Synthesis and crystal structure of a new bismuth tin titanate with the pyrochlore-type structure

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A pyrochlore-type compound, Sn0.34Bi1.52Ti1.86Sn0.14O6.62, was synthesized using a solid-state reaction in a N2 atmosphere. The crystal structure was refined using the synchrotron powder X-ray diffraction data. This compound comprised mixed-valence states Sn2+ and Sn4+. The morphology of this compound was irregular shapes with particle size approximately 1–5 μm. The band gap of this compound was estimated to be 2.83 eV from the ultraviolet–visible spectrum. The dielectric constant of this compound was 78 under 100 Hz frequency and weak photocatalytic activity for methylene blue degradation under visible light irradiation.

Key-words : Bismuth tin titanate, Pyrochlore, Crystal structure

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1. Introduction

The phase diagram of the Bi2O3–TiO2 system published⁵ in 1965 did not indicate the presence of pyrochlore-type (A₂B₂O₇) bismuth titanate (Bi₂Ti₂O₇). In 1995, Kahlenberg and Böhm³ reported the existence of pyrochlore-type bismuth titanate with Bi³⁺ and O²⁻ deficiencies (Bi₁.₈₃Ti₂O₆.₇₃) in addition to a mixture of Bi₂Ti₃O₁₂ and Bi₂Ti₄O₁₁ phases. After this discovery, many researchers have tried to synthesize a single phase of the pyrochlore-type bismuth titanate. Radosavljevic et al.³) prepared for the first time almost a single phase of pyrochlore-type bismuth titanate, Bi₁.₇₄Ti₂O₆.₆₂, by a low temperature route at 600°C, and this product contained very small impurity phases of Bi₂Ti₄O₁₁ and TiO₂. Su and Li⁴) prepared a single phase of Bi₂Ti₂O₇ by the sol–gel method. By using the same method, Kim et al.⁵) obtained the pyrochlore-type bismuth titanate, Bi₁.₈₆Ti₂O₆.₈₈₄, and the crystal structure was refined using neutron powder diffraction data. In addition to the above reports, many papers report the synthesis of a single phase of pyrochlore-type bismuth titanate by various methods such as coprecipitation,⁶ solvothermal,⁷ and hydrothermal reactions.⁸ These low temperature synthesis procedures are more suitable than a high temperature reaction for synthesizing a pyrochlore-type bismuth titanate because the pyrochlore-type Bi₂Ti₂O₇ decomposes above 650°C.⁹,¹⁰ Among the above methods, hydrothermal reaction is the interesting one which produced different shape of Bi₂Ti₂O₇ particles such as nanorods¹¹ and microspheres,¹² and both particles exhibited photocatalytic activity under visible light irradiation for degradation of organic pollutants, methylene blue (MB) and Rhodamine B.¹¹,¹² Besides photocatalytic activity, it was reported that Bi₂Ti₂O₇ showed dielectric property¹³ with the value of dielectric constant 104.2 under 1 MHz frequency. Additionally, there have been many reports for pyrochlore-type bismuth titanates where the A-site (Bi³⁺) partially substituted with Li¹⁴,¹⁵ alkaline earth elements (Mg, Ca, Sr, Ba),¹⁴ transition elements (Y, Mn, Fe, Cu, Co),¹⁵–¹⁹ for synthesis of new compounds. Previously, we succeeded to prepare a pyrochlore-type bismuth titanate²⁰ [Na₀.₃₂Bi₁.₆₈Ti₂O₄.₄₆(OH)₀.₄₄] by hydrothermal reactions, where Na incorporated in the A-site, and this compound exhibited no photocatalytic activity for degradation of MB under visible light irradiation.

On the other hand, the A-site in pyrochlore-type structure can accommodate Sn²⁺ ion as found in Sn₄TiNbO₁₄, Sn₅Ti₀.₉Ta₀.₁(O,F)₇, Sn₂⁺(Sn⁴⁺M₂⁻)O₇–x–y/2 [M= Nb, Ta]²¹,²² The presence of Sn²⁺ makes static displacement of A-site from the ideal pyrochlore structure.²³ Avdeev et al.²³ found that this static displacement was caused by lone electronic pair on the A-site cation for Bi₂−xMₓRu₂O₇−y (M = Cu, Co; x = 0, 0.4) pyrochlores. The similar displacement phenomenon was also found for the Bi³⁺ in the A-site of bismuth titanate pyrochlore.⁵ Thus, Sn²⁺ could be a good choice for partially incorporated with Bi-site for bismuth titanate pyrochlore.

