}_{0.10})\text{Ta}_2\text{O}_7$. The excitation (broken line) and emission (solid line) peaks of $\text{Rb}(\text{La}_{0.90}\text{Bi}_{0.10})\text{Ta}_2\text{O}_7$ were 305 nm and 553 nm (greenish yellow), respectively.

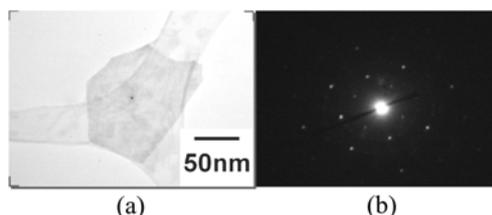


Fig. 4. (a) TEM image and (b) SAED pattern of $(\text{La}_{0.90}\text{Bi}_{0.10})\text{Ta}_2\text{O}_7$ nanosheet.

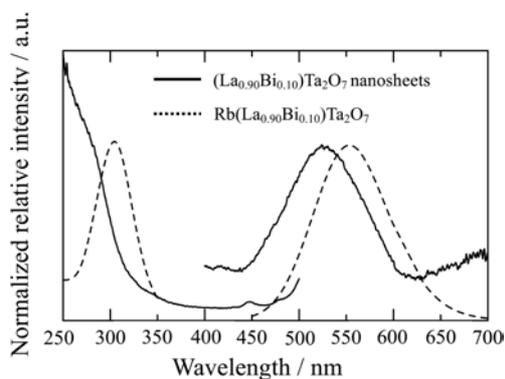


Fig. 5. Excitation and emission spectra of $(\text{La}_{0.90}\text{Bi}_{0.10})\text{Ta}_2\text{O}_7$ nanosheets solution and $\text{Rb}(\text{La}_{0.90}\text{Bi}_{0.10})\text{Ta}_2\text{O}_7$. The emission peak of $(\text{La}_{0.90}\text{Bi}_{0.10})\text{Ta}_2\text{O}_7$ nanosheets solution was obtained at 524 nm (green) when the sample was excited at 281 nm (solid line). The excitation and emission peaks of $\text{Rb}(\text{La}_{0.90}\text{Bi}_{0.10})\text{Ta}_2\text{O}_7$ were 305 nm and 553 nm (yellowish green), respectively (broken line).

allowed transition, the ground state of the Bi^{3+} ion is $^1\text{S}_0$, and the four excited states of the Bi^{3+} ion are $^3\text{P}_0$, $^3\text{P}_1$, $^3\text{P}_2$, $^1\text{P}_1$, the optical absorption is expected to be much stronger than forbidden f-f transition of Eu^{3+} , Tb^{3+} ion. The luminescence properties of Bi^{3+} ion have been studied in many compounds, YOCl [15], $\text{Gd}_2\text{GaSbO}_7$ [16], LaBO_3 [17], LaGaO_3 [18], SrBiO_2Cl [19]. In general, Bi^{3+} doped phosphors exhibits blue or purple emission at room temperature. However, synthesized $\text{Rb}(\text{La}_{0.90}\text{Bi}_{0.10})\text{Ta}_2\text{O}_7$ exhibited yellowish green emission at room temperature. The emission property did not ascribe to $^3\text{P}_{0,1} \rightarrow ^1\text{S}_0$, but probably metal-to-metal charge transfer (MMCT), $\text{Bi}^{3+} (6s^2) \rightarrow \text{Ta}^{5+} (d^0)$. The empirical model of MMCT in closed

shell d^0 transition metal complex oxide doped with Bi^{3+} ion have been proposed by Boutinaud et al. [20].

Figure 4(a) shows TEM image of the nanosheets prepared by the exfoliation process. This results indicated successful exfoliation of Layered Perovskite $\text{Rb}(\text{La}_{0.90}\text{Bi}_{0.10})\text{Ta}_2\text{O}_7$ to the mononanosheet. The result of the crystallinity of nanosheet characterized by SAED (selected-area electron diffraction) the result was shown in Figure 4(b). The SAED pattern of a nanosheet $(\text{La}_{0.90}\text{Bi}_{0.10})\text{Ta}_2\text{O}_7$ exhibited diffraction spots, indicating its single-crystal nature.

Figure 5 shows the excitation and emission spectra of $(\text{La}_{0.90}\text{Bi}_{0.10})\text{Ta}_2\text{O}_7$ nanosheets solution and of $\text{Rb}(\text{La}_{0.90}\text{Bi}_{0.10})\text{Ta}_2\text{O}_7$. The emission peak of $(\text{La}_{0.90}\text{Bi}_{0.10})\text{Ta}_2\text{O}_7$ nanosheets solution was at 524 nm when the sample was excited at 281 nm at room temperature. The excitation and emission peaks of $(\text{La}_{0.90}\text{Bi}_{0.10})\text{Ta}_2\text{O}_7$ nanosheets solution were different from the excitation and emission peaks of the bulk $\text{Rb}(\text{La}_{0.90}\text{Bi}_{0.10})\text{Ta}_2\text{O}_7$ because of the effect of size of nanosheet on the band-gap widening [21, 22], and thereby the energy transfer between Bi^{3+} and Ta^{5+} probably was influenced.

In this study, the new green emitting Bi^{3+} doped nanosheet phosphor was synthesized.

Conclusions

We have successfully prepared yellowish green emitting phosphor $\text{Rb}(\text{La}_{0.90}\text{Bi}_{0.10})\text{Ta}_2\text{O}_7$ using a solid-state reaction method, and green emitting nanosheets phosphor by the soft chemical exfoliation of the Layered Perovskite $\text{Rb}(\text{La}_{0.90}\text{Bi}_{0.10})\text{Ta}_2\text{O}_7$. The $(\text{La}_{0.90}\text{Bi}_{0.10})\text{Ta}_2\text{O}_7$ nanosheets are promising candidates for thin film inorganic EL or luminescence sheet to prevent counterfeiting currency.

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