FABRICATION AND PROPERTIES OF Co DOPED 
\( \text{Bi}_{0.5}\text{K}_{0.5}\text{TiO}_3 \) – \( \text{BiFeO}_3 \) SOLID SOLUTION

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ABSTRACT

In this study, we present some results on the structure and properties of the solid solution of 
\( \text{Bi}_{0.5}\text{K}_{0.5}\text{TiO}_3 \) – \( \text{BiFeCoO}_3 \) (BKT – BFCO) by Sol-gel method. Crystal structures of BKT – BFCO solid solutions were studies by XRD and Raman spectroscopy. The results were in good agreement with the previous reports of \( \text{Bi}_{0.5}\text{K}_{0.5}\text{TiO}_3 \) – \( \text{BiFeO}_3 \) (BKT – BFO) and \( \text{Bi}_{0.5}\text{K}_{0.5}\text{TiO}_3 \) – \( \text{BiCoO}_3 \) (BKT – BCO) solid solutions. The magnetic properties were investigated via unsaturated M-H loop, which showed the competition of paramagnetic and antiferromagnetic ordering in BKT – BFCO. However, differing from the BKT – BFO and BKT – BCO solid solutions, the unclear values of saturated magnetism in BKT – BFCO raised the unexplained question, which needed further studies.

Keywords: sol-gel, BKT, ferroelectric, multiferroic, solid solutions.

1. INTRODUCTION

Recently, much attention has been paid to multiferroic materials exhibiting simultaneously a combination of ferroelectric, ferromagnetic, and/or ferroelasticity behaviours. Also, the coupling effect of electrical and magnetic order parameters gives a rise to a wide range of novel applications, such as in magnetic sensors, transformers, multiple state memories and microwave devices [1–4]. Among all multiferroics, \( \text{BiFeO}_3 \) (BFO) is well-known as one of the most promising materials for device applications due to its high Curie temperature \( T_C \sim 1103 \)K and antiferromagnetic temperature \( T_N \sim 643 \)K [5,6]. In BFO, the antiferromagnetic spin structure is G-type. This spatially modulated cycloidal spin structure does not allow the appearance of net magnetization, and inhibits the observation of a notable linear magnetoelectric effect in BFO [7]. Therefore, it is expected to get non-zero magnetization and a linear magnetoelectric effect in BFO by suppressing or destroying the spin cycloid, which can be realized via chemical substitution. Naganuma et al. [8] found that the substitution of Co for Fe induces a spontaneous ferromagnetic ordering at room temperature (RT). However, BFO and doped compounds generally have a high leakage current density at room temperature [9]. It is known that a perovskite ceramic based on the mix of bismuth and alkali at A-cations, i.e., \( \text{Bi}_{0.5}\text{K}_{0.5}\text{TiO}_3 \) (BKT), is one candidate as a lead-free piezoelectric material with a large spontaneous
polarization and high Curie temperature [10–13]. Unfortunately, BKT ceramics do not exhibit ferromagnetism at RT. It suggested that the solid solution of BKT and BFO may possess the enhancement magnetism and ferroelectricity. Recently, some properties of BKT-BFO solid solutions have been also investigated intensively [14].

Recently, some properties of BKT-BFO solid solutions have been also investigated intensively by our group [14]. We had observed the reduction of optical band gap from 3.22 eV to 1.39 eV for 30 mol.% BFO solid solution in BKT materials. Besides, the results also exhibited room-temperature ferromagnetism as well as increasing the concentration of BFO solid solution in BKT materials. The optical band gap of the solid solution showed the reduction from 3.21 eV for pure BKT to 1.77 eV for 30 mol.% BiCoO$_3$ (BCO) solid solutions in BKT. And, it is interesting that the BKT-BCO solid solutions also exhibited the room-temperature ferromagnetism resulted from interaction between Co$^{2+/3+}$ through oxygen vacancies.

To understand the role of transition metal based perovskite in the solid solution of BKT, we performed the study of cobalt (Co) substitution in BiFeO$_3$ in BKT–BFO solid solutions. In this study, we synthesized nanoparticles of 0.9Bi$_{0.5}$K$_{0.5}$TiO$_3$ + 0.1BiFe$_{1-x}$Co$_x$O$_3$ ($x = 10, 30, 50, 70$ and $90 \%$mol) (BKT–BCO) via sol-gel method. The electronic and ferromagnetic properties in these materials was reported. The dependence of structure on on the doping level of Co ions was studied.