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By this motif we tried to incorporation of Sn\(^{2+}\) into A-site of the bismuth titanate pyrochlore, and obtained Sn\(_{0.34}\)Bi\(_{1.52}\)Ti\(_{1.86}\)Sn\(_{0.14}\)O\(_{6.62}\). Moreover, incorporation of Sn\(^{2+}\) in the A-site of bismuth titanate pyrochlore-type compound is always a challenge because during synthesis there are some possibilities of Sn\(^{2+}\) oxidized to Sn\(^{4+}\) which lead to Sn\(^{4+}\) present simultaneously with Ti\(^{4+}\) in the B-site due to the restriction of crystal radius. Previously reported\(^{21,22}\) some pyrochlore-type Sn\(^{2+}\) compounds always oxidation occurred during synthesis. This in turn led to some incorporation of Sn\(^{4+}\) into the B-site of the pyrochlore structure. Herein, we describe the synthesis of Sn incorporated into a new pyrochlore-type bismuth titanate by solid state reaction and crystal structure refinement by using synchrotron powder X-ray diffraction (SPXRD) data. The photocatalytic activity for phenol, MB, and methyl orange (MO) were checked under visible light irradiation. The dielectric property was also investigated.

2. Experimental

The starting compounds, SnO, Bi\(_2\)O\(_3\) and TiO\(_2\) with several molar ratios were taken such as 0.20:0.30:0.50, 0.14:0.24:0.62, 0.29:0.14:0.57 and 0.15:0.23:0.62 in a plastic bottle with ethanol and ball milling 6 h for uniform mixing after that heated 120°C to remove the ethanol. The sample is heated at 900–1100°C for 3 h in flow of N\(_2\) gas to resist the oxidation of Sn\(^{2+}\). All starting reagents were purchased from Kanto Chemical Co., Inc. (Tokyo, Japan). The crystal structure of the product was examined by XRD on a Rigaku X-ray diffractometer (RINT-2000, RIGAKU and MiniFlex 600) with Cu K\(\alpha\) radiation [\(\lambda = 1.54056\ \text{Å} (1 \text{Å} = 0.1 \text{nm})\)]. Sn oxidation state was determined by X-ray photoelectron spectroscopy (XPS) (JEOL-9200). SPXRD measurements were performed at the BL02B2 powder diffraction beamline at SPring-8, Hyogo, Japan. The powder samples were sealed in a glass capillary with an inner radius of 0.2 mm. The data was collected with a constant wavelength (\(\lambda = 0.412486\ \text{Å}\)) at room temperature. Crystal structure was refined using the Rietveld program RIETAN-FP\(^ {23}\) and was visualized using VESTA software.\(^ {25}\) Surface morphology was checked by scanning electron microscopy (SEM, JEOL F6500). Diffuse-reflectance spectra were collected using a spectrometer (JASCO V-550 spectrometer) and were converted using the Kubelka–Munk function. Aqueous phenol (20 ppm), MO and MB (10 ppm) solution were prepared with ultrapure water and catalyst was added at a concentration of 3 g/L for phenol and 2 g/L for MO and MB. 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 was evaluated by liquid chromatography (JASCO LC-2000) for phenol and the concentration of MO and MB was measured by UV–vis spectroscopy (V-550, JASCO). For dielectric property measurement the pellet sample was made with adding binder (polyethylene glycol) under pressing 10 KN. The pellet 10 mm in diameter and 1 mm in thickness. The ceramic samples were electrode on both sides using silver paint and heated at 600°C for 15 min under N\(_2\) atmosphere. The dielectric properties were measured over a frequency range from 10\(^2\) to 10\(^6\) Hz at room temperature.

