



Modulating the magnetic properties of BiFeO_3 by addition of $\text{Ba}_5\text{TbTi}_3\text{V}_7\text{O}_{30}$

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Abstract

$x\text{BiFeO}_3-(1-x)\text{Ba}_5\text{TbTi}_3\text{V}_7\text{O}_{30}$ ($x\text{BFO-BTTV}$) ceramic composites with different x values were prepared by high temperature solid state reaction technique and sintering at 1073 K. The formation of composite structure consisting of BFO and BTTV phases was confirmed by XRD study. Surface morphology was studied by scanning electron microscope (SEM) and shows that structure with high density was obtained in the composite 0.3BFO-BTTV whereas the average grain size increases by increasing x , i.e. by increasing amount of BiFeO_3 in the system. Magnetic measurements were done in a wide temperature range, i.e. from 10 to 350 K, by vibrating sample magnetometer (VSM) and showed that the magnetization changes by changing the value of x in the composite. BiFeO_3 is antiferromagnetic in nature with weak ferromagnetism. Addition of $\text{Ba}_5\text{TbTi}_3\text{V}_7\text{O}_{30}$ enhances magnetic properties of the composite and maximal coercivity and remnant magnetization are obtained in the composite 0.7BFO-BTTV.

Keywords: $\text{BiFeO}_3-\text{Ba}_5\text{TbTi}_3\text{V}_7\text{O}_{30}$ composites, structure, magnetization, multiferroic, VSM

I. Introduction

Since the discovery of multiferroic material BiFeO_3 [1], many similar materials, showing both ferroelectricity and ferromagnetism in single phase, have been studied. In these materials, an external magnetic field can induce electric polarization and electric field can induce change in magnetization [2]. Due to this unique property these materials have potential applications in magnetic as well as ferroelectric devices [3] such as dual storage devices, electric field controlled ferromagnetic resonance devices and transducers with magnetically modulated piezoelectrics [4].

Mahesh Kumar *et al.* [5] prepared the phase pure BiFeO_3 (BFO) ceramics and additionally it was confirmed that it has the frequency independent Neel temperature (T_N) at around 653 K [6]. BFO has a rhombohedrally distorted perovskite structure with the space group $R3c$ [7,8]. There are several reports on the modification of magnetic properties (Neel temperature, T_N) of BFO by addition of niobate ferroelectrics [9,10]. It has also been observed that the magnetic ordering param-

eters in BFO can be improved by employing the solid solution technique with other ferroelectric compounds [11]. $\text{Ba}_5\text{TbTi}_3\text{V}_7\text{O}_{30}$ (BTTV) is one such kind of ferroelectric compounds with high dielectric constant and low dielectric loss [12].

This work focuses on the modulation of the magnetic properties of BFO by addition of $\text{Ba}_5\text{TbTi}_3\text{V}_7\text{O}_{30}$ (BTTV) compound. Composites with different phase ratios $x\text{BiFeO}_3-(1-x)\text{Ba}_5\text{TbTi}_3\text{V}_7\text{O}_{30}$ where $x = 0, 0.3, 0.5, 0.7, 1$ are synthesized and systematic study of the relationship between their magnetic properties and composition is performed.

II. Experimental details

$x\text{BiFeO}_3-(1-x)\text{Ba}_5\text{TbTi}_3\text{V}_7\text{O}_{30}$ (abbreviated as $x\text{BFO-BTTV}$) composites, where $x = 0, 0.3, 0.5, 0.7$ and 1, were processed using conventional solid state reaction technique and conventional sintering. The starting precursor materials are: BaCO_3 , Tb_2O_3 , TiO_2 , V_2O_5 , Fe_2O_3 and Bi_2O_3 (99%+, Loba Chemie). At first stoichiometric amounts of Fe_2O_3 and Bi_2O_3 were thoroughly wet mixed and then calcined at 973 K for 4 h to form BFO. The as-obtained calcined powder

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was further ground. In the second stage, stoichiometric amounts of BaCO_3 , Tb_2O_3 , TiO_2 and V_2O_5 were mixed and ground thoroughly in agate mortar in methanol medium to maintain molecular level homogeneity. The thoroughly ground powder was calcined using alumina crucible at 1023 K for 12 h to form BTTV. The calcined powder was ground again and finally mixed with the calcined BFO powder in different proportions. The prepared powder mixtures with a small amount of PVB (polyvinyl butyral), added as a binder, were pressed as disks in a stainless steel die under a pressure of 7 tons to make pellets. The sizes of the obtained pellets

were 1–2 mm in thickness and 12–13 mm in diameter. Finally, the pellets were sintered at 1073 K for 6 h in ambient air followed by cooling at $2^\circ\text{C}/\text{min}$.

