Response to Comment on `Quantum-confinement effects on the optical and dielectric properties for mesocrystals of BaTiO₃ and SrBi₂Ta₂O₉'  
Kohiki Shigemi, Takada Syozo, Shimizu Akihiko, Yamada Kenichi, Higashijima Hirotaka, Mitome Masanori

journal or publication title
Journal of Applied Physics

volume
88

number
10

page range
6093-6095

year
2000-11-15

URL
http://hdl.handle.net/10228/543
doi: 10.1063/1.1318365
Response to “Comment on ‘Quantum-confinement effects on the optical and dielectric properties for mesocrystals of BaTiO$_3$ and SrBi$_2$Ta$_2$O$_9$’” [J. Appl. Phys. 88, 6092 (2000)]

Shigemi Kohiki,a) Syozo Takada, Akihiko Shimizu, Kenichi Yamada, and Hirotaka Higashijima
Department of Materials Science, Kyushu Institute of Technology, Tobata, Kita-kyusyu 804-8550, Japan

Masanori Mitome
National Institute for Research in Inorganic Materials, Tsukuba, Ibaraki 305-0044, Japan

(Received 13 March 2000; accepted for publication 3 August 2000)

In this reply, the authors show that the argument by Scott regarding the band gap of bulk SrBi$_2$Ta$_2$O$_9$ (SBT) is not based on concrete evidence. The authors will also show additional data from a Raman study of a powdered SBT sample to prove that the surface of the specimen was not covered by Bi$_2$O$_3$.

Scott claimed in his comment on our recent publication that (a) the band gap of bulk or large area thin film SrBi$_2$Ta$_2$O$_9$ (SBT) is 4.1 eV, and (b) the absorption edge of the SBT powder at 2.7 eV we showed is not that of crystalline SBT but that of Bi$_2$O$_3$ on the surfaces of SBT.

We first point out that the references mentioned by Scott, in which the band gap of bulk SBT is said to be measured as 4.1 eV, actually showed no data of absorption of SBT in the ultraviolet (UV) to visible portion of the spectrum. It seems to us that his argument regarding the band gap value of 4.1 eV has no clear evidence in the literature. A report by Scott et al., which is not referred to by him in his comment on our article, however, carries an UV-visible absorption spectrum of bulk SBT as reproduced here in Fig. 1 from their article. This figure clearly exhibits the existence of three intense peaks at 2.3, 3.4, and 4.1 eV. Although the absorption edge in this particular case can be estimated at 3.7 eV, there is no explanation of the origin for the other two peaks. We have no clear idea whatsoever about the rationale of pointing out Refs. 2–4 instead of Ref. 5. Figure 1 presented in Ref. 5 indicates that there is no evidence of the band gap of bulk SBT at 4.1 ± 0.1 eV. Since multiconstituent oxide materials can have a variety of structures due to factors such as crystallinity, nonstoichiometry, defects, and/or phases, it is highly likely that an oxide under a common name actually has varied values of a certain material constant. One of the representative examples is indium–tin–oxide, which has different material constants, such as transmittance and resistivity, depending on the conditions of preparation. In the other report by Watanabe et al. not referred to by Scott in his comment on our article, for SBT they have claimed a 2 eV gap depending on the specimen composition. In Ref. 6 the composition and band gap were different between the surface and bulk of the specimen, and the compositions for both the surface and bulk were nonstoichiometric. Based on these facts, so far there is no concrete evidence of a single universal value for the absorption edge at 4.1 eV for bulk SBT.

Scott said that the band gap of SBT cannot be 2.7 eV because SBT crystals are transparent. Materials with the band gap of about 3.2 eV or larger look completely transparent to the human eye because the light in the visible range is not absorbed at all. A band gap in the visible portion of the spectrum gives colors depending on the value of the band gap. The 2.7 eV value corresponds to the blue portion of the spectrum, resulting in slightly white or yellowish color but still giving a transparent look to crystals. An example of a crystal having a similar band gap is ZnSe; the band gap is 2.67 eV at 300 K, and ZnSe is transparent with a yellowish appearance. Even if the SBT crystal has to be transparent as claimed by Scott, it is totally possible for SBT, therefore, to have the band gap of 2.7 eV as our absorption measurements clearly showed in Ref. 1.

Scott claimed in his comment on our recent publication that (a) the band gap of bulk or large area thin film SrBi$_2$Ta$_2$O$_9$ (SBT) is 4.1 eV, and (b) the absorption edge of the SBT powder at 2.7 eV we showed is not that of crystalline SBT but that of Bi$_2$O$_3$ on the surfaces of SBT.

