We investigated the photocurrent characteristics for ferroelectric single crystals of non-doped barium titanate (BT) and Mn-doped barium titanate (Mn-BT). The introduction of 90° domain structures into the BT crystals markedly raised the photocurrent, which suggests that the separation of photoinduced carriers is significantly enhanced around 90° domain walls (DWs). The Mn doping led to a drastic increase in the photocurrent, with photon energy less than the band gap. Density functional theory calculations show that the large photocurrent observed for the Mn-BT crystals originates from the electron excitation from the O-2p valence band to the Mn-ε defect level followed by the carrier (hole) injection.

Key words: barium titanate, ferroelectric, single crystals, bulk photovoltaic effect, domain structure, impurity

1. INTRODUCTION

Barium titanate (BaTiO₃) has drawn renewed attention as a representative ferroelectric and piezoelectric material, and has been intensively studied from both experimental [1-8] and theoretical [9-15] points of view. There exist lots of works on the control of its polarization and piezoelectric properties by the doping of acceptor-type impurities such as aluminum (Al), iron (Fe), or manganese (Mn), etc. [16-24] Mn-doped barium titanate has especially attracted research interests because of (1) the multivalent character of Mn ions (Mn⁴⁺, Mn³⁺ and Mn²⁺) at the Ti⁴⁺ site and (2) the impurity levels located at deep positions above the top of the valence band.

Historically speaking, bulk photovoltaic effects which arises from the non-centrosymmetric nature of ferroelectric crystals were first discovered in barium titanate, [25-28] and were subsequently studied in various ferroelectric materials such as lithium niobate (LiNbO₃) [29,30], lead zirconate titanate (Pb(Zr,Ti)O₃) [31,32], bismuth ferrate (BiFeO₃) [33,34] and so forth. These studies were conducted with the aim mainly of the applications for non-linear optics using photorefractive effects and two-wave mixing. These phenomena are closely related with the bulk photovoltaic effect originating from photogenerated carriers. In this context, the doping effect, which is expected to simultaneously cause an increase in optical absorbance and the trap or generation of carriers, has also been studied [35,36].

Recently, a large photovoltage resulting from ferroelastic domain walls has been reported in bismuth ferrate thin films [37], which has ignited considerable research interests in investigating a novel working principle of solar batteries using ferroelectric and piezoelectric materials.

In this study, we investigated the photocurrent characteristics in the single crystals of barium titanate (BT) and Mn-doped barium titanate (Mn-BT). It is reported that the irradiation of photons with a lower energy than the band gap (E_g) generates a large photocurrent for Mn-doped BT crystals compared with BT ones.

2. EXPERIMENTAL DETAILS

Samples for photocurrent measurements were prepared from commercial non-doped BT single crystals (Neutron Co. Ltd.) and from Mn-doped BT single crystals [Mn(0.03%) and Mn(0.25%)] grown by a top-seeded solution growth (TSSG) method. After annealing in air at 1200°C for 24 h, Au electrodes were fabricated on the opposite two lateral sides (the [110] surfaces of the crystals) by sputtering. The top side of each samples (the [1 1 0] surface for the BT and Mn(0.03%)-BT crystals, the [0 0 1] surface for the Mn(0.25%)-BT crystals) was polished for optical contact with sample surfaces. A typical modulation image detailed domain structures using a reduced spring constant of 2 N/m and a free-resonance frequency of ~70 kHz were used as a scanning probe. In order to observe the fine domain structures, Ir-coated Si cantilevers with a spring constant of 2 N/m and a free-resonance frequency of ~1.0 MHz for
the in-plane vibration mode.

For the measurements of photocurrent characteristics, infrared and visible light beams with an intensity of ~14 mW/cm² from a halogen lamp in a wavelength of 350-1000 nm range and in an energy 1.2-3.5 eV range were irradiated to the crystal surfaces. Photocurrents normal to the incident light were measured along the \( (100) \) or \( (110) \) direction. A chopper frequency for the lock-in detection of the photocurrents was changed in the range of 20-270 Hz. We confirmed that a pyroelectric current caused by the photothermal effect was at one order of magnitude lower than the photocurrents. Optical filters were used to obtain the light with \( h\nu > 2 \text{ eV} \) or \( h\nu < 2 \text{ eV} \), where \( h\nu \) is the photon energy. The intensity ratio of the light of \( (h\nu > 2 \text{ eV}) \) to that of \( (h\nu = 2 \text{ eV}) \) was approximately 5:9:5. The polarization was fixed parallel to the poling direction (the \( (110) \) direction of the crystals) by a polarizer through the photocurrent measurements.

