Supporting Information

Preparation of Blue Luminescent Nanosheet derived from Layered Perovskite $\text{Bi}_2\text{SrTa}_2\text{O}_9$

Shintaro Ida*, Chikako Ogata, Ugur Unal, Kazuyoshi Izawa, Taishi Inoue, Ozge Altuntasoglu, and Yasumichi Matsumoto

Graduate School of Science and Technology, Kumamoto University, 2-39-1 Kurokami, Kumamoto 860-8555, Japan

Figure S-1. XRD patterns of; (a) $\text{Bi}_2\text{SrTa}_2\text{O}_9$, (b) protonated $\text{Bi}_2\text{SrTa}_2\text{O}_9$.

Comparison of the blue luminescence between BST-nanosheet and $\text{Sr}_2\text{Ta}_3\text{O}_{10}\text{-nanosheet}$

In order to discuss the mechanism of the blue luminescence of BST-nanosheet , $\text{Sr}_2\text{Ta}_3\text{O}_{10}\text{-nanosheet}$ with the similar structure of BST-nanosheet was prepared and its luminescence properties were measured as follows as follows.

The synthesis of $\text{CsSr}_2\text{Ta}_3\text{O}_{10}$ was conducted by a conventional solid-state procedure according to that reported by Thangadurai et al.^{S1} The starting materials were a mixture of CsNO_3 , SrCO_3 , and Ta_2O_5 . An excess amount of CsNO_3 (50 mol%) was added to compensate for the loss due to the volatilization of alkali component. The mixtures were heated at 900 °C for 12 h and 1150 °C for 12 h with intermittent grinding. $\text{HSr}_2\text{Ta}_3\text{O}_{10}$ were prepared by ion-exchanging $\text{CsSr}_2\text{Ta}_3\text{O}_{10}$ (1 g) in 1 M HNO_3 (200 mL) for 3 days at room temperature. The acid was replaced daily to ensure complete exchange. After the reaction, the solid products were washed with distilled water. The $\text{HSr}_2\text{Ta}_3\text{O}_{10}$ (1g) was stirred in 0.1 M tetrapentylammonium (TPA^+) hydroxide solutions (100 mL) for 7 days at 30 °C. The ratio of tetraalkylammonium/ H^+ was about 8. After the reaction, the suspension was centrifuged under 3000rpm for 30 min, and then the sediment was collected. Next, the sediment was stirred in water (100 mL) for 1 day at 30 °C. After the stirring, a supernatant solution was obtained by centrifugation of the suspension under 3000rpm for 30 min. The supernatant solution was coated on mica substrate by spin coating technique, which was used for AFM measurements. Fig. S-2 shows the AFM image of $\text{Sr}_2\text{Ta}_3\text{O}_{10}\text{-nanosheet}$. The observed thickness of the nanosheet was about 1.7 nm, which correspond to the thickness of a mono-layer of the $\text{CaSr}_2\text{Ta}_3\text{O}_{10}$.

Fig. S-3 shows the excitation and emission spectra of BST-nanosheet solution and $\text{Sr}_2\text{Ta}_3\text{O}_{10}\text{-nanosheet}$ solution. BST-nanosheet showed visible blue luminescence, while the $\text{Sr}_2\text{Ta}_3\text{O}_{10}\text{-nanosheet}$ solution showed no blue luminescence. The structure of $\text{Sr}_2\text{Ta}_3\text{O}_{10}$ nanosheet is similar to that of the BST . The former has a triple perovskite sheet of Sr-Ta-O and the latter has a double

perovskite sheet of Sr-Ta-O of which Sr^{2+} ions of A site were partly substituted with Bi^{3+} . The partial substitution of the A site in the BST-nanosheet presumably has a role in the generation of the defect levels related to the emission.

(S1) Venkataraman Thangadurai, Peter Schmid-Beurmann, Werner Weppner, *Journal of Solid State Chemistry* **2001**, 158, 279-289.

Figure S-2. AFM image of $\text{Sr}_2\text{Ta}_3\text{O}_{10}$ -nanosheet

Figure S-3. Excitation and emission spectra of; (a) BST-nanosheet solution and (b) $\text{Sr}_2\text{Ta}_3\text{O}_{10}$ -nanosheet solution.

Preparation method of mono layer LBL film of BST-nanosheet.

The mono layer LBL film of BST-nanosheet was prepared as follows. Quartz was used as a substrate in this study. Substrates were primed in an aqueous polyethyleneimine (PEI) 2.5 g/L solution for 20 min to charge the surface of the substrate positively. The Primed substrates were dipped into the BST-nanosheets solution for 10 min. The substrate was rinsed and dried under a N₂ stream after each process. The excitation and emission spectra of the mono layer LBL film of BST-nanosheet were measured using the cell unite as shown in Fig. S-4. The triangular cell was filled out with 0.1 M HCl or 0.1 M NaOH.

Figure S-4. Cell unit for photoluminescence measurement

The repeatability of pH response of the blue luminescence

Fig. S-5 shows the repeatability of pH response of the blue luminescence using the same mono layer LBL film of BST-nanosheet. It was found that the pH response for LBL film had a good repeatability.

Figure S-5. The repeatability of pH response of the blue luminescence for mono layer LBL film of BST-nanosheet in 0.1 M HCl or 0.1 M NaOH ($\lambda_{ex}: 285 \text{ nm}$, $\lambda_{em}: 475 \text{ nm}$).

Chemical composition analysis

The chemical compositions for both the protonated sample and the nanosheet sample were analyzed by ICP spectrometer. The protonated sample (50mg) or the exfoliated nanosheet sample (2.5 mL) was dissolved in 25 mL of HF:HNO₃=(4:1) solution prior to analysis. As standard solutions, HF:HNO₃=(4:1) solutions containing Bi(NO₃)₃, Sr(NO₃)₂ and TaF₅ with adequate concentrations were used.

The purity of all starting materials

Bi₂O₃ (99.9%, Kishida Chemical Co., Ltd.), SrCO₃ (99.9%, Sigma-Aldrich, Inc.) and Ta₂O₅ (99.9%, Wako Pure Chemical Industries, Ltd.) were used as starting materials of Bi₂SrTa₂O₉. CsNO₃ (99.99% Nakarai Tesque, Inc.), SrCO₃ (99.9%, Sigma-Aldrich, Inc.) and Ta₂O₅ (99.9%, Wako Pure Chemical Industries, Ltd.) were used as starting materials of CsSr₂Ta₃O₁₀.