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Effects of Mn doping on the polarization and leakage current properties in $Bi_4Ti_3O_{12}$ single crystals

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Abstract

Single crystals of $Bi_4Ti_3O_{12}$ and $Bi_4Ti_{2.97}Mn_{0.03}O_{12-\delta}$ (Mn-BiT) were grown in air by a self-flux method, and the leakage current and polarization properties at 25 °C have been investigated along the *a* axis direction. The substitution of Mn at the Ti site is shown to be effective for suppressing leakage current. Mn-BiT crystals exhibits a leakage current density ($\sim 10^{-8}$ A/cm^2) by about two orders of magnitude lower than that of BiT crystals. Electron spin resonance measurements demonstrate that valence increase of Mn during the subsequent annealing in air plays an essential role in the low leakage current property. A superior polarization property (remanent polarization of 38 μC/cm^2 and coercive field of 25 kV/cm) was obtained for Mn-BiT crystals.

Keywords: Defects; X-ray methods; Perovskite; Ferroelectric properties

1. Introduction

Since ferroelectric bismuth titanate ($Bi_4Ti_3O_{12}$, BiT) has been demonstrated to show a high Curie temperature of 675 °C, a large spontaneous polarization and a large electrooptic coefficient,[1,2] BiT has attracted a great deal of attention for its potential applications to non-volatile memories, piezoelectric devices and uncooled infrared detectors.[3,4] However, leakage current arising from defects often interferes with polarization switching and poling process of the BiT-based materials,[5–8]. The control of polarization states is the underlying basis of these functional devices, and domain switching by applying an electric field can only be achieved with a high insulating property. Poor insulating property makes BiT unsuitable for these practical applications.

It is well recognized that defects strongly affect the ferroelectric-related properties such as leakage current and polarization switching.[9–16] Takahashi et al.[17] have revealed the conduction mechanism of BiT single crystals and polycrystalline ceramics at high temperatures. The electrical conductivity along the *a* axis is higher by several orders of magnitude than that along the *c* axis. Oxide-ion conduction originating from a large number of oxygen vacancies in the perovskite layers gives rise to the high electrical conduction along the *a* axis at around 700 °C. Recently, Noguchi et al.[10] have proposed the defect structure in BiT through the study by ab initio electronic structure calculations in addition to high-temperature neutron diffraction. The calculations show that the vacancy formation of Bi preferentially proceeds at the perovskite A site rather than in the Bi_2O_2 layers, yielding oxygen vacancies in the perovskite layers.

In this paper, we have shown that Mn doping is effective for reducing leakage current of BiT single crystals. BiT crystals indicated a relatively high leakage current density (*J*), while Mn-doped BiT crystals exhibited a *J* by about two orders of magnitude lower than that of undoped crystals.

2. Experiments

Powder samples of $Bi_4Ti_3O_{12}$ and $Bi_4Ti_{3-x}Mn_xO_{12-\delta}$ (Mn-BiT, $x = 0.1$) were prepared by a solid-state reaction. The raw materials of Bi_2O_3 (99.9999%), TiO_2 and MnO with 99.99% purity were mixed and sintered at 800 °C for several times. Powder X-ray diffraction (XRD) data were analyzed by the Rietveld method using the program RIETAN-2000[18] based on *B*2*cb* orthorhombic symmetry.

Single crystals of BiT and Mn-BiT were grown by a self-flux method. The crystals of BiT were obtained from the raw powders of Bi_2O_3 (99.9999%) and TiO_2 (99.99%).[10] Mn-doped powder prepared by a solid-state reaction was used

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for the crystal growth of Mn-BiT. The crystals were grown in air (oxygen partial pressure of 0.02 MPa) The mixed materials in Pt crucible were soaked at 1200 °C for 10 h, slowly cooled to 1000 °C for 40 h and then furnace cooled to room temperature. The crystals were annealed at 700 °C for 5 h in air. The composition of Mn-BiT crystals determined by inductively coupled plasma emission spectroscopy was $Bi_4Ti_{2.97}Mn_{0.03}O_{12-\delta}$. Leakage current and polarization properties were measured at a frequency of 1 Hz at 25 °C along the *a* axis (the major polar direction). X-band electron spin resonance (ESR) spectroscopy was employed to study the valence state of Mn in the crystals.

