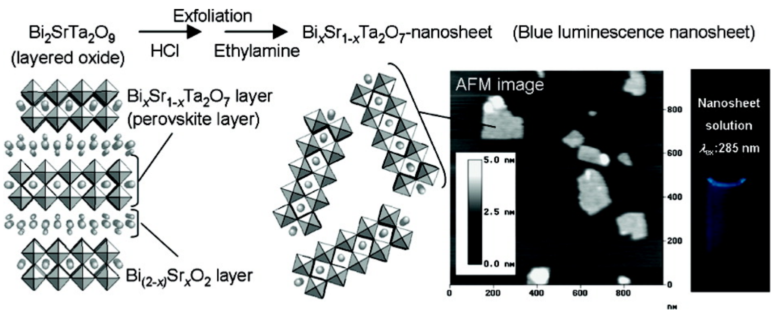
JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

Communication

Preparation of a Blue Luminescent Nanosheet Derived from Layered Perovskite BiSrTaO

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

J. Am. Chem. Soc., **2007**, 129 (29), 8956-8957• DOI: 10.1021/ja073105b • Publication Date (Web): 30 June 2007



Journal of the American Chemical Society is published by the American Chemical Society. 1155 Sixteenth Street N.W., Washington, DC 20036

J|A|C|S
COMMUNICATIONS

Preparation of a Blue Luminescent Nanosheet Derived from Layered Perovskite $Bi_2SrTa_2O_9$

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

Received May 3, 2007; E-mail: s_ida@chem.chem.kumamoto-u.ac.jp

Metal oxide nanosheets, which can be synthesized by the exfoliation of layered oxides, are two-dimensional semiconductor nanocrystals.[1] The thickness of a nanosheet is about 1 nm, and the lateral size ranges from several hundred square nanometers to several square micrometers. The multilayer films composed of the nanosheets can be prepared with a layer-by-layer (LBL) assembly method.[2−4] It is possible to create new materials by building up various functional nanosheets together with the intercalated guest ions. We have developed the layered films of nanosheets intercalated with rare earth ions as new luminescent materials.[5] In this system, the red and green luminescence based on the intercalated rare earth ions is observed. It is, however, difficult to obtain blue luminescence from the current systems to achieve photodevices working in the range of the whole color spectrum. If a nanosheet with a blue luminescent property can be developed, the photodevices with luminescence of all colors may be created by building up nanosheets.

On the basis of the above point of view, we have investigated the exfoliation of various layered oxides and their luminescence properties. In this study, we report, for the first time, the blue photoluminescence of an oxide mono-nanosheet derived from layered perovskite $Bi_2SrTa_2O_9$ (BST).

BST is one of the Aurivillius phases and consists of bismuth oxide layers and perovskite slabs.[6,7] The synthesis of BST was carried out using a conventional solid-state procedure. The starting material was a stoichiometric mixture of Bi_2O_3, $SrCO_3$, and Ta_2O_5. The mixture was heated at 900 °C for 4 h and 1200 °C for 4 h. Protonation was carried out by stirring 0.3 g of BST powder in 100 mL of a 3 M aqueous HCl solution for 5 days at room temperature. After the reaction, obtained solid product was centrifuged and washed with distilled water.

Protonation of the starting material resulted in $H_{1.67}Bi_{0.21}Sr_{0.85}Ta_2O_7$ (H-BST) as determined by inductively coupled plasma (ICP) spectrophotometry (Seiko Instruments, SPS7800). Tsunoda et al. have also reported that protonation of BST resulted in the formation of $H_{1.8}Bi_{0.20}Sr_{0.80}Ta_2O_7$.[8] The composition of the protonated form is close to that of the Ruddlesden−Popper phase. However, the host layer charge decreases from −2 to −1.8 because of the cation disorder between the Sr^{2+} ions of the A site in the perovskite layer and the Bi^{3+} ions in the bismuth oxide sheets.[8,9]

