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Local structure investigation and properties of Mn-doped $BiFeO_3$–$BaTiO_3$ ceramics

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Abstract

$Bi_{0.75}Ba_{0.25}(Fe,Ti)_{1-x}Mn_xO_3$ with $x=0$, 3 and 5 mol% Mn ceramics were prepared by a solid state reaction method. The relationships between site substitution of Mn in Mn-doped 0.75BF–0.25BT ceramics, phase formation and their properties were investigated. The addition of Mn was shown to improve densification, electrical and magnetic properties, especially ME coefficient. The Synchrotron X-Ray Absorption Near Edge Structure (XANES) spectra showed that Mn substituted for Fe/Ti atom and did not affect the oxidation state of Ti and Bi. However, a significant change of oxidation state was observed in Fe, Mn and Ba atoms.

Keywords: B. Spectroscopy; B. X-ray methods; C. Dielectric properties; C. Ferroelectric properties

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1. Introduction

Multiferroic materials exhibit ferroelectric and magnetic properties simultaneously [1]. One of the multiferroic materials, $BiFeO_3$–$BaTiO_3$ (BF–BT), has been widely studied on phase formation, electrical and magnetic properties, as well as magnetoelectric effect and related ferroic properties [2,3]. Previous work reported by Leontsev and Eitel [4] found that Mn doped 0.75BF–0.25BT showed the highest value of dielectric and ferroelectric properties and expected that high performance lead-free 0.75BF–0.25BT ferroelectric could be obtained with processing improvement and composition modification. In addition, Itoh et al. [3] showed that the very weak ferromagnetism of BF–BT (observed from *M–H* hysteresis loop) could be improved by doping with Mn, and that Mn-doped BF–BT exhibited reasonable ferroelectric characteristics [3]. Therefore, the influence of Mn addition in BF–BT has since been widely studied and the possible causes of the improvement can be investigated through the determination of the local structure and oxidation states to confirm the substituting site of Mn in BF–BT structure.

In this work, Synchrotron X-ray absorption spectroscopy (SXAS) was employed to investigate local structure of absorber atoms which is useful for the study of the relationships among site substitution of Mn in Mn-doped 0.75BF–0.25BT ceramics, phase formation and relevant properties.

2. Experimental procedure

The $Bi_{0.75}Ba_{0.25}(Fe,Ti)_{1-x}Mn_xO_3$ ceramics with $x=0$, 3 and 5 mol% Mn were prepared by a solid-state reaction method via vibro-milling mixing technique. All mixtures were calcined at 900 °C for 5 h and sintered at 1025 °C for 2 h. The influence

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of Mn addition in a BF–BT system was investigated to examine phase formation, local structure, microstructure, electrical, magnetic and magnetoelectric (ME) properties. Phase formation was studied by X-ray Diffraction (XRD) technique. The X-ray Absorption Spectroscopy (XAS) measurement at Beamline 8, Synchrotron Light Research Institute (Public Organization), Thailand, was carried out to study the local structure around absorber atoms in undoped and Mn-doped ceramics. This investigation was done by using 13-element Ge detector for Fluorescence (FL) Mode. The spectra were obtained in X-Ray Absorption Near Edge Structure (XANES) region. Microstructure of all ceramics was obtained by a scanning electron microscope (SEM: JOEL JSM-6400). Dielectric and ferroelectric measurements were carried out by a typical LCR meter, and a computer controlled modified Sawyer–Tower circuit, respectively. Magnetic behavior was obtained by a Vibrating Sample Magnetometer (VSM). Finally, magnetoelectric (ME) coefficient was measured by using a dynamic lock-in technique at a constant frequency 1 kHz and constant bias AC magnetic field of 5 Oe. In addition, the static ME coefficient was determined as a function of DC magnetic field (H_{dc}) up to 4.6 kOe at room temperature. ME coefficient was calculated by

$$\text{ME coefficient} = V(\text{volt})/\text{thickness(cm)} \times H_{dc}(\text{Oe}) \qquad (1)$$

3. Results and discussions

Room temperature XRD patterns of all ceramics over Bragg angles up to 60° are shown in Fig. 1. The results demonstrate the perovskite structure without traces of secondary phase and, that, in these selected compositions the added Mn was completely soluble in BF–BT. Distorted rhombohedral structure, similar to the observation in rhombohedral BF–BT as reported by Itoh et al. [3], can be seen in $x=0$ ceramic. The addition of Mn in 0.75BF–0.25BT plays a dominant role on structural symmetry of BF–BT. Structural distortion of BF–BT is lower (no peak splitting) with the addition of 3 mol% Mn. However, the distortion was again observed at 5 mol% Mn addition. This structural alteration will be later confirmed with changes in the relevant properties.