3. Results and discussion

3.1 Sample preparation

We used four different starting material compositions, as mentioned in the experimental section. When the molar ratios of the starting materials SnO, Bi\(_2\)O\(_3\), and TiO\(_2\) (rutile) were 0.15:0.23:0.62 at above 1000°C, the X-ray powder pattern of the product showed almost single phase pyrochlore-type compound [Fig. 1(a)]. A small amount of impurity phase was identified as rutile-type TiO\(_2\) and SnO\(_2\) for the samples prepared above 1000°C. The X-ray powder pattern of the product showed almost single phase pyrochlore-type compound [Fig. 1(a)]. A small amount of impurity phase was identified as rutile-type TiO\(_2\) and SnO\(_2\) for the samples prepared above 1000°C. The sample synthesized at 1100°C showed the lowest impurity level and was selected for further characterizations. SEM images [Fig. 1(b)] showed that the particle shape of the products were irregular, and the particle size was approximately 1–

![Fig. 1. XRD patterns at various temperatures. Sn\(_{0.34}\)Bi\(_{1.52}\)Ti\(_{1.86}\)Sn\(_{0.14}\)O\(_{6.62}\) sample obtained at 1100°C (a), SEM image of Sn\(_{0.34}\)Bi\(_{1.52}\)Ti\(_{1.86}\)Sn\(_{0.14}\)O\(_{6.62}\) sample prepared at 1100°C (b).]
3.2 Crystal structure

The structure refinement was carried out with the assumption of the crystal structure of bismuth titanate pyrochlore-type Bi$_2$Ti$_2$O$_7$. When the A-site cation of pyrochlore structure (A$_2$B$_2$O$_7$) possessed lone pair electrons, generally the A-site cation was displaced from 16d to the 96-fold site. In the case of our sample, Sn$^{2+}$ and Bi$^{3+}$ partially occupied in the A-site and both ions have the lone pair electrons so it was assumed that these ions located to the 96g. SPXRD data was used to refine the crystal structure considering the chemical composition obtained from the starting material composition (Sn$_{0.48}$Bi$_{1.52}$)Ti$_2$O$_6.76$, however synthesized sample lattice parameter ($a = 10.439$ Å) was determined from the XRD data. This lattice parameter was higher than those of the earlier reported bismuth titanate pyrochlore-type [10.3523(2) Å for Bi$_{1.74}$Ti$_2$O$_6.62$ and 10.3735(3) Å for Bi$_{1.896}$Ti$_2$O$_6.884$] compounds and also A-site incorporated bismuth titanate compounds had the range of lattice parameter $a= 10.30$–10.37 Å. Thus, it was considered that some of the Sn$^{2+}$ oxidized to Sn$^{4+}$ and located to the B-site of pyrochlore structure along with Ti$^{4+}$, this is because of smaller ionic radius of Sn$^{4+}$ that unable to occupy in the A-site. XPS data confirmed the presence of Sn$^{4+}$. Figure 2 shows XPS data having two peaks at 485.8 and 487.1 eV were indexed to Sn$^{2+}$ and Sn$^{4+}$, respectively. That was close to the refined data (71%–Sn$^{2+}$ and 29%–Sn$^{4+}$). From the Rietveld refinement the lowest $R_p$ with reasonable crystal structure obtained when 7% of Sn$^{4+}$ occupied in the B-site. The crystallographic data and structural parameters of this structural model are summarized in Tables 1 and 2, respectively. Rietveld refinement pattern represents in Fig. 3. The final chemical composition ([Sn$_{0.34}$Bi$_{1.52}$]–Ti$_{1.86}$Sn$_{0.14}$O$_{6.62}$) was determined from the SPXRD refinement data.

