Analysis of Crystal System of $BaBiO_3$ by Synchrotron X-ray Diffraction and Convergent-beam Electron Diffraction

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Introduction

Semiconducting property of $BaBiO_3$ is attributed to charge density wave (CDW) gap originating from ordering arrangement of "Bi^{3+}" and "Bi^{5+}" in the distorted-perovskite structure [1]. It has been reported that the collapse the CDW gap by modulation of crystal structure with cation substitution generate the electron carrier and superconducting transition in $BaPb_{1-x}Bi_xO_3$ and $Ba_{1-x}K_xBiO_3$ [2, 3].

So far, crystal system of $BaBiO_3$ has been reported to be monoclinic-distorted perovskite [4]. However, there has no decisive study on crystal structure of $BaBiO_3$ since so far reported studies has been based on diffraction measurements assuming the space group. In this study, crystal system of $BaBiO_3$ has been determined by using synchrotron x-ray diffraction. The obtained result has been confirmed by convergent-beam electron diffraction (CBED) [5].

Experimental

Ceramic $BaBiO_3$ specimen was prepared from the mixture of nominal amount of $BaCO_3$ and Bi_2O_3. The powdery mixture was calcined at 720 ^{o}C for 12 h in air and pressed into pellet followed by sintering at 800 ^{o}C for 16 h under O_2 atmosphere. X-ray diffraction measurement revealed that the sample was the single phase distorted-perovskite. Cation and oxide ion content were confirmed by inductively-coupled plasma emission analysis (ICP) and iodometry, respectively.

Synchrotron x-ray diffraction measurements were performed by using BL-4B2 beam line at Photon Factory, KEK. Wavelength of x-ray was measured to be 1.5384 Å from Si 422 peak. Diffraction signals in 2θ range of 75~77^{o} and 89.5~91.0^{o} were employed for determination of crystal system of $BaBiO_3$. CBED measurements on the same specimen were performed by using JEOL-JEM2010.

Results and discussion

If the often reported monoclinic symmetry of $BaBiO_3$ [4] with a=6.186 Å, b=6.140 Å, c=8.670 Å and β=90.17^{o} is applicable, two x-ray diffraction peaks indexed as 440 and 008 should be observed in 2θ range of 89.5~91.0^{o}. Fig. 1(a) shows x-ray diffraction peaks of $BaBiO_3$ observed in this work. Observed two peaks apparently suggested the monoclinic symmetry of $BaBiO_3$. However, full width at half maximum (FWHM) of the peak indexed by open circle was larger than those of the other peaks in 75~77^{o} and 89.5~91.0^{o} This suggested that the apparent single diffraction peak represented by open circle was composed of overlapping two peaks, indicating the triclinic symmetry in $BaBiO_3$.

Fig. 1(b) shows curve fitting result of diffraction peak represented by open circle in Fig. 1(a), assuming triclinic symmetry in $BaBiO_3$. It was indicated that the apparent broad single peak in Fig. 1(a) was composed of overlapping $\bar{4}40$ and 440 peaks of triclinic $BaBiO_3$. The lattice constants of $BaBiO_3$ calculated from the observed peaks were a=6.188 Å, b=6.139 Å, c=8.671 Å, α=89.99^{o}, β=90.14^{o} and γ=90.02^{o} , which were so close to monoclinic ones that the triclinic symmetry was not distinguished in the preceding studies.

Triclinic symmetry of $BaBiO_3$ was also supported by CBED. Neither CBED pattern which showed symmetry of 2 nor m was obtained, indicating that the crystal system was not monoclinic but triclinic[5].

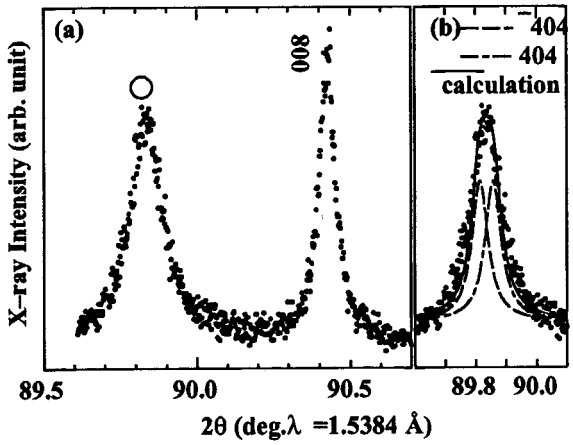

Fig. 1(a) X-ray diffraction peaks of $BaBiO_3$ obtained by using synchrotron light source. The FWHM of the peak represented by open circle is larger than that of the peak assigned to 008. (b) Curve fitting of the peak indexed by open circle in Fig. 1(a) assuming triclinic symmetry. Dashed curve: $\bar{4}40$ peak. Chain curve: 440 peak. Solid curve: calculation. Dot : observed data.

References

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