



## Magnetic properties of $(1 - x)\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3 + x\text{MnTiO}_3$ materials



### ARTICLE INFO

#### Keywords:

MnTiO<sub>3</sub>  
Bi<sub>0.5</sub>Na<sub>0.5</sub>TiO<sub>3</sub>  
Ferromagnetism  
Lead-free ferroelectric  
Sol-gel

### ABSTRACT

MnTiO<sub>3</sub>-doped Bi<sub>0.5</sub>Na<sub>0.5</sub>TiO<sub>3</sub> materials were fabricated by sol-gel technique. According to X-ray diffraction and Raman scattering analyses, MnTiO<sub>3</sub> was suitable to be used as solid solution in Bi<sub>0.5</sub>Na<sub>0.5</sub>TiO<sub>3</sub> but resulted in distorted structure. The optical band gaps decreased from 3.06 eV for pure Bi<sub>0.5</sub>Na<sub>0.5</sub>TiO<sub>3</sub> to 1.69 eV for 9 mol% MnTiO<sub>3</sub> solid solution in Bi<sub>0.5</sub>Na<sub>0.5</sub>TiO<sub>3</sub>. The magnetic properties of Bi<sub>0.5</sub>Na<sub>0.5</sub>TiO<sub>3</sub> materials were tuned from ferromagnetism to combination of ferromagnetism and paramagnetic-like property with varying MnTiO<sub>3</sub> concentration. The reduction of the optical band gap and the tunable magnetic properties of Bi<sub>0.5</sub>Na<sub>0.5</sub>TiO<sub>3</sub> materials were due to the random distribution of Mn cation in the host lattice as a function of MnTiO<sub>3</sub> amounts. This work provides a new trend of selecting dopants to induce ferromagnetism in lead-free ferroelectric materials.

### 1. Introduction

Inducing new functions of materials to be applied to smart multifunctional electronic devices remains challenging [1]. Green lead-free ferroelectric materials, specifically Bi<sub>0.5</sub>Na<sub>0.5</sub>TiO<sub>3</sub>-based materials, have been developed and extensively investigated because of their satisfactory piezoelectric and ferroelectric properties comparable with those of toxic ferroelectric PbTiO<sub>3</sub>-based materials [2]. Bi<sub>0.5</sub>Na<sub>0.5</sub>TiO<sub>3</sub> materials, which were first reported by Smolenskii et al. exhibit a high Curie temperature of ~320 °C and strong ferroelectricity ( $P_r$ ) of ~38  $\mu\text{C}/\text{cm}^2$  [2,3]. Bi<sub>0.5</sub>Na<sub>0.5</sub>TiO<sub>3</sub> materials have optical band gap of 3.00–3.14 eV, depending on the type of method used for fabrication [4]. Pure Bi<sub>0.5</sub>Na<sub>0.5</sub>TiO<sub>3</sub> materials exhibit weak ferromagnetism at room temperature, and the magnetic signal strongly influences the diamagnetism of empty Ti<sup>4+</sup> as 3d<sup>0</sup> cell [5]. Weak ferromagnetism in Bi<sub>0.5</sub>Na<sub>0.5</sub>TiO<sub>3</sub> materials possibly originated from self-defects, such as Na or Ti, and the results are consistent with theoretical prediction [5–8]. However, pure Bi<sub>0.5</sub>Na<sub>0.5</sub>TiO<sub>3</sub> materials have low magnetization and thus cannot be applied to electronic devices. Therefore, enhancing the magnetization of materials is important to be successfully applied to electronic devices. Introduction of ferromagnetic properties for lead-free ferroelectric materials can be achieved in several methods: *i*) translating transition metals, such as Fe, Co, Mn, or Cr, as impurity [5,6,9,10]; *ii*) applying solid solution with various ferromagnetic materials, such as MgFeO<sub>3- $\delta$</sub>  or SrFeO<sub>3- $\delta$</sub>  [11,12]; *iii*) combining ferromagnetic materials with ferroelectric materials, such as MgFe<sub>2</sub>O<sub>4</sub> or CoFe<sub>2</sub>O<sub>4</sub>, as composites [13,14]; or *iv*) advancing the magnetic properties of multiferroic materials, such as BiFeO<sub>3</sub>, as solid solution or composite [15,16]. Therefore, the magnetic properties of Bi<sub>0.5</sub>Na<sub>0.5</sub>TiO<sub>3</sub> materials could be enhanced by the exchange interaction of transition metals randomly substituted at the Ti site as solid solution formed or controlled at the interface of ferromagnetic/ferroelectric composites.