2. EXPERIMENTAL

The solid solutions 0.9Bi$_{0.5}$K$_{0.5}$TiO$_3$ + 0.1BiFe$_{1-x}$Co$_x$O$_3$ ($x = 10, 30, 50, 70$ and $90 \%$mol) (BKT–BCO) samples were synthesized by using the sol-gel technique. The bismuth nitrate pentahydrate (Bi(NO$_3$)$_2$.5H$_2$O), potassium nitrate (KNO$_3$), iron (III) nitrate (Fe(NO$_3$)$_3$.9H$_2$O) and cobalt (III) nitrate (Co(NO$_3$)$_3$.6H$_2$O) were dissolved in acetic acid (CH$_3$COOH) and distilled water until transparency. Thus, the acetylaceton (CH$_3$COCH$_2$COCH$_3$) was introduced into a prepared solution before adding the tetraisopropoxytitanium (IV) (C$_{12}$H$_{28}$O$_4$Ti) and kept stirring around until transparency. Then, the dry gels were prepared by heating the sol at 90 °C. The samples powders were prepared by grounding and calcining at 400 °C for 2 h to following sintering at 800°C for 3 h. The potassium was added to excess around 20 mol% to prevent the potassium loss during gel and sintering process.

The crystalline structures of the samples were characterized by X-ray diffraction (XRD). The vibrational and rotational modes in samples were characterized by Raman spectroscopy. The magnetic properties were characterized by using vibration sample magnetometer (VSM) at room temperature.

3. RESULTS AND DISCUSSION

Figure 1a. shows the XRD patterns of the 0.9Bi$_{0.5}$K$_{0.5}$TiO$_3$ + 0.1BiFe$_{1-x}$Co$_x$O$_3$ solid solution with various Co concentrations ($x = 10, 30, 50, 70, 90 \%$mol). All the patterns can be indexed to a single phase with a perovskite type structure at room temperature. The peaks were indexed as the tetragonal structure of BKT phase for all samples, indicating that BiFe$_{1-x}$Co$_x$O$_3$ materials were well-dissolved in BKT materials to form a single phase, which was followed by the crystal structure of host BKT materials.
Fabrication and properties of Co doped Bi$_{0.5}$K$_{0.5}$TiO$_3$ – BiFeO$_3$ solid solution.

Figure 1. (a) XRD patterns of 0.9Bi$_{0.5}$K$_{0.5}$TiO$_3$ + 0.1BiFe$_{1-x}$Co$_x$O$_3$ solid solution with various Co concentrations ($x = 10, 30, 50, 70$ and $90$ %mol) and (b) The magnification of XRD peaks in the range of $29^\circ$ to $35^\circ$ of 0.9Bi$_{0.5}$K$_{0.5}$TiO$_3$+0.1BiFe$_{1-x}$Co$_x$O$_3$ solid solution with various Co concentrations.

An enlarged comparison of the location of (110) diffraction peaks in the range of $29^\circ$ to $35^\circ$ shows that the peak positions of the samples slightly shift toward lower 2θ values as the Co amount is increased, as shown in Figure 1b. The results indicated that the Co$^{3+}$ ions diffused and substituted to Fe$^{3+}$ sites caused shrinkage the lattice parameters because the ionic radius of Co$^{3+}$ (0.061 nm) is smaller than ionic radius of Fe$^{3+}$ (0.064 nm). The result was consistent with recent observation in lattice distortion in Co doped BiFeO$_3$ or BKT materials [15, 16].

The role of the BiFe$_{1-x}$Co$_x$O$_3$ in solid solution exhibited through the wave number in the range from $150$ cm$^{-1}$ to $450$ cm$^{-1}$. Fig. 2 showed the shift to low wave number at $380$ cm$^{-1}$ when increasing the Co concentration. Due to the difference of the Co ionic radius from the Fe ionic radius, the distance between ions in crystal structure reduced, and leading to the distortion of perovskite structures, as shown in XRD results.

Figure 2. Room-temperature Raman spectra of 0.9Bi$_{0.5}$K$_{0.5}$TiO$_3$ + 0.1BiFe$_{1-x}$Co$_x$O$_3$ solid solution with various Co concentrations.

The clear changes of the peaks at 630 cm$^{-1}$ and 920 cm$^{-1}$ were obtained to clarify the change of octahedral TiO$_6$ structures. These were the result from the random substitution at A-sites of Ti in the octahedron when BFCO evaporated in BKT to form solid solution. Besides, the substitution also supported the appearance of O-vacancies in the crystal structures.

Figure 3-1(a) shows the absorbance spectroscopy of 0.9 Bi$_{0.5}$K$_{0.5}$TiO$_3$ + 0.1 BiFe$_{1-x}$Co$_x$O$_3$ samples at room temperature. The single absorption band tailored with small absorbance tail
band which was shown for Bi_{0.5}K_{0.5}TiO_{3} samples. The small tail in absorbance tail band in Bi_{0.5}K_{0.5}TiO_{3} materials was observed which was suggested to origin from self-defect such as O-vacancies [19].

