Hydrothermal synthesis and crystal structure of a mixed-valence pyrochlore-type strontium bismuthate, (Sr$_{0.75}$Bi$_{0.25}$)$_2$Bi$_2$O$_{6.83}$

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A pyrochlore-type strontium bismuthate, (Sr$_{0.75}$Bi$_{0.25}$)$_2$Bi$_2$O$_{6.83}$ was synthesized by a hydrothermal method using NaBiO$_3$·nH$_2$O as a starting material. The crystal structure was refined using synchrotron powder X-ray diffraction data. The final R-factors were $R_{wp}$ = 8.07 % and $R_p$ = 5.87 %, and the lattice parameter was $a$ = 11.0195 (2) Å. This compound had a mixed bismuth valence state involving Bi$^{3+}$ and Bi$^{5+}$, where Bi$^{3+}$ partially occupied the A-site (Sr$^{2+}$) as well as the B-site (Bi$^{5+}$) in the pyrochlore-type structure. Moreover, the present compound was found to be a diamagnetic semiconductor with electrical resistivity of ~90 Ωm at room temperature.

Key-words : Hydrothermal synthesis, Strontium bismuthate, Pyrochlore

A variety of bismuth oxides have been prepared by hydrothermal reactions using a hydrated sodium bismuth oxide, NaBiO$_3$·nH$_2$O$_{n=10}$. Although the crystal structure of NaBiO$_3$·nH$_2$O had been unknown for a long time, we recently clarified it using synchrotron powder X-ray diffraction (SPXRD) data. $^{1,2}$ NaBiO$_3$·nH$_2$O had a layered structure related with that of PbSb$_2$O$_6$, and the removal of water molecules in the interlayer resulted in the transformation to the ilmenite-type structure. $^6$ We reported that the reaction with NaBiO$_3$·nH$_2$O in alkaline-earth metal solutions yielded trirutile-type MgBi$_2$O$_6$. $^5$ PbSb$_2$O$_6$-type ABi$_2$O$_6$ ($A$ = Ca, Sr, Ba), $^7,8,13$ pyrochlore-type compounds (Ca, Sr, Ba), $^{1,2}$ and perovskite-type Ba$_{0.96}$Bi$_{0.86}$O$_{2.59}$O$_{0.41}$. $^4$ When a barium chloride solution was used in the room-temperature reaction, the crystallinity of the PbSb$_2$O$_6$-type BaBi$_2$O$_6$ product was very low. $^{1,4}$ However, a highly crystalline BaBi$_2$O$_6$ was obtained using a barium hydroxide solution at 120 °C. $^{13}$ These results suggested that the room-temperature reaction in barium chloride solution was an ion exchange one, $^{1,4}$ whereas the reaction in barium hydroxide solution at 120 °C was a dissolution-recrystallization process. $^{1,3}$ On the other hand, the hydrothermal reaction in strontium nitrate solution at 180 °C produced pyrochlore-type (Sr$_{0.52}$Bi$_{0.48}$)$_2$Bi$_2$O$_6$·58(CO$_3$)$_{30.14}$, $^2$) however, the hydrothermal reaction in strontium hydroxide solution at 80 °C yielded pyrochlore-type Sr$_2$Bi$_2$O$_7$. $^7$ The different crystal phases were attributed to the different reaction temperature and pH of the solutions, which influence on Bi valence ratio and/or crystal growth speed of the product. Recently, Wang et al. reported $^3$ the photocatalytic properties of pyrochlore-type (Sr$_{0.60}$Bi$_{0.30}$)$_2$Bi$_2$O$_7$, prepared by hydrothermal reaction using NaBiO$_3$·2H$_2$O in a pH-adjusted solution of Sr(NO$_3$)$_2$ and NaOH at 160 °C. However, no crystal structure data were included in their study. Recently, we obtained pyrochlore-type (Sr$_{0.75}$Bi$_{0.25}$)$_2$Bi$_2$O$_{6.83}$ by hydrothermal reaction using NaBiO$_3$·nH$_2$O in a strontium hydroxide solution at 240 °C; the chemical composition of this sample was close to that reported by Wang et al. $^3$ Crystal structure refinement of the (Sr$_{0.75}$Bi$_{0.25}$)$_2$Bi$_2$O$_{6.83}$ sample was carried out using SPXRD; the differences among three pyrochlore-type strontium bismuthates [Sr$_2$Bi$_2$O$_7$, (Sr$_{0.60}$Bi$_{0.30}$)$_2$Bi$_2$O$_7$, and (Sr$_{0.75}$Bi$_{0.25}$)$_2$Bi$_2$O$_{6.83}$] will be discussed in this work.