3. COMPUTATIONAL PROCEDURE

Density functional theory (DFT) calculations via the local density approximation (LDA) [39] with a plane wave basis set were performed to investigate the electronic states of Mn-doped BT with the supercell approach. The projector-augmented wave (PAW) method [40] was applied by the Vienna \textit{ab-initio} simulation package (VASP) [41]. First, \( \text{BaTiO}_3 \) (BT) with \( P4mm \) symmetry was structurally optimized until the Hellmann–Feynman force on each atom was smaller than 0.1 eV/nm. The Hellmann–Feynman force on each atom was smaller than 0.1 eV/nm. The parameter configuration, although the position of Mn is not exactly fixed parallel to the poling direction, was adjusted to the crystal structure: (a) vertical phase, and (b) in-plane phase.

Next, the supercell of \( 2 \times 2 \times 3 \) (\( \text{Ba}_2\text{Ti}_3\text{MnO}_{16} \)) using the optimized BT unit cell was constructed. One Ti atom in this supercell was replaced by one Mn atom in order to obtain the Mn-BT supercell (\( \text{Ba}_2\text{Ti}_3\text{MnO}_{16} \)).

4. RESULTS AND DISCUSSION

Density functional theory (DFT) calculations via the local density approximation (LDA) [39] with a plane wave basis set were performed to investigate the electronic states of Mn-doped BT with the supercell approach. The projector-augmented wave (PAW) method [40] was applied by the Vienna \textit{ab-initio} simulation package (VASP) [41]. First, \( \text{BaTiO}_3 \) (BT) with \( P4mm \) symmetry was structurally optimized until the Hellmann–Feynman force on each atom was smaller than 0.1 eV/nm. The k-mesh of \( 5 \times 5 \times 5 \) centered at the \( \Gamma \) point was used for the geometry optimization (lattice parameters and fractional coordinates) of the BT unit cell. In all of our calculations, a plane-wave cutoff energy of 400 eV was adopted and electronic energy was converged to at least \( 1 \times 10^{-5} \text{ eV} \). The lattice parameters of the optimized BT cell was \( a = 0.3925 \text{ nm} \) and \( c = 0.3964 \text{ nm} \), which is smaller than the experimental data by ~2%. Although the use of the modified Perdew-Burke-Ernzerhof functional for bulk properties and surface energies (PBEsol) [42] leads to the lattice parameters in good agreement with the experiments, we applied LDA to the calculations of Mn-doped BT because of the better convergence for a correction for strongly correlated electrons.

Next, the supercell of \( 2 \times 2 \times 3 \) (\( \text{Ba}_2\text{Ti}_3\text{MnO}_{16} \)) using the optimized BT unit cell was constructed. One Ti atom in this supercell was replaced by one Mn atom in order to obtain the Mn-BT supercell (\( \text{Ba}_2\text{Ti}_3\text{MnO}_{16} \)). The geometry optimization of the Mn-BT supercell, a simplified local spin density approximation LSDA+U approach [43] was adopted as a correction for localized and strongly correlated electrons within on-site Coulomb terms for \( U-J = 4 \text{ eV} \) both for Mn-3d and Ti-3d. The \( \kappa \) mesh for this structural optimization of the Mn-BT supercell was performed at the \( \Gamma \) point. The optimized structure is shown in Fig. 1. The lattice parameters obtained were \( a = 0.7875 \text{ nm} \) and \( c = 1.1947 \text{ nm} \). The parameter \( a \) was larger by about 0.2% than those of the original \( \text{Ba}_2\text{Ti}_3\text{O}_{16} \) supercell before structural optimization, while the difference in the parameter \( c \) was almost zero. The increase only in the parameter \( a \) indicates the decrease in tetragonal distortion \((c/a)\) by Mn doping, which is consistent with a lower Curie temperature for Mn-doped BT ceramics. [29] The total magnetic moment of the Mn-BT supercell was \( 3.000 \mu_B \) (\( \mu_B \): Bohr magnetons), which agrees well with the magnetic susceptibility measurements. [20] This DFT calculation shows that the electronic state of Mn-3d is described roughly as \( t_{2g}^{-1}e_g^{0} \) with the spin-up configuration, although the position of Mn is not exactly with the \( O_b \) symmetry at the center of the oxygen octahedral, as can be seen in Fig. 1.