The crystalline phase formation of the samples was confirmed by X-ray diffraction (Rigaku, Miniflex) with CuK_α radiation of wavelength $\lambda = 1.5405 \text{ \AA}$ in the range of Bragg's angles $2\theta = 10^\circ\text{--}65^\circ$ with scanning rate of $3^\circ/\text{min}$. Surface morphologies were analysed using scanning electron microscope (SEM, JEOL-IT300). The average grain sizes of the obtained ceramics were calculated by linear intercept method. Magnetization measurements were carried out using vibrating sample magnetometer (VSM) at a temperature range of (10–350 K). Hysteresis (M - H) loops were reported at room temperature (300 K).

III. Results and discussion

3.1. Structure

Figure 1 shows the room temperature XRD patterns of the calcined $x\text{BFO-BTTV}$ powders with $x = 0, 0.3, 0.5, 0.7$ and 1. The peak values for $x = 1$, i.e. for the pure BiFeO_3 (BFO), are in close agreement with those reported earlier [13]. These peaks are also visible in XRD patterns of the sample with $x = 0.3, 0.5$ and 0.7. Thus it seems that the samples with $x = 0.3, 0.5$, and 0.7 are composites in which one phase is BFO. XRD patterns of the samples with $x = 0.3, 0.5$ and 0.7 are similar and in addition to XRD peaks of BFO phase there are some