NaBiO$_3$·nH$_2$O (2 g, 6.5 mmol) and Sr(OH)$_2$·8H$_2$O with 1:1–1.5 molar ratios were placed into a Teflon-lined autoclave (70 ml). The autoclaves were closed, heated to 240 °C in an oven, and kept at that temperature for several hours (1–48 h). The crystal structure of the products were examined by X-ray diffraction (XRD), using a Miniflex-600 Rigaku diffractometer with Ni-filtered CuK$_\alpha$ radiation ($\lambda$ = 1.54056 Å). SPXRD measurements were performed on the BL02B2 beamline at SPring-8, Hyogo, Japan. The data were collected with a constant wavelength ($\lambda$ = 0.413356 Å). The crystal structure of the sample was refined using the Rietveld program RIETAN-FP$^{15}$ and visualized using the VESTA software.$^{16}$ The bismuth

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These values are longer than that of pyrochlore-type Sr$_2$Bi$_2$O$_7$ may be due to the lower reaction to obtain the single phase. The slow crystallization of zero-dimensional of the DC magnetic susceptibility was measured in spectroscopy (XPS, JEOL-9200). The temperature dependence of the DC magnetic susceptibility was measured in zero-dimensional of the DC magnetic susceptibility was measured in spectroscopy (XPS, JEOL-9200).

The room-temperature electrical resistivity of the pressed pellet (at 6 GPa for 30 min in a cubic anvil-type high-pressure apparatus at room temperature) was measured using a standard four-probe method (PPMS, Quantum Design), with Ag paste electrodes connected to an Au wire. Aqueous methyl orange (MO, 10 ppm) solutions were prepared with ultrapure water, and the catalyst was added at a concentration of 2 g/L. The solution was stirred and irradiated by visible light from a 300 W Xe lamp (UXR-300DU, Ushio Inc.), using a 420 nm sharp cut filter (GG420, Shibuya Optical Co., Ltd.). The time-dependent concentration of MO was evaluated by ultraviolet-visible (UV-Vis) spectroscopy.

A single-phase pyrochlore-type compound was observed for a Bi:Sr molar ratio of 1:1 at 48 h, whereas an impurity phase was observed in the products with Bi: Sr molar ratios between 1:2 and 1:5 at the same time. The XRD patterns of the products with Bi: Sr = 1:1 for 1–48 h, revealing that the product for 1 h was close to a single phase. In the case of pyrochlore-type Sr$_2$Bi$_2$O$_7$, a longer time was required$^1$ to obtain the single phase. The slow crystallization of pyrochlore-type Sr$_2$Bi$_2$O$_7$ may be due to the lower reaction temperature (80 °C). The single-phase product obtained after 24 h was used for further characterizations.

Rietveld refinement was carried out on the SPXRD data. The SPXRD pattern of the synthesized (Sr$_{0.75}$Bi$_{0.25}$)$_2$Bi$_2$O$_{6.83}$ sample could be indexed to a pyrochlore-type structure $Fd\bar{3}m$ (227, origin choice 2) with cubic cell parameter $a = 11.0195$ (2) Å, in agreement with the previous data for pyrochlore-type mixed-valence Sr bismuthates such as (Sr$_{0.52}$Bi$_{0.48}$)$_2$Bi$_2$O$_{6.83}$(CO$_3$)$_{0.14}$ ($a = 11.01$ Å) and (Sr$_{0.60}$Bi$_{0.40}$)$_2$Bi$_2$O$_{7}$ ($a = 11.0161$ Å)$^{2,3}$ These values are longer than that [10.94132 (6) Å] of the pyrochlore-type Sr$_2$Bi$_2$O$_7$ prepared by a low-temperature (80 °C) hydrothermal method.$^1$ In this compound the Bi site was occupied only by Bi$^{5+}$ and the valence distribution of Bi affected the length of the lattice parameter.

The SPXRD refinement pattern for the (Sr$_{0.75}$Bi$_{0.25}$)$_2$Bi$_2$O$_{6.83}$ sample is shown in Fig. 1, and the corresponding crystal structure is shown in the inset of the figure. The final R-factors were $R_{wp} = 8.07$ % and $R_p = 5.87$ %. The chemical composition of (Sr$_{0.75}$Bi$_{0.25}$)$_2$Bi$_2$O$_{6.83}$ was determined from the refinement data. The Sr:Bi molar ratio (0.60:1) obtained from the refined data is close to the energy-dispersive X-ray spectroscopy (EDX) result (Sr:Bi = 0.64:1). The oxygen (O2) occupancy (0.83) at the 32e site was kept fixed for charge balance. The structural parameters are summarized in Table 1.