No study has reported on the properties of ilmenite materials influencing Bi<sub>0.5</sub>Na<sub>0.5</sub>TiO<sub>3</sub> materials as solid solution. Ilmenite materials have a common formula of ATiO<sub>3</sub>, where A is the transition metal (A = Fe, Co, Ni, Mn). Ribeiro et al. predicted that ilmenite can be potentially applied to multiferroic materials, in which the

antiferromagnetic super-exchange coupling is favored via A–O–A bond and the polar component prolongs the A–O interaction, as predicted for ferroelectric materials [16]. However, the antiferromagnetic ordering in ATiO<sub>3</sub> is extremely low (lower than the room temperature); as such, this material cannot be applied to electronic devices operated at room temperature. Among ilmenite materials, MnTiO<sub>3</sub> has been investigated because it is theoretically predicted to have magnetic and ferroelectric properties [17,18]. MnTiO<sub>3</sub> materials undergo paramagnetic-to-antiferromagnetic transition around 64 K with a broad anomaly around 100 K, which originated from the setting of the 2D intra-layer antiferromagnetic interaction [19]. A powder neutron diffraction study of MnTiO<sub>3</sub> materials indicated that the spins are directed along the [1 1 1] direction and a magnetic structure with Mn<sup>2+</sup> spin antiparallel within each layer [20]. Maurya et al. provided direct evidence for the existence of Mn<sup>2+</sup> and Mn<sup>3+</sup> in MnTiO<sub>3</sub> [21]. Mn-doped Bi<sub>0.5</sub>Na<sub>0.5</sub>TiO<sub>3</sub> materials exhibit room-temperature ferromagnetism with magnetization around 8 memu/g at room temperature and under 6 kOe magnetic application [6]. Therefore, we expected that room-temperature ferromagnetism could be observed in MnTiO<sub>3</sub>-doped Bi<sub>0.5</sub>Na<sub>0.5</sub>TiO<sub>3</sub> materials during solid solution.

This work is the first to fabricate MnTiO<sub>3</sub>-doped Bi<sub>0.5</sub>Na<sub>0.5</sub>TiO<sub>3</sub> materials as solid solution by using sol-gel method. The reduction of the optical band gap and the induction of room-temperature ferromagnetism in Bi<sub>0.5</sub>Na<sub>0.5</sub>TiO<sub>3</sub> materials via MnTiO<sub>3</sub>-modified materials were due to the random distribution of Mn cation into the host lattice of Bi<sub>0.5</sub>Na<sub>0.5</sub>TiO<sub>3</sub>.

### 2. Experimental

$(1 - x)\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3 + x\text{MnTiO}_3$  samples were fabricated by sol-gel technique. Bi(NO<sub>3</sub>)<sub>3</sub>·5H<sub>2</sub>O, NaNO<sub>3</sub>, and Mn(NO<sub>3</sub>)<sub>2</sub> were dissolved in acetic acid and deionized H<sub>2</sub>O (20 ml of H<sub>2</sub>O:5 ml of CH<sub>3</sub>COOH). The solution was added dropwise with tetraisopropoxytitanium (IV, C<sub>12</sub>H<sub>28</sub>O<sub>4</sub>Ti) followed by acetylacetone. The solution was magnetically stirred for 3 h until it became transparent to prepare homogeneous gel. The gel was prepared by drying the solution at 100 °C. The gel was ground and sintered at 800 °C for 5 h. Sodium nitrate was weighed to

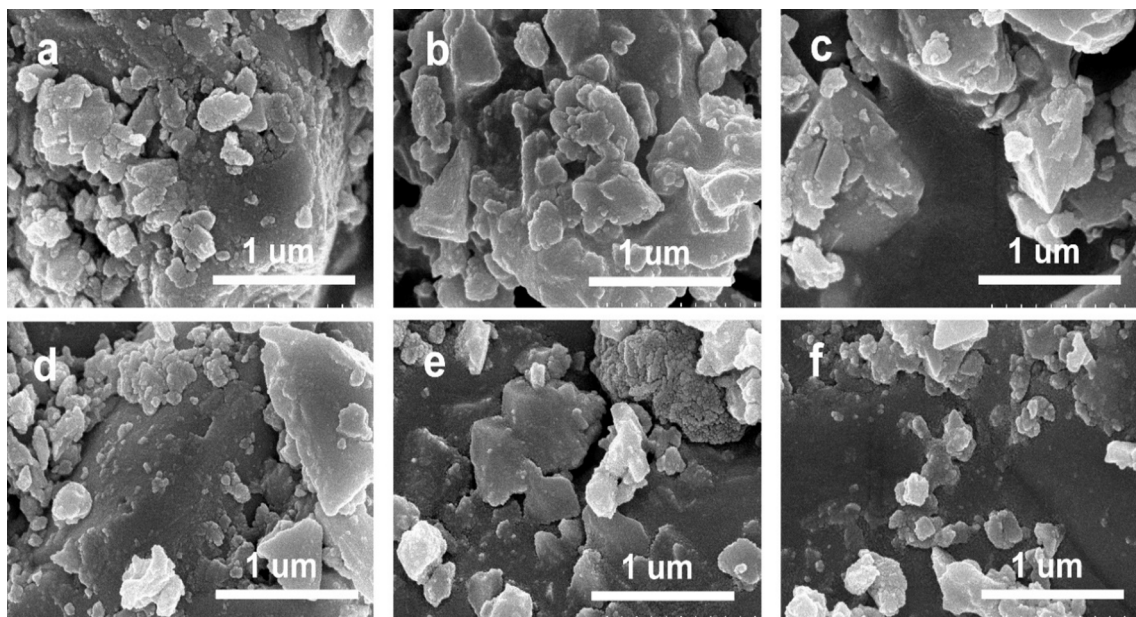


Fig. 1. The FE-SEM image of (a) pure  $\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3$  and  $\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3$  solid solution with different concentrations of  $\text{MnTiO}_3$ : b)  $x = 1$  mol%, c)  $x = 3$  mol%, d)  $x = 5$  mol%, e)  $x = 7$  mol%, and f)  $x = 9$  mol%.