We first point out that the references mentioned by Scott, in which the band gap of bulk SBT is said to be measured as 4.1 eV, actually showed no data of absorption of SBT in the ultraviolet (UV) to visible portion of the spectrum. It seems to us that his argument regarding the band gap value of 4.1 eV has no clear evidence in the literature. A report by Scott et al., which is not referred to by him in his comment on our article, however, carries an UV-visible absorption spectrum of bulk SBT as reproduced here in Fig. 1 from their article. This figure clearly exhibits the existence of three intense peaks at 2.3, 3.4, and 4.1 eV. Although the absorption edge in this particular case can be estimated at 3.7 eV, there is no explanation of the origin for the other two peaks. We have no clear idea whatsoever about the rationale of pointing out Refs. 2–4 instead of Ref. 5. Figure 1 presented in Ref. 5 indicates that there is no evidence of the band gap of bulk SBT at 4.1 ± 0.1 eV. Since multiconstituent oxide materials can have a variety of structures due to factors such as crystallinity, nonstoichiometry, defects, and/or phases, it is highly likely that an oxide under a common name actually has varied values of a certain material constant. One of the representative examples is indium–tin–oxide, which has different material constants, such as transmittance and resistivity, depending on the conditions of preparation. In the other report by Watanabe et al. not referred to by Scott in his comment on our article, for SBT they have claimed a 2 eV gap depending on the specimen composition. In Ref. 6 the composition and band gap were different between the surface and bulk of the specimen, and the compositions for both the surface and bulk were nonstoichiometric. Based on these facts, so far there is no concrete evidence of a single universal value for the absorption edge at 4.1 eV for bulk SBT.

Scott said that the band gap of SBT cannot be 2.7 eV because SBT crystals are transparent. Materials with the band gap of about 3.2 eV or larger look completely transparent to the human eye because the light in the visible range is not absorbed at all. A band gap in the visible portion of the spectrum gives colors depending on the value of the band gap. The 2.7 eV value corresponds to the blue portion of the spectrum, resulting in slightly white or yellowish color but still giving a transparent look to crystals. An example of a crystal having a similar band gap is ZnSe; the band gap is 2.67 eV at 300 K, and ZnSe is transparent with a yellowish appearance. Even if the SBT crystal has to be transparent as claimed by Scott, it is totally possible for SBT, therefore, to have the band gap of 2.7 eV as our absorption measurements clearly showed in Ref. 1.

Scott claimed in his comment on our recent publication that (a) the band gap of bulk or large area thin film SrBi$_2$Ta$_2$O$_9$ (SBT) is 4.1 eV, and (b) the absorption edge of the SBT powder at 2.7 eV we showed is not that of crystalline SBT but that of Bi$_2$O$_3$ on the surfaces of SBT.

We first point out that the references mentioned by Scott, in which the band gap of bulk SBT is said to be measured as 4.1 eV, actually showed no data of absorption of SBT in the ultraviolet (UV) to visible portion of the spectrum. It seems to us that his argument regarding the band gap value of 4.1 eV has no clear evidence in the literature. A report by Scott et al., which is not referred to by him in his comment on our article, however, carries an UV-visible absorption spectrum of bulk SBT as reproduced here in Fig. 1 from their article. This figure clearly exhibits the existence of three intense peaks at 2.3, 3.4, and 4.1 eV. Although the absorption edge in this particular case can be estimated at 3.7 eV, there is no explanation of the origin for the other two peaks. We have no clear idea whatsoever about the rationale of pointing out Refs. 2–4 instead of Ref. 5. Figure 1 presented in Ref. 5 indicates that there is no evidence of the band gap of bulk SBT at 4.1 ± 0.1 eV. Since multiconstituent oxide materials can have a variety of structures due to factors such as crystallinity, nonstoichiometry, defects, and/or phases, it is highly likely that an oxide under a common name actually has varied values of a certain material constant. One of the representative examples is indium–tin–oxide, which has different material constants, such as transmittance and resistivity, depending on the conditions of preparation. In the other report by Watanabe et al. not referred to by Scott in his comment on our article, for SBT they have claimed a 2 eV gap depending on the specimen composition. In Ref. 6 the composition and band gap were different between the surface and bulk of the specimen, and the compositions for both the surface and bulk were nonstoichiometric. Based on these facts, so far there is no concrete evidence of a single universal value for the absorption edge at 4.1 eV for bulk SBT.