In the case of Sn$_{0.34}$Bi$_{1.52}$Ti$_{1.86}$Sn$_{0.14}$O$_{6.62}$, (Sn$^{4+}$,Ti$^{4+}$)–O$^2$– distance in the B-site of the pyrochlore-type structure is 1.989(6) Å as shown in Table 3, this is the highest value among others pyrochlore-type bismuth titanate compounds; Bi$_{1.74}$Ti$_2$O$_6.62$, [Ti$^{4+}$–O$^2$– = 1.9635(3) Å] and Bi$_{1.896}$Ti$_2$O$_6.884$ [Ti$^{4+}$–O$^2$– = 1.9652(8) Å]. This higher bond length value supported the incorporation of some Sn$^{4+}$ in the B-site with Ti$^{4+}$. Because, Sn$^{4+}$–O$^2$– distance [2.067(15) Å] in the B-site for the pyrochlore-type Bi$_2$Sn$_2$O$_7$ is longer than Ti$^{4+}$–O$^2$– distance of pyrochlore-type bismuth titanate compounds. This was caused by the fact that Sn$^{4+}$ ionic radius is bigger than Ti$^{4+}$ one, for coordination number 6. In the case of A-site of Sn$_{0.34}$Bi$_{1.52}$Ti$_{1.86}$Sn$_{0.14}$O$_{6.62}$, (Sn$^{3+}$,Bi$^{3+}$)–O$^2$– average bond length in the A-site is 2.554(1) Å as shown in Table 3, this value is well agreement with the Bi$^{3+}$–O$^2$– bond length for Bi$_{1.74}$Ti$_2$O$_6.62$ [2.547(8) Å] and Bi$_{1.896}$Ti$_2$O$_6.884$ [2.559(6) Å] titanate compounds. Whereas, Sn$^{2+}$ has almost similar ionic radius (1.18 Å) compared to Bi$^{3+}$ (1.17 Å). The crystal structure and polyhedral structure are shown in Figs. 4(a) and 4(b) respectively.

3.3 Photocatalytic and dielectric properties

The optical absorption spectrum for SBT sample is shown in Fig. 5 (insert). Band gap energy was estimated by assuming of direct transition similar to Bi$_2$Ti$_2$O$_7$.

Figure 2: X-ray photoelectron spectrum of the Sn$^{3d_{5/2}}$ signal.
line samples have been reported to give accurate values for monazite-type oxides. The band gap was found 2.83 eV as shown in Fig. 5.

The photocatalytic activity of Sn0.34Bi1.52Ti1.86Sn0.14O6.62 compound was checked for MB, MO and phenol. This compound does not show photocatalytic activity for phenol and MO degradation under visible light. Weak photocatalytic activity was observed for MB and the time profile of C/C0 under visible-light irradiation (λ ≥ 420 nm) shown in Fig. 6(a). The degradation of MB under visible light was monitored by recording the UV–vis absorption spectra (λmax = 664 nm) as display in Fig. 6(b). The absorption peak centered at 664 nm for MB. The intensity of the absorption peak at 664 nm decreased with irradiation time. Some Sn2+ pyrochlore compounds showed visible light driven photocatalytic activities such as Sn0.92Sb2O6·2H2O showed photocatalytic activity for MO and Sn2Sb2O7 showed for H2 evaluation. Nanorod Bi2Ti2O7 showed much higher photocatalytic activity for MB degradation under visible light compared to pyrochlore-type Sn0.34Bi1.52Ti1.86Sn0.14O6.62 probably due to the nano size and lower band gap (2.58 eV).

Figure 7 showed the frequency dependent dielectric constant and tan δ for Sn0.34Bi1.52Ti1.86Sn0.14O6.62 sample.
at room temperature. The dielectric constant of this compound was 78 under 100 Hz frequency. Previously, Sn\textsuperscript{2+} incorporated in the A-site for pyrochlore structure also exhibited dielectric constant in the range (31–149).\textsuperscript{21)} From the frequency dependent dielectric constant curve indicated that Sn\textsubscript{0.34}Bi\textsubscript{1.52}Ti\textsubscript{1.86}Sn\textsubscript{0.14}O\textsubscript{6.62} dielectric constant was independent on frequency.

4. Conclusion

Sn\textsubscript{0.34}Bi\textsubscript{1.52}Ti\textsubscript{1.86}Sn\textsubscript{0.14}O\textsubscript{6.62} pyrochlore-type compound was synthesized by solid state reactions. This pyrochlore-type compound had dielectric constant 78 under 100 Hz frequency with weak photocatalytic activity under visible light irradiation for MB degradation, while no photocatalytic activity was observed for MO and phenol degradation.

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