Exfoliation was performed by stirring 0.1 g of the protonated powder in a 0.1 M aqueous ethylamine solution for 5 days at room temperature. The ethylamine was the most suitable amine for the exfoliation process. After the reaction, the suspension was centrifuged to separate the sediment and supernatant solution. According to the XRD analysis, the basal distance for the sediment was 1.54 nm and larger than that of 1.00 nm for H-BST. This indicates that ethylamine was intercalated into the interlayer. The supernatant solution (nanosheet solution) was coated on a mica substrate by a spin coating technique in order to carry out atomic force microscopy (AFM, Molecular Imaging) measurements.

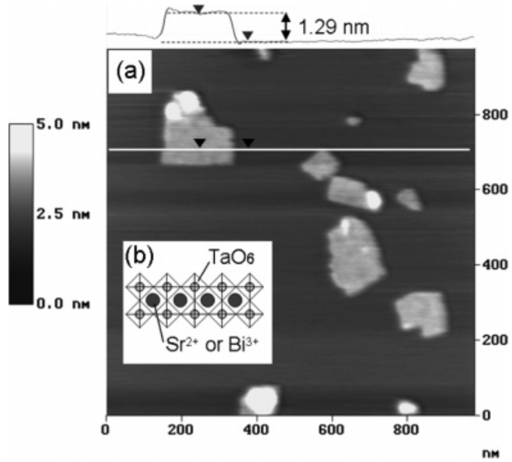


Figure 1. (a) AFM image; and (b) structural model of the nanosheet derived from $Bi_2SrTa_2O_9$.

Figure 1a shows an AFM image of the nanosheets prepared by the exfoliation process. The observed thickness of the nanosheets was about 1.3 nm, which corresponds to the thickness of a monolayer of the layered perovskite (0.93 nm). This result indicates successful exfoliation of the layered perovskite BST to the mono-nanosheet. The chemical composition of a nanosheet was Bi/Sr/Ta = 0.16:0.75:2, indicating that Sr^{2+} ions of the A site are substituted with Bi^{3+}. The concentration of the nanosheet solution was about 150 mg/L. Comparison of the compositions of the protonated bulk form (Bi/Sr/Ta = 0.21:0.85:2) and the nanosheet revealed that the amount of Bi^{3+} and Sr^{2+} ions slightly decreased by the exfoliation reaction. This indicates that the guest species that were not exchanged during the protonation process were removed by the exfoliation reaction.

Figure 2 shows the photoluminescence spectra of BST, H-BST, and the ethylamine intercalated form (EA-BST) obtained by the exfoliation processes. The excitation and emission spectra were analyzed by a Jasco FP-6500 spectrofluorometer with a 150 W Xe lamp source ($\lambda_{ex} = 305$ nm, $\lambda_{em} = 475$ nm). It should be noted that relatively strong blue emission appeared for EA-BST powder. The intensity of the blue emission increased after the process of protonation and exfoliation. This is presumably due to the removal of the guest bismuth layer, which is considered to act as a quenching species for the blue emission in the interlayer. The emission spectra of EA-BST and H-BST have one main peak at 475 nm with a shoulder peak at around 510 nm. Comparing the excitation spectra monitored at $\lambda_{em} = 475$ nm (Figure 2) and $\lambda_{em} = 510$ nm (not given), the excitation peak positions for EA-BST and H-BST remained constant at 305 and 302 nm, respectively, regardless of