Figures 2(a)-2(d) show the optical microscopy images of the BT and Mn-BT crystals poled along the \( (110) \) direction observed by polarization microscopy, together with (e)-(g) the schematic views of the electrode configurations with respect to their crystallographic orientations. The length, width, and thickness of all crystals were 1.0, 1.5, and 0.2 mm, respectively. The crystals with the poling treatment had a domain structure with 90° domains with an average size of 2–3 \( \mu \text{m} \), as shown in Figs. 2(b)–2(d). These crystals were characterized after approximately a day had passed from the poling treatment. For obtaining BT crystals with a single domain state, the BT crystal with the 90° domain structure was aged for approximately a month at room temperature, which led to almost the single domain state,
as shown in Fig. 2(a). Hereafter, these BT crystals are called single-domain BT crystals.

Figures 3(a) and 3(b) show the PFM phase images observed for the BT crystals with the 90° DWs [Fig. 2(b)], the schematic of which is depicted in Fig. 2(f). In Fig. 3(a) of the vertical phase image, the black and bright regions correspond to the 90° domains with the spontaneous polarization vectors (P_s) toward downward and upward directions, respectively. A striped 90° domain structure with an average width of 2-3 µm, in which the 90° DWs exist along the [1 1 0] direction, was clearly observed. It is interesting to note that the 90° DWs did not necessarily have facet faces and that complicated and curved 90° DWs were present.

Next, effects of the photon energy of the irradiated light on the photocurrent properties are discussed. Figure 4(a) also shows the J properties of the BT crystals with the 90° DWs under the irradiation of lights with different photon energy spectra. The light irradiation with the low-energy photons (hν < 2 eV) led to a J of 30 pA/cm², which is comparable to that in the case of the WL irradiation (36 pA/cm²). A J of 3 pA/cm² was observed with the light with hν > 2 eV, which was much smaller than that in the case of light with hν < 2 eV. As mentioned above, the intensity ratio of light with hν > 2 eV to that with hν < 2 eV was approximately 5.95. The J value is considered to be proportional to the light intensity in our experimental conditions with the total light intensity of ~14 mW/cm². The relatively large J observed by the irradiation of the photons with an energy smaller than the E_g of BT (3.2–3.4 eV) suggests that impurity state inside the band gap plays a crucial role in the excitation of electrons and dynamics of the resultant photogenerated carriers, as discussed later.

Figure 4(b) and 4(c) show the J properties of the Mn-BT crystals with the 90° DWs. It should be noted that the photocurrent properties were markedly enhanced by Mn doping. The J values increased with Mn concentration and exceeded 280 pA/cm² in the Mn(0.25%)-BT crystals with the WL irradiation. As a result of the comparison between the crystals with similar 90° DW sizes, the J value of 255 pA/cm² for the Mn(0.25%)-BT crystals was 8.5 times as large as that for the BT crystals by light irradiation with hν < 2 eV. It is suggested that the J properties obtained with hν < 2 eV for the Mn-BT crystals are dominated by electron excitation through the Mn-d states inside the band gap. In general, the photocurrent caused by the bulk photovoltaic effect (J_b) can be expressed as the following equation using the light intensity (I):

$$J_b = k_b \alpha I,$$

where α is the absorption coefficient and k_b is the Glass constant characterizing the photovoltaic activity of the given impurities in a non-centrosymmetric lattice and expressed with the unit of cm/V [29]. We first discuss the effects of the 90° DWs in the BT crystals. Because α is not significantly affected by the presence of the 90° DWs, the increased J by introducing the 90° DWs is attributed to the increase in k_b under the light irradiation with the same J.

Figure 5 shows the relation between J and α. For a semiquantitative discussion using Eq. (1), we use the values of α measured at 2.0, 2.5, and 1.8 eV as representatives for the J values observed by light irradiations with the WL, hν > 2 eV, and hν < 2 eV spectra, respectively, in the plot of Fig. 5. As exhibited in Fig. 5(a) for the relationship with the WL irradiation, the Mn(0.25%)-BT crystals showed a drastically large J density (J) of ~36 pA/cm² [see Fig. 4(a)], while single-domain BT crystals exhibited a photocurrent density (J) of ~13 pA/cm². That is, the photocurrent was increased by the factor of 2.8 when the 90° DWs were introduced. Photovoltaic properties enhanced by introducing ferroelastic DWs have been qualitatively established in bismuth ferrate (BiFeO3) films [37].
compared with the value extrapolated from the data point for the BT and Mn(0.03\%)\textendash BT crystals, as is expected from Eq. (1). This large $J$ was apparently increased by $h\nu>2$ eV irradiation [Fig. 5(c)], although $J$ maintained a small value with $h\nu>2$ eV irradiation [Fig. 5(b)]. The large $J$ observed for the Mn(0.25\%)\textendash BT crystals by $h\nu<2$ eV irradiation cannot be explained only by the increase in $\alpha$ by Mn doping. These results suggest that Mn doping leads to two effects on the photocurrent properties in the visible light region: one is the increase in $\alpha$ and the other is the increase in $k_c$.