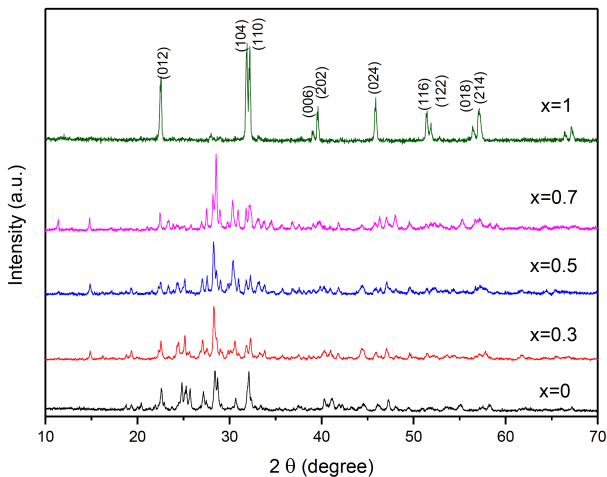


Figure 1. XRD patterns of $x\text{BFO-BTTV}$ ceramics

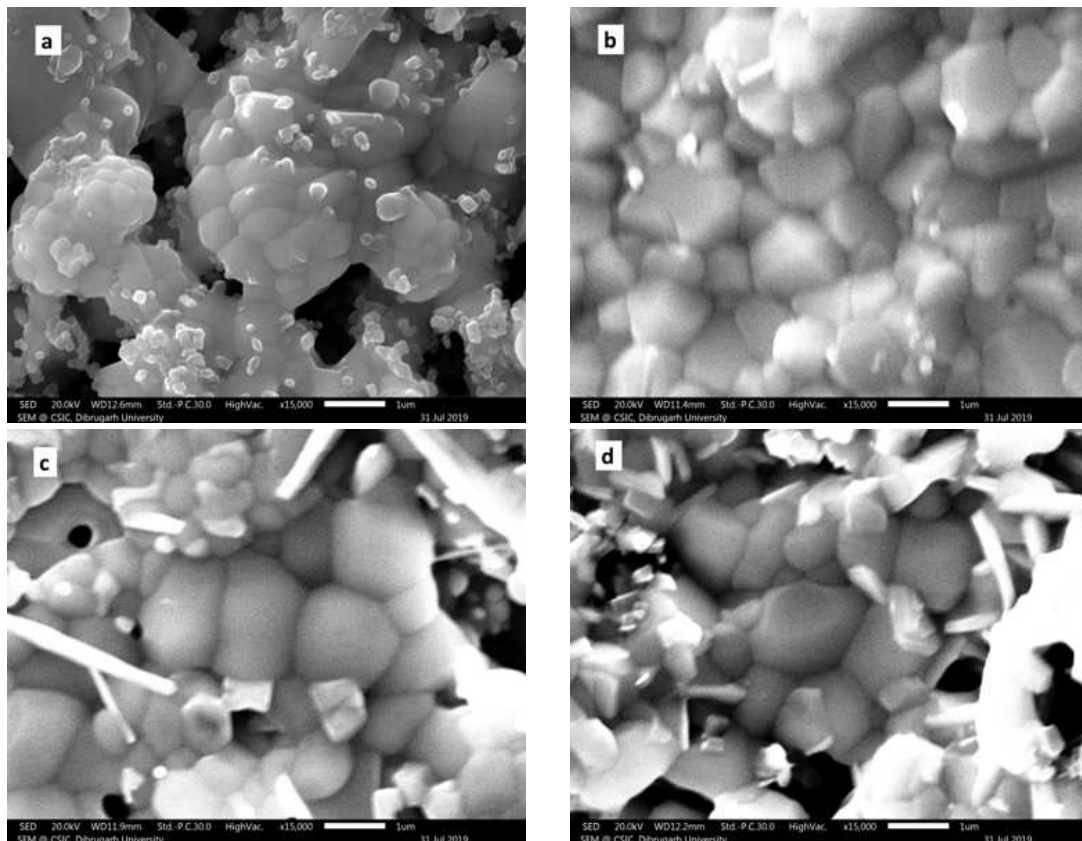


Figure 2. SEM micrographs of $x\text{BFO-BTTV}$ composites: a) $x = 0$, b) $x = 0.3$, c) $x = 0.5$ and d) $x = 0.7$

additional XRD peaks belonging to another phase. This secondary phase could be tungsten bronze phase corresponding to the pure BTTV i.e. $x = 0$, or solid solution formed with some of Bi and/or Fe ions. Thus, the XRD results justify the existence of composite structure of the prepared ceramics.

Figure 2 shows the SEM micrographs of the samples x BFO-BTTV for $x = 0, 0.3, 0.5$ and 0.7 . For $x = 0$, i.e. for the pure BTTV, relatively large portion of porosity is obvious. The grains are elongated and oval having the average grain size around $0.9 \mu\text{m}$. As x increases to $x = 0.3$ the compactness also increases and the structure looks more dense. However, as x increases further ($x = 0.5$ and 0.7), the average grain size also increases and the appearance of columnar shape grains with higher portion of porosity is obvious. It may be due to the presence of a secondary phase in the composites and the increased in the content of BFO where there may be loss of Bi_2O_3 during high temperature processing resulting in the formation of porosity [13].

3.2. Magnetization studies

Figure 3 depicts the magnetisation M vs. temperature for the composite samples with $x = 0.3, 0.5, 0.7$. It is observed that the magnetisation decreases as the temperature increases, which is an expected trend. Magnetization increases with the increase in the content of BTTV in the composites. Also, at around $\sim 230 \text{ K}$ there is a kink, indicating the development of local weak ferromagnetism.

Figure 4 is plot between the inverse of susceptibility ($1/\chi$) and temperature which shows that the extrapolation of the straight line makes an almost zero intercept on the temperature axis which indicates the samples have nearly perfect antiferromagnetic ordering. However, there is a sharp change of the slope after $\sim 222 \text{ K}$. The slope makes positive intercept on x -axis and after about $\sim 239 \text{ K}$, it makes negative intercept. This indicates that there is the development of local ferromagnetism and canted antiferromagnetism [14].

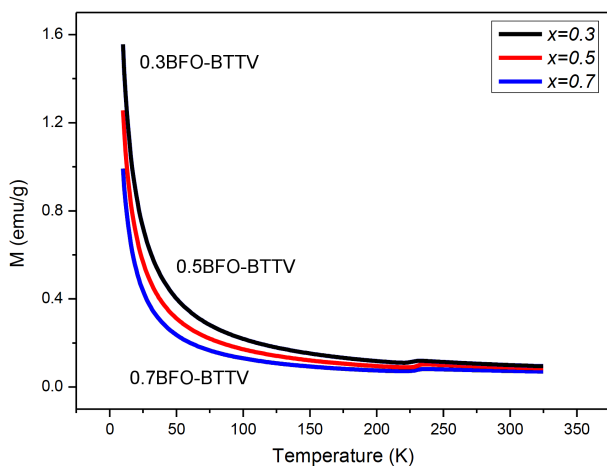


Figure 3. Variation of magnetization, M with temperature for x BFO-BTTV ceramic composites