10.1021/ja073105b CCC: $37.00 © 2007 American Chemical Society

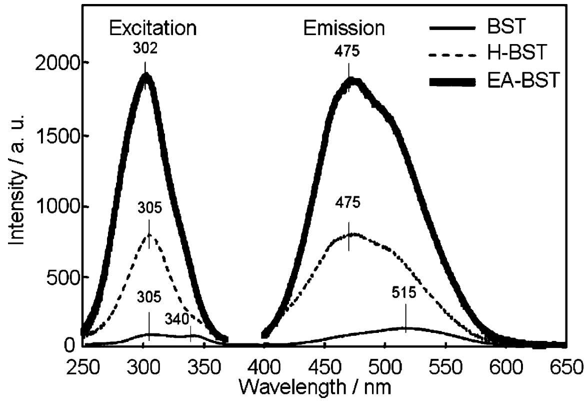


Figure 2. Excitation and emission spectra of BST, H-BST, and EA-BST powders ($\lambda_{ex} = 300$ nm, $\lambda_{em} = 475$ nm).

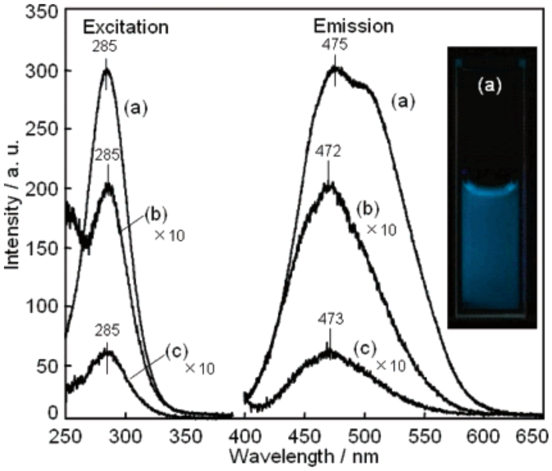


Figure 3. Excitation and emission spectra of (a) BST-nanosheet solution; (b) monolayer LBL film of BST-nanosheet in 0.1 M NaOH; and (c) monolayer LBL film of BST-nanosheet in 0.1 M HCl ($\lambda_{ex} = 285$ nm, $\lambda_{em} = 475$ nm).

the emission wavelength. This indicates that the observed emissions are based on the same excitation process.

In the excitation spectrum of BST, two excitation peaks were observed at 305 and 340 nm. The excitation peak of BST at around 340 nm was close to its UV−vis spectra. The valence band maximum of BST is dominated by the O 2p states. The conduction band minimum of BST is formed from the Bi 6p and Ta 5d states, and the Bi 6p state has lower energy than the Ta 5d state has.[10] Therefore, the excitation peak at around 340 nm may be assigned to the excitation from the O 2p state to Bi 6p state. The excitation peak at around 300 nm was observed in the excitation spectra of all samples. The position of the excitation peaks was not appreciably affected by the type of guest species. As described below, the nanosheet solution also showed a blue emission under the 285 nm excitation. This means that the excitation peaks at around 300 nm can be assigned to the excitation of the host layer, presumably, from O 2p to Ta 5d.

Figure 3a shows the photoluminescence spectra of the solution of the nanosheet derived from BST (BST-nanosheet). It should to be noted that visible blue emission with a peak at 475 nm was observed under the 285 nm excitation. So far, the blue luminescence based on the silicon nanosheet derived from $CaSi_2$ was reported.[11] With regard to oxide nanosheets, a weak blue luminescence of TiO-nanosheet prepared from $Cs_{0.76}Ti_{1.81}O_4$ was reported.[12] However, no or very weak blue luminescence was observed in the present measurement. In conclusion, this is the first report on the visible blue luminescence based on the oxide nanosheet.

On the blue luminescence, the $Sr_2Ta_3O_{10}$ nanosheet solution derived from $CsSr_2Ta_3O_{10}$ showed no blue luminescence (see Supporting Information). The structure of the $Sr_2Ta_3O_{10}$ 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 results in the generation of the defects of the A site. The defects in the BST-nanosheet may be related to the blue emission.

