Research on new precursor for nanosheets phosphors


dGraduate School of Science and Technology, Niigata University, Japan
bDepartment of Chemistry and Chemical Engineering, Niigata University, Japan
cCenter for Transdisciplinary Research, Niigata University 8050 Ikarashi 2-nocho, Niigata, 950-2181, Japan
dSchool of Advanced Materials Science and Engineering, Sungkyunkwan University, Korea
eAdvanced Materials and Process Research Center for IT, AMPIT, Sungkyunkwan University, Sunwon, 440-746, Korea

Photoluminescence properties of Rb(La0.90Bix)Ta2O7, Layered Perovskite compound, and its exfoliated form, (La0.90Bix)Ta2O7-nanosheet were characterized. The excitation and emission peaks of Rb(La0.90Bix)Ta2O7 were 305 nm and 553 nm, respectively. The emission peak of (La0.90Bix)Ta2O7-nanosheets solution was at 524 nm when the sample was excited at 281 nm. (La0.90Bix)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 are promising candidates for thin film inorganic EL or luminescence sheet to prevent counterfeiting currency. Nanosheets phosphors are prepared by exfoliating RbLaTa2O7 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(La0.90Bi0.10)Ta2O7 exhibited yellowish green emission and (La0.90Bi0.10)Ta2O7 nanosheets solution exhibited green emission, and investigated its photoluminescence properties.

Experiments

Rb(La0.90Bi0.10)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(La0.90Bi0.10)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 Kα 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
This compound has a tetragonal structure ($a = 0.38820 \text{ nm}, c = 1.11053 \text{ nm}$) with an $P4/mmm$ space group, and is member of the Dion-Jacobson series of compound with the general formula $A[M_{n-1}B_nO_{3n+1}]$ ($A = \text{alkali metal}$) 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 $\text{Bi}^{3+}$ ion was doped more than $x = 0.1$, impurity $\beta - \text{Rb}_4\text{Ta}_6\text{O}_{17}$ phase observed.

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 $6s^2 \to 6s6p$ transition of $\text{Bi}^{3+}$ ion is allowed transition, the ground state of the $\text{Bi}^{3+}$ ion is $^1S_0$, and the four excited states of the $\text{Bi}^{3+}$ ion are $^3P_0$, $^3P_1$, $^3P_2$, $^1P_1$, the optical absorption is expected to be much stronger than forbidden $f$-$f$ transition of $\text{Eu}^{3+}$, $\text{Tb}^{3+}$ ion. The luminescence properties of $\text{Bi}^{3+}$ ion have been studied in many compounds, YOCl [15], $\text{Gd}_2\text{GaSbO}_7$ [16], $\text{LaBO}_3$ [17], $\text{LaGaO}_3$ [18], $\text{SrBiO}_2\text{Cl}$ [19]. In general, $\text{Bi}^{3+}$ 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 $^3P_0,1 \to ^1S_0$, but probably metal-to-metal charge transfer (MMCT), $\text{Bi}^{3+}$ ($6s^2$) $\to \text{Ta}^{5+}$ ($d^0$). 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 Rb(La\(_{0.90}\)Bi\(_{0.10}\))Ta\(_2\)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 (La\(_{0.90}\)Bi\(_{0.10}\))Ta\(_2\)O\(_7\) exhibited diffraction spots, indicating its single-crystal nature.

Figure 5 shows the excitation and emission spectra of (La\(_{0.90}\)Bi\(_{0.10}\))Ta\(_2\)O\(_7\) nanosheets solution and of Rb(La\(_{0.90}\)Bi\(_{0.10}\))Ta\(_2\)O\(_7\). The emission peak of (La\(_{0.90}\)Bi\(_{0.10}\))Ta\(_2\)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 the bulk Rb(La\(_{0.90}\)Bi\(_{0.10}\))Ta\(_2\)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\(^{4+}\) 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 Rb(La\(_{0.90}\)Bi\(_{0.10}\))Ta\(_2\)O\(_7\) using a solid-state reaction method, and green emitting nanosheets phosphor by the soft chemical exfoliation of the Layered Perovskite Rb(La\(_{0.90}\)Bi\(_{0.10}\))Ta\(_2\)O\(_7\). The (La\(_{0.90}\)Bi\(_{0.10}\))Ta\(_2\)O\(_7\) nanospheres are promising candidates for thin film inorganic EL or luminescence sheet to prevent counterfeiting currency.

Acknowledgements

This work was supported by a project from the Center for Transdisciplinary Research, Niigata University.

References