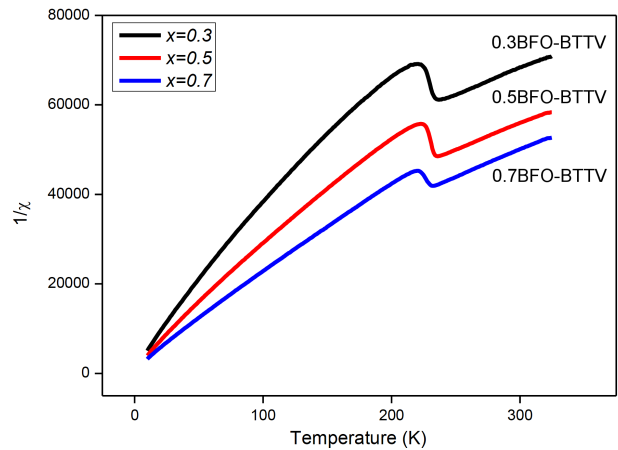


Figure 4. Variation of susceptibility with temperature for x BFO-BTTV ceramic composites

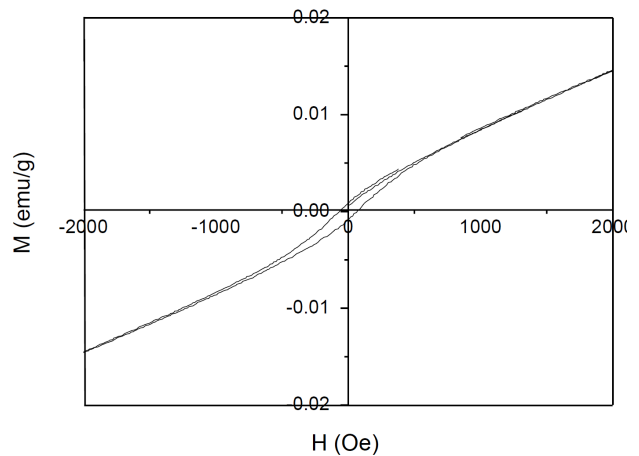


Figure 5. M - H hysteresis loops for BFO at 300 K

Figure 5 shows the hysteresis curve for the pure BFO. The curve does not saturate which indicates typical antiferromagnetic behaviour [15]. There is an appearance of hysteresis loop in the pure BFO having low value of $H_c \sim -65 \text{ Oe}$ and $M_r \sim 8.5068 \times 10^{-4} \text{ emu/g}$ suggesting that it is also a weak ferromagnetic in nature [13]. The appearance of hysteresis loop may be due to the canting of antiferromagnetic ordering of Fe–O–Fe chains of spins resulting in weak spontaneous magnetic moment. The low values of magnetization and non-saturation even at high magnetic field may be due to the uncompensated antiferromagnetism.

Figure 6 shows the M - H curves of the composite x BFO-BTTV at 300 K (for $x = 0.7, 0.5, 0.3$ and 0) and corresponding remnant magnetizations and coercivities are given in Table 1. It can be seen that addition of BTTV to the pure BFO increases the spontaneous magnetic moment and hence there is the appearance of hysteresis loop. It shows that there is the development of parallel spin clusters or canting spins in an antiferromagnetic material. It may be due to the distortion in the perovskite layers of superstructure of the pure BFO which results in magnetic anisotropy and canting of spin structure of the compound. As a result