Scott said that the band gap of SBT cannot be 2.7 eV because SBT crystals are transparent. Materials with the band gap of about 3.2 eV or larger look completely transparent to the human eye because the light in the visible range is not absorbed at all. A band gap in the visible portion of the spectrum gives colors depending on the value of the band gap. The 2.7 eV value corresponds to the blue portion of the spectrum, resulting in slightly white or yellowish color but still giving a transparent look to crystals. An example of a crystal having a similar band gap is ZnSe; the band gap is 2.67 eV at 300 K, and ZnSe is transparent with a yellowish appearance. Even if the SBT crystal has to be transparent as claimed by Scott, it is totally possible for SBT, therefore, to have the band gap of 2.7 eV as our absorption measurements clearly showed in Ref. 1.
Doubt has been raised about the surface of SBT, showing that Bi$_2$O$_3$ is formed on the surface of SBT depending on the process conditions, and that our powder sample of SBT may have been covered with Bi$_2$O$_3$. We show that this is not the case in our specimen by presenting the Raman spectrum in Fig. 2. Raman scattering measurements were made at room temperature in air using a JASCO NR-1800. A near backscattering configuration was adopted, using the 514.5 nm line of an Ar$^+$ ion laser with an intensity of $3.8 \times 10^9$ W/m$^2$. The major peaks at around 210, 600, and 810 cm$^{-1}$ are associated with the LO phonons of SBT.$^{7,8}$ In the backscattering configuration only the LO phonon is clearly seen. No intense and sharp peaks were seen at around 210, 310, and 450 cm$^{-1}$, which are of Bi$_2$O$_3$. The small humps at around 310 and 450 cm$^{-1}$ are also due to SBT.$^{7,8}$ We also carried out high-resolution transmission electron microscopy and x-ray photoelectron spectroscopy studies of the SBT powder sample, both showed no clear evidence of the presence of Bi$_2$O$_3$ at the sample surface.$^{10}$ Based on these measurements, we can safely state that the surface of our SBT powder is not covered by Bi$_2$O$_3$.

The penetration depth of the 514.5 nm line is a few hundred nanometers, which is approximately the same as for the UV-visible diffuse reflectance measurement that provides evidence of a band gap at around 2.7 eV. X-ray diffraction measurements in our previous study also showed that the structure of SBT powder we used was not of Bi$_2$O$_3$ but actually of SBT.$^1$ The fact that there is no Bi$_2$O$_3$ on the surface of the SBT powder and that both Raman and reflectance measurements give the properties of this region at the same depth as the sample, proves that the SBT powder we used was not covered with Bi$_2$O$_3$, the bulk structure of SBT extended close to the surface, and the band gap is about 2.7 eV.

Scott further argued that the quantum confinement energy varies as the inverse of the dimension. In the case of nanoscale crystallites prepared from solution as a precursor, however, the dependence of the value of the absorption edge on the initial concentration of the precursor solution, which is known as the dilution effect, is a reliable indication of the confinement effect as shown for BaTiO$_3$ mesocrystals in Ref. 1. Figure 3 shows the diffuse reflectance spectrum of SBT confined in the MCM-41 molecular sieve, prepared from precursor solutions with different concentrations. The measurement was made using a JASCO V-550 spectrometer with a resolution of 0.002 eV. The solution of lower concentration gives an absorption edge at higher energy; the samples made from solutions of $5 \times 10^{-3}$, $5 \times 10^{-4}$, and $5 \times 10^{-5}$ mol/l have absorption edges at 3.6, 4.2, and 4.3 eV, respectively. Although x-ray diffraction measurement showed no clear peaks of the crystal structure of SBT confined in the mesopores of the MCM-41 molecular sieve, the transmission electron microscopy study revealed the presence of microcrystalline SBT.$^{10}$ These facts suggest that the SBT in the pores of MCM-41 is in a crystalline state, is exhibiting a dilution effect, and the shift in position of its absorption edge is the result of confinement.

In conclusion, we have demonstrated that there is no clear evidence of a band gap for bulk SBT uniquely at 4.1 $\pm$ 0.1 eV, it is totally possible for SBT to have its band gap of 2.7 eV as in our absorption spectrum measurement, the surface of our SBT powder is not covered by Bi$_2$O$_3$, and the nanoscale crystallites prepared from solution in the mesopores of MCM-41 show a dilution effect which is an indication of a confinement effect.

Note added in Proof. Recently, theoretical band gap of 2 eV has been reported for SBT by Stachiotti et al.$^{11,12}$ They performed first-principles electronic structure calculation of SBT using the full-potential linearized augmented plane-wave method (WIEN97) within the local-density approximation (LDA) to density functional theory. They also revealed the following; in the valence band there is strong hybridization of O 2$p$ with Ta 5$d$ and Bi 6$s,p$ states, the valence band maximum (VBM) at X point is primarily of O 2$p$ character is also substantial above the conduction band minimum.
(CBM), and the VBM and CBM are not localized in the Bi–O layer as mentioned by the tight-binding calculation. Stachiotti et al. have pointed out that the 4 eV band gap claimed by Scott is twice as large as the theoretical 2 eV gap. It is well known that the LDA calculation tends to underestimate the band gap of semiconductor. The experimental 2.7 eV gap reported by Kohiki et al. is rather agreement with the theoretical one.

Finally, we would like to thank the author of the comment for presenting his views and giving us an opportunity to have this discussion.