3. Results and discussion

Fig. 1 shows the fitting profile of the Rietveld analysis of the XRD data for Mn-BiT ($x = 0.1$) powder. The resultant *R*-weighted pattern (R_{wp}) was 17.03% and the goodness of fit ($S = 1.28$) was close to 1.0. A satisfactory profile fitting was obtained. The refined lattice parameters of Mn-BiT were $a = 0.5451(1)$ nm, $b = 0.5413(1)$ nm and $c = 3.2854(4)$ nm, which were smaller than those of BiT [$a = 0.5457(2)$ nm, $b = 0.5419(2)$ nm and $c = 3.2891(1)$ nm]. While the ionic radii of Mn^{3+} (low spin: 0.0605 nm) and Mn^{4+} (0.0530 nm) at the six-fold coordinated site are smaller than that of Ti^{4+} (0.0605 nm), the radius of Mn^{2+} (high spin: 0.083 nm, low spin: 0.067 nm) is larger. The shrinkage of the lattice volume by Mn substitution and ionic-size consideration suggest that the majority of Mn ions for the powder at 25 °C (calcined at 800 °C in air) are substituted at the Ti^{4+} site as Mn^{3+} with the low-spin configuration, as expressed by,

$$Mn_2O_3 \xrightarrow{2TiO_2} 2Mn'_{Ti} + 3O_O^* + V_O^{\bullet\bullet}, \qquad (1)$$

where Mn'_{Ti} denotes Mn^{3+} at the Ti^{4+} site, O_O^* is oxide ion at the O^{2-} site and $V_O^{\bullet\bullet}$ indicates oxygen vacancy.

Fig. 2 shows the leakage current density (*J*) along the *a* axis of BiT and Mn-doped crystals at 25 °C. The data of BiT crystals[10] are plotted for comparison. BiT crystals exhibited a relatively high *J* of the order of $\sim 10^{-6}$ A/cm^2. Note that Mn doping led to a marked decrease in *J* to $\sim 10^{-8}$ A/cm^2. Mn-BiT crystals showed a *J* by about two orders of magnitude lower than BiT crystals.

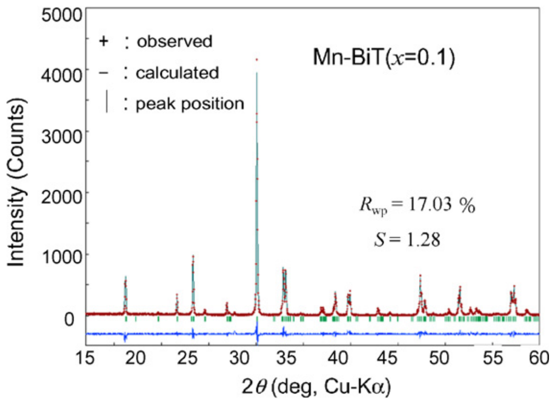

Fig. 1. Fitting profile of the Rietveld analysis of the XRD data for Mn-BiT ($x = 0.1$) powder.

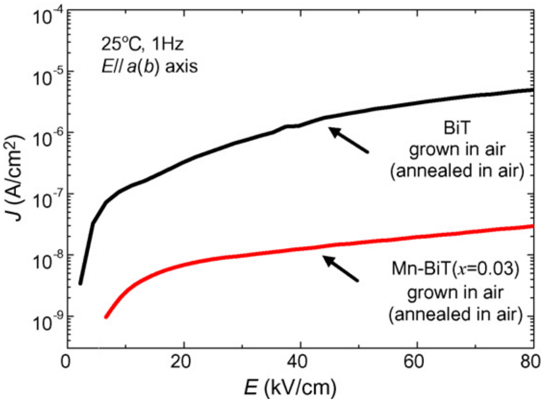

Fig. 2. Leakage current density along the *a* axis of the crystals annealed in air at 700 °C for 5 h. The data of BiT crystals (Ref. [10]) are plotted for comparison.