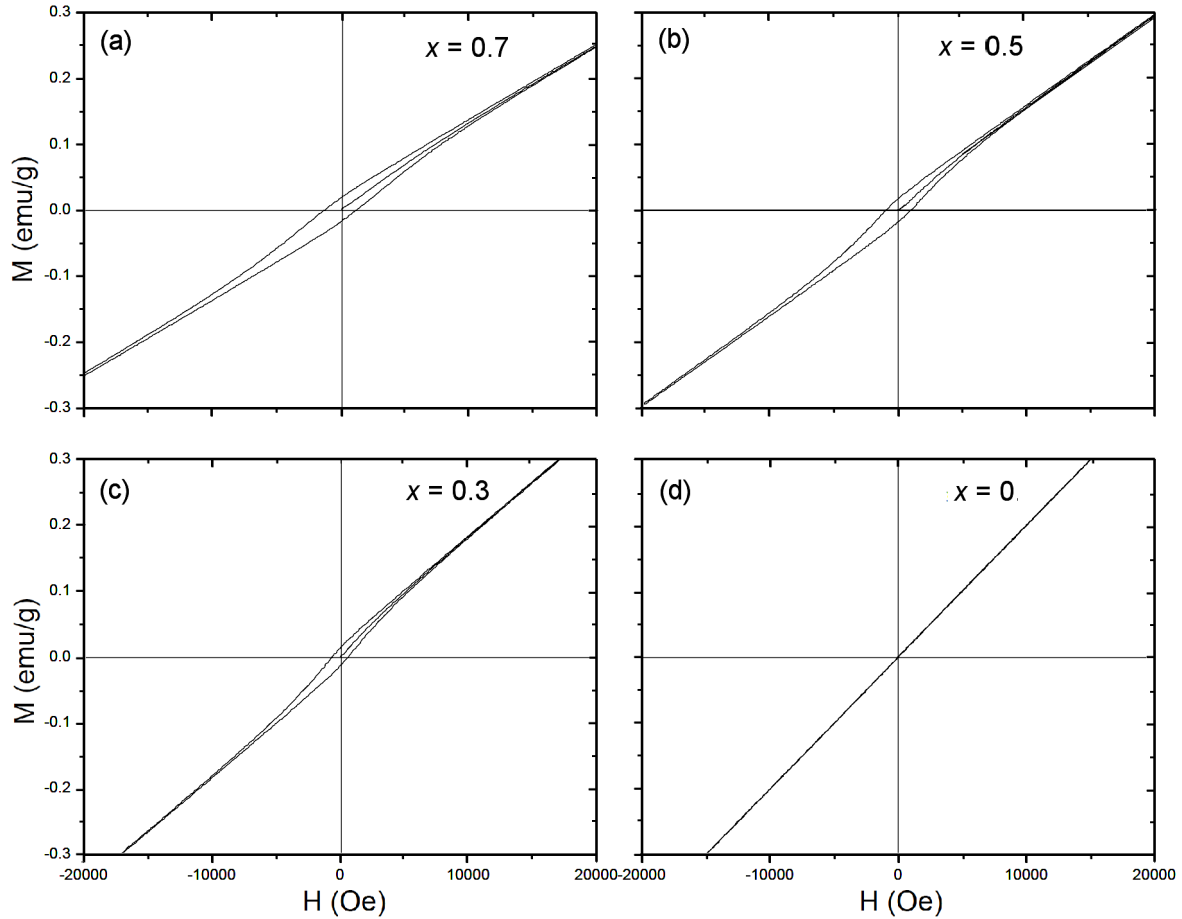


Figure 6. M - H hysteresis loops of x BFO-BTTV at 300 K for: a) $x = 0.7$, b) $x = 0.5$, c) $x = 0.3$ and d) $x = 0$

Table 1. Magnetic properties (coercivity H_c , and remnant magnetization M_r) of x BFO-BTTV ceramics at 300 K

Sample	H_c [Oe]	M_r [10^{-4} emu/g]
BFO	-65	8.51
0.7BFO-BTTV	-1206	180.57
0.5BFO-BTTV	-966	173.94
0.3BFO-BTTV	-612	139.99
BTTV	0	0

local ferromagnetism or weak antiferromagnetism is developed increasing ferromagnetic order. The composite sample 0.7BFO-BTTV has maximal remnant magnetization $M_r = 180.57 \times 10^{-4}$ emu/g and maximal coercivity $H_c = -1206$ Oe. Thus, its hysteresis loop is the most developed. However, with further increase in BTTV content, magnetization decreases. Finally, for $x = 0$ (the pure BTTV) the graph is linear with $M_r = 0$ and $H_c = 0$. It is because the pure BTTV is paramagnetic in nature.

IV. Conclusions

x BiFeO₃-(1- x)Ba₅TbTi₃V₇O₃₀ ceramic composites with different x values were prepared by high temperature solid state reaction technique and sintering. The formation of composite structure consisting of BFO and

BTTV phases was confirmed by XRD study. Comparative SEM study confirms that there is increase in sinterability and average grain size by increasing BTTV content.

Detailed magnetization study shows that the pure BFO is antiferromagnetic with weak ferromagnetism. Magnetization changes by changing the value of x in the investigated system. The addition of BTTV increases spontaneous magnetization, and at $x = 0.7$ (0.7BFO-BTTV) the hysteresis loop is the most developed with maximal remnant magnetization $M_r = 180.57 \times 10^{-4}$ emu/g and coercivity $H_c = -1206$ Oe. Thus the magneto-electric coupling is the most effective in this composite sample.

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