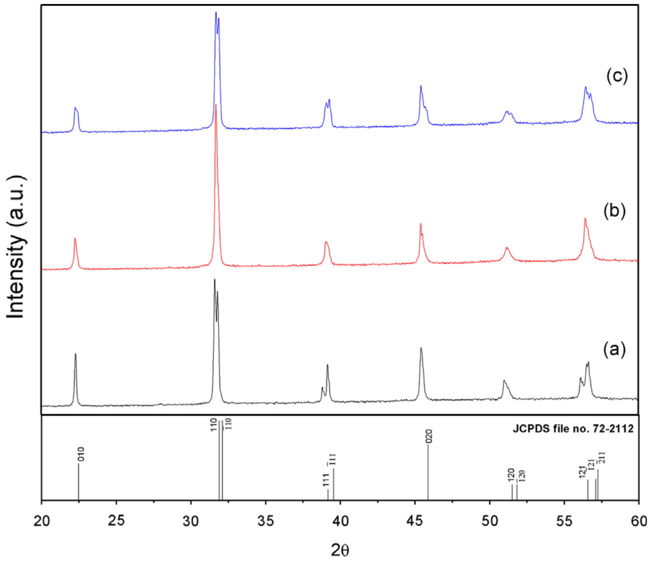

Fig. 1. XRD patterns of $Bi_{0.75}Ba_{0.25}(Fe,Ti)_{1-x}Mn_xO_3$ ceramics: (a) $x=0$, (b) $x=3$ and (c) $x=5$ mol%.

The results on XANES spectra are shown in Fig. 2. The experimental spectra are shown at Fe, Ti and Mn K-edges, with comparison with standards (inset) Fe_2O_3, $BaTiO_3$ and Mn_2O_3 and MnO_2, respectively, and Bi M_5- and Bi L_3-edges without standard comparison. XANES spectra are sensitive to local symmetry, oxidation state and electronic structure of the absorbing atom and XANES structure is used as a fingerprint of the local environment of an atom [5,6]. As shown in Fig. 2(a), XANES spectra of Mn-doped ceramics measured at Mn K-edge show very similar features to those of B-site absorber atoms (Ti and Fe K-edges) of undoped and Mn-doped ceramics, an indication of Mn substitution for Ti and Fe B-site atoms in a perovskite BF–BT system. More interestingly, the pre-edge peak A, which is sensitive to oxidation state of standards and ceramic samples (Fig. 2(a)) [7,8], measured at Fe and Mn K-edges was fitted perfectly using Gaussian function after background subtraction as shown in Fig. 2(b). The fitting results are listed in Table 1.

Three components of Fe_2O_3 pre-edge fitting were studied previously by Pinakidou et al. [7], in which it was reported that the last peak (A3) appeared at higher energy than 7115.0 eV which is attributed to $1s \rightarrow 3d$ dipole allowed transitions of Fe^{3+} in octahedral complexes due to the clustering of Fe. Peak positions A1 of undoped and doped ceramics shift toward lower energy than Fe_2O_3, indicating the presence of both Fe^{2+} and Fe^{3+} ions in BF–BT ceramics [7]. The highest average Fe valence was observed in undoped ceramic while lower average Fe valences were observed in 3 mol% and 5 mol% doped ceramics.

On the other hand, two components (A1 and A2) of Mn pre-edge fitting are shown in Fig. 2(c) and reveal that oxidation states of Mn in Mn-doped ceramics are Mn^{2+} and Mn^{3+} as decided by the energy position of A1 [5]. In addition, the highest average Mn valence was observed in $x=3$ ceramic.

As seen in Fig. 2(a), the addition of MnO_2 into a 0.75BF–0.25BT system does not affect oxidation state of Ti and Bi in 0.75BF–0.25BT. However, it affects Ba oxidation state significantly. As seen in Fig. 2(a), Ba L_3-edge XANES spectra of Mn-doped ceramics shift toward lower energy (about 0.2 and 0.5 eV) than that of the undoped. This behavior is possibly caused by a defect of chemistry and vacancy formation when Mn^{2+} and Mn^{3+} substitute for Fe and Mn^{3+} substitutes for Ti [8].

The microstructures of all ceramics are shown in Fig. 3. Undoped ceramics exhibit high residual porosity while Mn-doped ceramics show high density with undetectable porosity. Furthermore, inhomogeneous grain size can be observed in all ceramics. The average grain size (calculated by mean linear intercept) of all ceramics is also listed in Fig. 3 and it is found that the grain size increases with the addition of Mn, but there is no change of grain size between $x=3$ and $x=5$ doped-ceramics. Hence, it can be noted that Mn addition can improve sintering ability and the density, and a small addition of Mn results in grain grown promotion.

Fig. 4 shows dielectric constant (ε_r) and dielectric loss ($\tan \delta$) of undoped and doped-ceramics. The undoped ceramic