The mean Bi–O distance in the BiO$_6$ octahedral site of (Sr$_{0.75}$Bi$_{0.25}$)$_2$Bi$_2$O$_{6.83}$ [2.142 (5) Å] is longer than that of Sr$_2$Bi$_2$O$_7$ [Bi–O = 2.09 (14) Å]$^3$ The longer Bi–O distance of the sample in this study indicates the presence of Bi$^{3+}$ ions in the B-site, along with Bi$^{5+}$ species. The combination of XPS and Rietveld refinement results confirmed that approximately 21 % of Bi$^{3+}$ ions partially occupied the B-site, along with Bi$^{5+}$. Thus, the valence distribution of bismuth atoms was determined to be (Sr$_{0.75}$Bi$_{0.25}$)$_2$Bi$_2$O$_{6.83}$, while that of bismuth in (Sr$_{0.60}$Bi$_{0.40}$)$_2$Bi$_2$O$_7$ was (Sr$_{0.60}$Bi$_{0.40}$)$_2$Bi$_2$O$_{6.83}$. The mean (Sr,Bi–O) distance of our synthesized sample was 2.609 (3) Å, which is shorter than the Sr–O distance [2.650 (3) Å] in Sr$_2$Bi$_2$O$_7$.$^1$ This was due to the 25 % partial occupancy of the A-site by the Bi$^{3+}$ species, along with Sr$^{2+}$ ions.

The presence of Bi$^{3+}$ was confirmed by the XPS data shown in Fig. 2(a). The two peaks at 162.9 and 164 eV (or

| Atom | Site | x | y | z | g | B$_D$(Å$^2$) |
|------|------|---|---|---|---|-----------|
| Sr   | 16d  | 1/2 | 1/2 | 1/2 | 0.75*  | 0.60 (2)   |
| Bi1  | 16d  | 1/2 | 1/2 | 1/2 | 0.25*  | = B (Sr)   |
| Bi2  | 16e  | 0   | 0   | 0   | 1      | 0.67 (2)   |
| O1   | 48f  | 1/8 | 1/8 | 0.3310 (6) | 0.85 (2)  |
| O2   | 32e  | 0.5635 (5) | = x | = x | 0.83*  | 1.5*       |

* denotes a fixed parameter.
157.6 and 158.8 eV) were attributed to Bi$^{5+}$ and Bi$^{3+}$, respectively, as indicated in the previous report for Bi$_{0.75}$-Pb$_{0.25}$NiO$_{3}$. The average valence of Bi atoms was found to be 4.26, with 63\% of Bi$^{5+}$ and 37\% of Bi$^{3+}$.

This pyrochlore-type strontium bismuthate follows the linear relationship between the lattice parameter of the cubic unit cell and the sum of the ionic radii of the A- and B-site cations, as shown in various pyrochlore-type oxides [Fig. 2(b)]. Slightly deviation (U) from straight line position could be due to the charge distribution of bismuth.

The temperature dependence of the magnetic susceptibility and electrical resistivity indicates that the present compound is a diamagnetic semiconductor. The electrical resistivity of the pressed sample decreased with increased temperature, and the room-temperature electrical resistivity was found to be $\approx90\ \Omega \cdot \mathrm{m}$. This value was higher than that (0.03 $\Omega \cdot \mathrm{m}$) of Sr$_2$Bi$_2$O$_7$. The difference may be due to the higher amount of Bi present in (Sr$_{0.75}$Bi$_{0.25}$)$_2$Bi$_2$O$_{6.83}$, because the formation of a covalent bond between Bi 6s and O1 2p orbitals through sp hybridization\(^1\) may lead to a high resistivity, while negligible mixing takes place between O2 2p bands and Sr sites.\(^1\)

The strontium bismuthate, (Sr$_{0.75}$Bi$_{0.25}$)$_2$Bi$_2$O$_{6.83}$, absorption edges lie within the visible region [Fig. 3(a)] and the band gap was found to be 0.20 eV by assuming direct transitions\(^1,3\) as shown in Fig. 3(b). Three types of strontium bismuthates show decrease of MO concentration under dark conditions [Fig. 4(a)]. On the other hand, it was reported that (Sr$_{0.60}$Bi$_{0.30}$)$_2$Bi$_2$O$_7$ had photocatalytic activity for MO, but its activity was not checked under dark conditions.\(^3\) Under dark and visible light irradiation, the decrease of MO concentration followed the same trend as the experiments in dark conditions for all three Sr bismuthates, as shown in Fig. 4(b). If these samples have photocatalytic activity, their slopes should change at the switching point from dark to light irradiation. However, there are no changes of slopes as shown in Fig. 4(b). Thus, we can conclude that the decrease of MO concentration under dark experiment could be due to adsorption; a similar result was found for phenol by Sr$_2$Bi$_2$O$_7$ in dark experiment.\(^1\)

In summary, the crystal structure of pyrochlore-type mixed bismuth-valence (Sr$_{0.75}$Bi$_{0.25}$)$_2$Bi$_2$O$_{6.83}$ was refined by SPXRD. Bi$^{5+}$ partially occupied the A-site as well as the B-site of the pyrochlore structure along with Sr$^{2+}$ and Bi$^{3+}$, respectively. The present compound possessed higher electrical resistivity compared to that of Sr$_2$Bi$_2$O$_7$ at room temperature.

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