Noguchi et al. have proposed the defect formation mechanism in BiT at high temperatures that the vacancy formation of Bi (V_{Bi}''') at the perovskite A site is the trigger for generating oxygen vacancy ($V_O^{\bullet\bullet}$) near V_{Bi}'''.[10] It has been reported that the electrical conduction along the *a* axis at 700 °C is governed by oxide-ion conduction through $V_O^{\bullet\bullet}$.[17] The vacancy formation in the perovskite layers of BiT is expressed as

$$2Bi_{Bi}^* + 3O_O^* \rightarrow 2V_{Bi}''' + 3V_O^{\bullet\bullet} + Bi_2O_3\,(\text{gas}), \qquad (2)$$

and electronic defects play a minor role for charge compensation at high temperatures. During cooling, the influence of oxide-ion conduction is suppressed, while the electrical conduction arising from electron hole ($h^\bullet$) becomes dominant.[17] In the cooling process to room temperature, the crystals absorb oxygen, and the oxide ion occupies $V_O^{\bullet\bullet}$ with the formation of $h^\bullet$ according to the reaction

$$\frac{1}{2}O_2 + V_O^{\bullet\bullet} \rightarrow O_O^* + 2h^\bullet \qquad (3)$$

The higher *J* caused by high-pressure O_2 annealing is direct evidence that $h^\bullet$ conduction plays a detrimental role in leakage current at room temperature in the BiT system.[10]

In order to investigate the effects of Mn doping, the valence state of Mn was analyzed by ESR study for crushed powders of Mn-BiT crystals. Fig. 3 shows the X-band ESR spectra observed at −170 °C. The crystals annealed in air (Fig. 3(a)) exhibited a broad signal at around 300 mT, while the crystals quenched from 900 °C to room temperature (Fig. 3(b)) showed the hyperfine structure probably originating from typical isolated Mn^{2+}.[19] The structural analysis of the powder annealed in air by the Rietveld method has indicated that the majority of Mn ions occupies the Ti^{4+} site with Mn^{3+}. Our ESR study on the crystals annealed in air did not provide the hyperfine structure ascribed to Mn^{2+} or Mn^{4+} (Mn^{3+} is silent in X-band ESR measurements). These results demonstrate that Mn in the BiT powder annealed in air is present as Mn^{3+}. For the quenched crystals, apparent hyperfine structure was observed at around 300 mT. It is reasonable to consider that the ESR signals of the quenched crystals are attributed to Mn^{2+}. The presence of Mn^{2+} at the perovskite B site has been observed also for $PbTiO_3$[20] and $KNbO_3$.[21] When

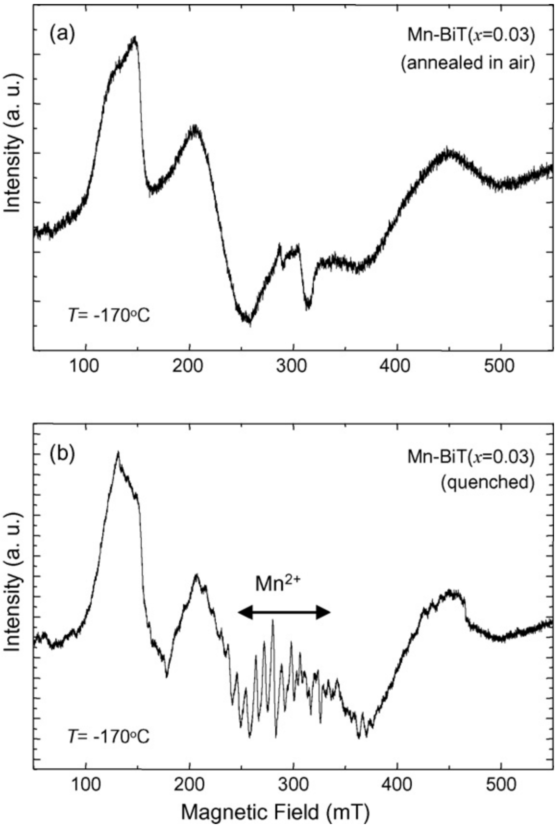

Fig. 3. X-band ESR spectra of the crushed powder of Mn-BiT ($x = 0.03$) crystals observed at −170 °C: (a) the crystals annealed in air and (b) the crystals quenched from 900 °C to room temperature. The measurements were performed for crushed powder of the crystals.