exceed at around 50 mol% to prevent sodium loss during gelling and sintering [4–6]. The surface morphology was observed with field emission scanning electron microscope (FE-SEM). The crystalline structures of the samples were characterized through X-ray diffraction (XRD) analysis. The vibrational and rotational modes of the samples were determined by Raman spectroscopy. Optical properties were studied by UV-Vis spectroscopy. Magnetic properties were characterized by a vibrating-sample magnetometer (VSM) at room temperature.

### 3. Results and discussion

The FE-SEM images of  $\text{MnTiO}_3$ -modified  $\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3$  samples with different molar ratios are shown in Fig. 1(a)–(f). It can be seen that the different molar ratios of  $\text{MnTiO}_3$  show the same surface morphology in each case. The particles were aggregated to form block and the granular structures which were not seen clearly in all samples. It seems

that the particles were sintered more at a higher doped concentration.

Fig. 2(a) shows the XRD patterns of pure  $\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3$  and  $\text{MnTiO}_3$ -modified  $\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3$  materials with various amounts of  $\text{MnTiO}_3$ . The XRD spectra show that all samples exhibited a single perovskite structure with rhombohedral symmetry. This finding indicates that  $\text{MnTiO}_3$  could be used as solid solution in  $\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3$  materials.  $\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3$  has a rhombohedral crystal structure at room temperature, similar to the crystal structure of  $\text{MnTiO}_3$  materials [2,3,19]. Therefore, the solid solution of  $\text{MnTiO}_3$  into  $\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3$  materials could be possibly understood by considering the Hume-Rothery rules [22]. In addition, no impurity phase was observed from the XRD pattern. Furthermore, the role of the randomly distributed Mn cations in the crystal structure of  $\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3$  materials is shown in Fig. 2(b). The XRD patterns were magnified within the  $2\theta$  range of  $30^\circ$  to  $35^\circ$ . The  $(012)/(110)$  settle peak position shifted to high angle, resulting in compressed lattice parameter. The Mn ions have various

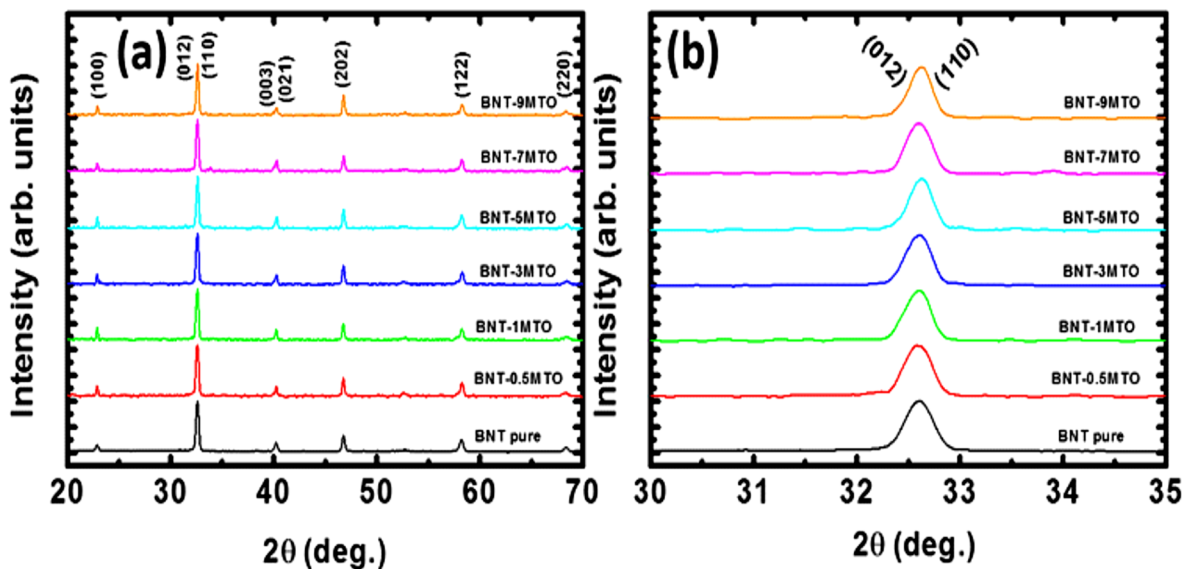


Fig. 2. (a) XRD pattern of pure and  $\text{MnTiO}_3$ -modified  $\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3$  at room temperature, and (b) magnification of the XRD pattern within the  $2\theta$  range of  $30^\circ$  to  $35^\circ$  for undoped and  $\text{MnTiO}_3$ -modified  $\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3$  materials.

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