Figure 6 schematically shows the defect states in the electronic band structure for BT and Mn-BT. Although $E_g$ in BT has been reported to be 3.2\textendash 3.4 eV, the BT crystals exhibited a significant optical absorption in the visible light region, which suggests the presence of defect states inside the band gap due to unintentional impurity acceptors such as Cu and Fe, with an effective acceptor concentration of $\sim$100 ppm [44]. The defect chemistry established on the basis of electric transport data (electric conductivities and Seebeck coefficient measurements) [45] suggests that the average defect levels originating from acceptors (A) dominant for the transport properties are present at $\sim 0.5$ eV above the valence band maximum (VBM), as depicted in Fig. 6, as the $\text{A}^0$/\text{A}^+ states. In addition, the majority carrier and its conduction mechanism have respectively been reported to be holes ($h^+$) and the $p$-type conduction for BT ceramics annealed or sintered at a relatively high oxygen partial pressure ($P_{O_2}$), e.g., in air, at 600\textendash 1200 °C [26]. The thermally activated electron excitation from the VBM to the $\text{A}^0$/\text{A}^+ states results in $h^+$ at the VBM and then the concentration of $h^+$ ($p$) is determined by temperature and $P_{O_2}$. The $\text{A}^0$/\text{A}^+ states at the lowest energy above the VBM dominate the overall transport properties, while the deep defect states at a higher level in energy with respect to the VBM are inactive for the transport properties but active for the optical properties. The measurable $\alpha$ in the 1-3 eV range observed for the BT crystals implies that not only the $\text{A}^0$/\text{A}^+ states but also the deep defect states play an important role in their photocurrent properties.

Mn doping led to a marked increase in $\alpha$ in the low energy range of 2-3 eV, and the Mn(0.25\%)\textendash BT crystals exhibited a high $\alpha$ of 20-260 cm$^{-1}$. These experimental results suggest that the optical absorption originates from an interband electron excitation, i.e., the electron excitation from the VBM to empty Mn-$3d$ states inside the band gap. As shown in Fig. 6, there has been a report on two Mn-$d$ related defect states, namely, the Mn$^9$/Mn$^{10}$ state at 1.8 eV and the Mn$^{11}$/Mn$^{10}$ state at 1.2 eV with respect to the VBM [20]. These defect levels were determined by the analysis of the oxidation states for Mn-BT ceramics on the basis of the defect chemistry. $\Delta H_{h1}$ and $\Delta H_{h2}$ represent the first and second $h^+$-generation enthalpies, respectively, expressed by

$$\text{Mn}^{9+}\leftrightarrow\text{Mn}^{10+} + h^+ ; \quad \Delta H_{h1} = 1.8 \text{ eV} \quad (2a)$$

$$\text{Mn}^{10+}\leftrightarrow\text{Mn}^{11+} + h^+ ; \quad \Delta H_{h2} = 1.2 \text{ eV} \quad (2b)$$

where the Krö ger-Vin c notation is used for showing the above $h^+$-generation reactions. The valence states of Mn at the Ti$^{4+}$ site are described as follows: $\text{Mn}^{11+}$ for $\text{Mn}^{9+}$, $\text{Mn}^{10+}$ for $\text{Mn}^{11+}$, and $\text{Mn}^{11+}$ for $\text{Mn}^{10+}$. The values of $\Delta H_{h1}$ and $\Delta H_{h2}$ were determined by the experiments at high temperatures (600\textendash 1200 °C). Although $\Delta H_{h1}$ and $\Delta H_{h2}$ near room temperature should be corrected because of the changes in lattice size and its symmetry, the exact values have not been reported as far as we know. However, the reactions expressed by Eq. (2) still occur without any change in $h^+$-generation mechanism, and thus the values of $\Delta H_{h1}$ and $\Delta H_{h2}$ are described in Fig. 6 for understanding the optical absorption and the resultant $h^+$ generation reaction by the electron excitation from the VBM to the Mn-$d$ defect states.

Here, we discuss the electronic states of the Mn-BT crystals obtained by the DFT calculations. It is interesting to note that the off-center displacement from the center of the $O_{16}$ octahedra is found not only for Ti but also for Mn along the $c$-axis, as can be seen in Fig. 1. The off-center displacements of all of Ti atoms were almost the same therefore, the bond distance of Ti1 with the surrounding O atoms is indicated as a representative. Although the off-center character of Mn is a relatively small compared with that of Ti, a significant displacement is observed for Mn: the bond distance of Mn--O1 is 0.1775 nm, which is much smaller than that of Mn--O2 of 0.2204 nm. This bonding character of Mn with O1 and O2 is considered to be crucial for the increase in $k_c$ of the Mn-BT system.