Mn-BiT is maintained at 900 °C in air, the crystals are likely to be in a relatively reduced state. During cooling, the crystals absorb oxygen into lattice and then the average valence of Mn increases due to oxidation. In contrast, for the crystals quenched from 900 °C, the oxygen content at 900 °C in air is frozen and the partially reduced state at high temperatures is maintained at room temperature for the quenched crystals. Namely, the oxygen content of the quenched crystals is lower than that of the air-annealed ones. ESR investigations indicate that Mn^{2+} occupies the B site at high temperatures above 900 °C, and that Mn^{2+} is oxidized during cooling in air due to the absorption of oxygen from the ambient into the lattice.

Here, we discuss the role of Mn on the leakage current properties of BiT crystals. When BiT crystals are slowly cooled to room temperature in air, the crystals are gradually oxidized and a concentration of $V_O^{\bullet\bullet}$ decreases. This oxidation reaction leads to the formation of $h^\bullet$ according to Eq. (3). It has been demonstrated that $h^\bullet$ acts as a detrimental carrier for room temperature leakage current for the crystals of BiT and La-substituted BiT.[11] During the oxidation process of Mn-BiT, Mn^{2+} at the Ti^{4+} site can absorb $h^\bullet$ by the valence increase of Mn, as expressed by

$$\mathrm{Mn}''_{\mathrm{Ti}} + h^\bullet \rightarrow \mathrm{Mn}'_{\mathrm{Ti}} \quad (\mathrm{Mn}^{2+}\ \text{to}\ \mathrm{Mn}^{3+}), \tag{4}$$

where $\mathrm{Mn}''_{\mathrm{Ti}}$ indicates Mn^{2+} at the Ti^{4+} site. This reaction indicates that Mn acts as a buffering species for suppressing $h^\bullet$ generation by oxidation during cooling in air. The oxidation in the annealing process forces BiT crystals to accommodate $h^\bullet$, resulting in a higher J. For Mn-BiT crystals, a low J is achieved even though the oxidation occurs during cooling. The $h^\bullet$-absorbing function originating from the valence increase of Mn is a possible origin of the lower J observed for Mn-BiT crystals.

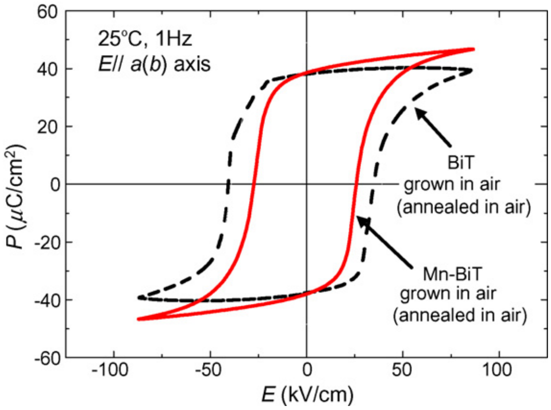

Fig. 4. Polarization hysteresis loops along the a axis of the crystals a annealed in air at 700 °C for 5 h. The data of BiT crystals (Ref. [10]) are plotted for comparison.

Fig. 4 shows the polarization hysteresis loops measured at 25 °C for the crystals annealed at 700 °C in air. The rectangularity of the hysteresis was improved by Mn doping. BiT crystals had a remanent polarization (P_r) of 37 μC/cm^2 and a coercive field (E_c) of 35–40 kV/cm. Mn-BiT crystals showed a larger P_r of 38 μC/cm^2. It is interesting to note that Mn-BiT exhibited a low E_c of 25 kV/cm compared with BiT. The doping of Mn induces $V_O^{\bullet\bullet}$ at high temperatures, as expressed by Eq. (1), and the following oxidation process (annealing in air) decreases $V_O^{\bullet\bullet}$ accompanied by an increase in average Mn valence (see Eq. (4)). The lower E_c observed for Mn-BiT crystals suggests that Mn doping does not deteriorate polarization switching properties.

4. Conclusions

The effects of Mn substitution on the leakage current and polarization properties of BiT crystals at 25 °C were investigated through Rietveld structural analysis and ESR study. The substitution of Mn is demonstrated to be effective for suppressing leakage current. ESR investigations show that the valence increase of Mn absorbs electron-hole (carrier) caused by oxidation during cooling in air, leading to the low leakage current for Mn-BiT crystals. It is concluded that Mn doping improves polarization-switching properties (lower E_c) as well as insulating property of BiT crystals.

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