The absorption band of 0.9Bi_{0.5}K_{0.5}TiO_{3} + 0.1BiFe_{1-x}Co_{x}O_{3} showed very complicated. However, the result clearly showed that the main absorption edge trend to red shift, indicating that the optical band gap of 0.9Bi_{0.5}K_{0.5}TiO_{3} + 0.1BiFe_{1-x}Co_{x}O_{3} samples decreased as increasing the Co concentration. At low Co concentration, BiFeO_{3} and Fe^{3+} were dominate, the minor absorption of the d orbital of Fe splits into threefold degenerate t_{2g} and e_{g} bands. Thus, two board absorbance bands in the range of approximately 500 nm to 900 nm were obtained.

The effect of Co doped BKT-BiFeO_{3} solid solution on the band gap was further calculated using the plot of (αhv)^2 versus photon energy hv, as shown in Figure 3-1(b), where α, h, and v are absorbance coefficient, the Planck constant, and the frequency, respectively. With previous result of BKT-BFO [14], The band gap values as function of Co concentration of the pure Bi 0.9Bi_{0.5}K_{0.5}TiO_{3} and 0.9Bi_{0.5}K_{0.5}TiO_{3} + 0.1BiFe_{1-x}Co_{x}O_{3} samples were show in Figure 3-2.

![Figure 3-1](image)

*Figure 3-1.* (a) UV–vis absorption spectra and (b) the dependence of (αhv)^2 on photon energy (hv) of the pure Bi_{0.5}K_{0.5}TiO_{3} and 0.9Bi_{0.5}K_{0.5}TiO_{3} + 0.1BiFe_{1-x}Co_{x}O_{3}.

![Figure 3-2](image)

*Figure 3-2.* The band gap values of the pure Bi 0.9Bi_{0.5}K_{0.5}TiO_{3} and 0.9Bi_{0.5}K_{0.5}TiO_{3} + 0.1BiFe_{1-x}Co_{x}O_{3} (x=0 [14], 0.1, 0.3, 0.5, 0.7, 0.9).

The optical band gap is 3.31 eV for pure BKT and was decreased to 2.29 eV for 90 % mol Co substituted at Fe site in BKT-BFO solid solution. The reduction of the optical bandgap was
possible originated from transition metal splitting under crystal field and oxygen vacancies was created due to unbalance charge between transition metal (Co$^{2+/3+}$) and host (Ti$^{4+}$) [16].

**Figure 4.** Magnetic hysteresis (M-H) loops of 0.9Bi$_{0.5}$K$_{0.5}$TiO$_3$+0.1BiFe$_{1-x}$Co$_x$O$_3$ solid solution with various Co concentrations.

Furthermore, the effect of Co concentrations in 0.9Bi$_{0.5}$K$_{0.5}$TiO$_3$+0.1BiFe$_{1-x}$Co$_x$O$_3$ solid solution on the ferromagnetic properties has been observed by determining the magnetic moment vs. magnetic field at room temperature. Figure 4 shows the magnetic hysteresis ($M-H$) loops of 0.9Bi$_{0.5}$K$_{0.5}$TiO$_3$+0.1BiFe$_{1-x}$Co$_x$O$_3$ solid solution. The unsaturated $M-H$ showed the competition between paramagnetism and antiferromagnetism. The RT magnetic properties of BKT were resulted in the $3d^0$ orbital in Ti$^{4+}$ [17-19]. Recent studies of the BKT – BFO and BKT – BCO solid solutions, as well as Fe/Co – doped BKT, also reported the enhancement of the RT magnetic ordering together with the increase of Co/Fe concentration [14, 16, 17]. It was explained that Fe$^{3+}$ and Co$^{3+}$ replaced randomly at Ti$^{4+}$ sites in crystal structure, and form O – vacancies. Our observed results were not only in good agreement, but also supportive for the above explanation. However, we had not observed a clear change in the values of unsaturated magnetism of these samples. It brought the difference between 0.9Bi$_{0.5}$K$_{0.5}$TiO$_3$+0.1BiFe$_{1-x}$Co$_x$O$_3$ and BKT – BFO/BCO solid solution, which raised the question for the further investigation.

**4. CONCLUSION**

In summary, we have studied the structural, magnetic properties of solid solution 0.9Bi$_{0.5}$K$_{0.5}$TiO$_3$+0.1BiFe$_{1-x}$Co$_x$O$_3$. The results were in good agreement with the previous reports of BKT – BFO and BKT-BCO solid solutions. The magnetic properties were investigated via unsaturated M-H loop, which showed the competition of paramagnetic and antiferromagnetic ordering in BKT – BFCO. Resulting in the competition between ferromagnetism and paramagnetism caused by the interaction between Fe, Co ions through oxygen vacancies and isolated random Fe, Co ions in the host lattice structure of BKT. We expected that our work will provide the simple way to obtained the room temperature ferromagnetism in lead-free ferroelectric materials.

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