Figure 7 shows the density of states (DOS) calculated for the Mn-BT supercell: (a) total and (b)-(f) partial DOS (PDOS) values of the constituent atoms. The DOS values of the majority spin and the minority spin are plotted in the upper and lower parts, respectively. In this
Note also that the majority Mn-e\(_g\) band is strongly hybridized with the 2\(p\) states of the nearest-neighbor oxygen (O1), which is evident from the presence of the PDOS of the O1-2\(p\) at 2.7 eV. Figure 8(b) illustrates the main feature of the PDOS shown in Fig. 7, where the orbital interaction between the Mn-3\(d\) and O1-2\(p\) is schematically depicted. The Mn-e\(_g\) character remains below the CBM, while the O1-2\(p\) character is the major part of the VBM. The orbital interaction between the Mn-e\(_g\) and the O1-2\(p\) leads to the \(\sigma\)-type bonding orbital with a lower energy than the original O1-2\(p\) states and to the \(\sigma^*\)-type anti-bonding orbital with a higher energy than the original Mn-e\(_g\) states. This hybridization of the Mn-e\(_g\) and O1-2\(p\) constitutes a critical factor affecting the Mn-e\(_g\) defect level from VBM. It is likely that the control of the defect level and its PDOS inside the band gap is a key strategy for enhancing the increase in Glass constant \(k_0\) of the BT system.

Fig. 8 Schematic images of the (a) PDOS of the constituents and (b) the orbital interaction between the Mn-3\(d\) and O1-2\(p\).

5. CONCLUSION

We have investigated the photocurrent characteristics of the BT and Mn-BT single crystals by the WL, \(h\nu>2\) eV, and \(h\nu<2\) eV light irradiations. The photocurrent of BT was increased by the introduction of 90° DWs. The photocurrent was drastically increased by Mn doping, especially under the \(h\nu<2\) eV light irradiation, which cannot be explained by the absorption coefficient of the visible light. DFT calculations show that the substantial photocurrents of the Mn-BT crystals induced by the irradiation of photons with energies less than the band gap originate from the photogenerated carriers from the VBM to the Mn-e\(_g\) defect state.

6. ACKNOWLEDGEMENT

This research is partly granted by JSPS through the Funding Program for Next Generation World-Leading Researchers (NEXT Program), initiated by the Council for Science and Technology Policy (CSTP).

7. REFERENCES

Conventional SIMS requires high vacuum conditions, which is higher than the water vapor pressure at room temperature. In addition, soft ionization techniques such as secondary ion mass spectrometry (SIMS) are commonly used to analyze volatile substances. For example, the technique of secondary ion mass spectrometry (SIMS) using an ion beam with MeV-energy Heavy Ion Beam can be obtained easily by using high-energy ions. The imaging mass spectrometry (IMS) technique for secondary ion mass spectrometry (SIMS) using an ion beam with MeV-energy Heavy Ion Beam is expected to obtain mass images of intact biological tissues. Accurate analysis of intact biological samples can be obtained by using high-energy ion beams. MeV-SIMS, is expected to obtain mass images of intact biological tissue. The results clearly allowed obtaining constant secondary ion intensity from volatile samples. The technique of secondary ion mass spectrometry (SIMS) using a high-energy ion beam is expected to affect the secondary ion yields. In this study, the vacuum in the target chamber was adjusted by He gas flow. Secondary ions were analyzed using an orthogonal acceleration (oa) time-of-flight mass spectrometer, AccuTOF, JEOL, Japan. Under low vacuum conditions with the aim of investigating the effects of evaporation of volatile samples on SIMS spectra, we obtained the mass spectra of higher alcohols and acids, and low vacuum conditions are essential for their application to IMS of biomolecules up to 100 kDa. On the other hand, IMS of ‘wet’ samples is crucial for visualizing the spatial distribution within a cellular state. In addition, under low vacuum conditions, IMS of ‘wet’ samples could not be detected. IMS of ‘wet’ samples using MeV-SIMS [8], although volatile substances could not be detected. IMS of ‘wet’ samples using MeV-SIMS [8], although volatile substances could not be detected. IMS of ‘wet’ samples using MeV-SIMS [8], although volatile substances could not be detected. IMS of ‘wet’ samples using MeV-SIMS [8], although volatile substances could not be detected. IMS of ‘wet’ samples using MeV-SIMS [8], although volatile substances could not be detected. IMS of ‘wet’ samples using MeV-SIMS [8], although volatile substances could not be detected.

References