We prepared a film of a monolayer of the BST-nanosheet on a quartz substrate with the LBL method, and its luminescence property of the film was measured in various pH conditions. As a result, it was found that the blue emission was influenced by pH. The blue emission intensity of the BST-nanosheet film in 0.1 M NaOH solution was about 3 times stronger than that in 0.1 M HCl solution, as shown in Figure 3b and c. Thus, the luminescence property of the nanosheet is largely sensitive to the change in the surface environment, such as adsorption of H^+ and/or OH^-, because almost all elements constituting the nanosheet are located on the surface of nanosheet, as shown in Figure 1b.

In conclusion, we succeeded in the exfoliation of $Bi_2SrTa_2O_9$ to a mono-nanosheet for the first time. The thickness of the nanosheet obtained by AFM measurement was about 1.3 nm. It should be noted that the BST-nanosheet itself shows blue luminescence under excitation at 285 nm at room temperature. This will allow the development of a new photoluminescence device constituted of luminescent nanosheets with all colors.

Acknowledgment. This work was supported by a Grant-in-Aid for Scientific Research (No. 440, Panoscopic Assembling and High Ordered Functions for Rare Earth Materials, and No. 16080215) from the Ministry of Education, Culture, Sports, Science and Technology.

Supporting Information Available: XRD patterns, AFM image, and the experimental method for the preparation of $Sr_2Ta_3Ta_3O_{10}$ nanosheet and LBL film of BST-nanosheet. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) (a) Sasaki, T.; Watanabe, M.; Hashizume, H.; Yamada, H.; Nakazawa, H. *J. Am. Chem. Soc.* **1996**, *118*, 8329−8235. (b) Schaak, R. E.; Mallouk, T. E. *Chem. Mater*. **2000**, *12*, 2513−2516. (c) Kudo, A.; Tanaka, A.; Domen, K.; Maruya, K.; Aika, K.; Onishi, T. *J. Catal.* **1988**, *111*, 67−76.
(2) Hata, H.; Kubo, S.; Kobayashi, Y.; Mallouk, T. E. *J. Am. Chem. Soc.* **2007**, *129*, 3064−3065.
(3) Zhou, Y.; Ma, R.; Ebina, Y.; Takada, K.; Sasaki, T. *Chem. Mater*. **2006**, *18*, 1235−1239.
(4) Sasaki, T.; Ebina, Y.; Watanabe, M.; Decher, G. *Chem. Commun.* **2000**, *21*, 2163−2164.
(5) Ida, S.; Araki, K.; Unal, U.; Izawa, K.; Altuntasoglu, O.; Ogata, C.; Matsumoto, Y. *Chem. Commum*. **2006**, 3619−3621.
(6) Aurivillius, B. *Ark. Kemi* **1949**, *1*, 463−480.
(7) Rae, A. D.; Thompson, J. G.; Withers, R. L. *Acta Crystallogr.* **1992**, *B48*, 418−428.
(8) (a) Tsunoda, Y.; Shirata, M.; Sugimoto, W.; Liu, Z.; Terasaki, O.; Kuroda, K.; Sugahara, Y. *Inorg. Chem.* **2001**, *40*, 5768−5771. (b) Tsunoda, Y.; Sugimoto, W.; Sugahara, Y. *Chem. Mater.* **2003**, *15*, 632−635.
(9) Tong, Z.; Takagi, S.; Shimada, T.; Tachibana, H.; Inoue, H. *Chem. Lett.* **2005**, *34*, 1406−1407.
(10) Shimizu, A.; Takada, S.; Shimooka, H.; Takahashi, S.; Kohiki, S.; Arai, M.; Oku, M. *Chem. Mater.* **2002**, *14*, 3971−3975.
(11) Sasaki, T.; Watanabe, M. *J. Phys. Chem. B* **1997**, *101*, 10159−10161.
(12) Nakano, H.; Mitsuoka, T.; Harada, M.; Horibuchi, K.; Nozaki, H.; Takahashi, N.; Nonaka, T.; Seno, Y.; Nakamura, H. *Angew. Chem., Int. Ed.* **2006**, *45*, 6303−6306.

JA073105B