Magnetic and Electric properties of the Multiferroic Composite (1-x)BiFeO$_3$ - xBa$_5$TbTi$_3$V$_7$O$_{30}$

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Abstract

Using high temperature solid state reaction technique ceramic composites (1-x)BiFeO$_3$ - xBa$_5$TbTi$_3$V$_7$O$_{30}$ having different x values are prepared. Basic crystal qualities are studied using XRD which shows that there's a formation of BiFeO$_3$ and Ba$_5$TbTi$_3$V$_7$O$_{30}$ phases. There observed change in the basic structure as x changes and is most distorted for x = 0.5. From SEM study, it is found that the grain size is minimum for pure ferroelectric sample and maximum for x = 0.5. Dielectric constant (ε_r) and Dielectric loss (tanδ) has been measured at wide temperature range (RT- 673 K). With increase in the value of x, there is also increase in Dielectric constant (ε_r) and is maximum for x = 1. Magnetic measurement is done at low temperature by VSM which shows that the magnetization is maximum for x = 0.3.

Keywords: Ferroelectric, Dielectric loss, Ferromagnetic, Multiferroic, VSM, Hysteresis

Introduction

Multiferroic material BiFeO$_3$ is a material which shows both ferroelectricity and (anti)ferromagnetism in a single phase [1,2]. The structure of BiFeO$_3$ is non-centrosymmetric rhombohedrally distorted perovskites structure having the space group R3c [3]. The characteristic of the material is that magnetization can be induced by an applied external electric field whereas an electric polarization can be induced by applying magnetic field [4]. It has ferroelectric-paraelectric phase transition temperature (Tc) at around 1,109 K [5] and antiferromagnetism (T$_N$) at around 653 K [6]. Till 1990s, the only reported value of ferroelectric polarization was ~ 6μC/cm^2 which was measured from BiFeO$_3$ bulk polycrystalline sample [1]. The low value of polarization at room temperature is may be due to semiconducting nature of BiFeO$_3$ because of which proper electrical poling is not possible results into low dielectric constant and high dielectric loss [7]. Dielectric constant of ~ 26 and Dielectric loss of ~ 0.26 was measured at frequency 10 kHz in Room temperature [6]. To improve the ferroelectric properties Smith *et al.* adopted a technique to make BiFeO$_3$ an insulator by doping it with other perovskites which are good ferroelectrics [8,9].

Preparing bulk pure BiFeO$_3$ without any traces of impurity still remain elusive. However, the proper characteristic of multiferroic can be obtained if BiFeO$_3$ suitably mixed with other kind of ferroic materials. It has been reported that the magnetic properties (Neel temperature, T$_N$) of BiFeO$_3$ is modified when mixed with niobate ferroelectrics [10]. It has been observed that the T$_N$ and T$_C$ both change considerably by addition of sodium potassium niobate in different proportions. It has also been observed that the magnetic order parameters in BiFeO$_3$ can be improved by employing the solid solution technique with pure ferroelectric compounds [11].

But the problem with niobate ferroelectrics (such as barium niobate titanate) is that high calcination and sintering temperature is required for their synthesis [12,13]. It was found that basic structure does not changes when R in Ba$_5$RTi$_3$Nb$_7$O$_{30}$ is substituted by rare earth elements [14]. Literature survey shows that in Ba$_5$RTi$_3$Nb$_7$O$_{30}$ when Nb is replaced by Vanadium the calcination and sintering temperature are reduced [15,16] without compromising ferroelectric properties. Also, thermal stability improves, leakage current reduces [17] and dielectric and ferroelectric properties enhances [18].

Though literature shows the mixing of BiFeO$_3$ of perovskite structure with different ferroelectrics of same family [11,19] but in our present work we decided to mix BiFeO$_3$ with Ba$_5$RTi$_3$V$_7$O$_{30}$ of different structural family (TB-structure). The open nature of the TB structure as compared to the perovskite

allows a wide range of cation and anion substitutions improving the ferroelectric properties. In our earlier work we have found interesting result with similar combination [20,21].

The objective of the work is to study the ferroelectric and magnetic characteristic of ceramic composite $(1-x)BiFeO_3-xBa_5TbTi_3V_7O_{30}$ (x = 0, 0.3, 0.5, 0.7, 1). Also, to see if there is any improvement in the ferroelectric and magnetic characteristic of $BiFeO_3$ by adding $Ba_5TbTi_3V_7O_{30}$ in different proportion and to see in which proportion both the electric and magnetic properties are most effective.

Materials and methods

Ceramics composite $(1-x)BiFeO_3-xBa_5TbTi_3V_7O_{30}$ (x = 0, 0.3, 0.5, 0.7, 1) are prepared using solid state reaction technique. The starting precursor materials are stoichiometrically mixed and then calcined at 1023 K for 12 h at a rate of 1℃/min. The calcined powders are mixed with a small amount of PVB (polyvinyl butyral) as a binder and the powders are pressed as disks in a stainless-steel die by applying pressure of 7 tons to make pellets (1-2 mm thick and 12 - 13 mm diameter). Then pellets are sintered at temperature of 1,073 K for 6 h followed by cooling at 2 ℃/min. X-ray diffractogram (Rigaku, Miniflex) with CuKα radiation of wavelength = 1.5405 Å in the range of Bragg's angles 2θ (10°< θ< 60°) with scanning rate of 3°/min is used to confirm the formation of crystalline phase formation. Scanning electron microscope (SEM: JOEL-IT300) is used to study the Surface morphology of the materials. Sintered pallets are polished on the both sides and applied silver paste. Impedance Analyzer (HIOKI-IM3536) is used to study Dielectric characteristics. Physical Property Measurement System (PPMS: Quantum Design, San Diago, USA) Vibrating Sample Magnetometer (VSM) is used to study the Magnetic properties. Hysteresis (M-H) loops are reported at room temperature 300 K).

Results and discussion

Structure

The XRD patterns of the calcined powder of samples $(1-x)BiFeO_3 - xBa_5TbTi_3V_7O_{30}$ for x = 0, 0.3, 0.5, 0.7 and 1 at room temperature are shown in **Figure 1**. There are additional peaks for x = 0.3, 0.5 and 0.7 which may be due to presence of $BiFeO_3$ resulting into additional XRD peaks belonging to another phase. The secondary phase may be tungsten bronze phase corresponding to $Ba_5TbTi_3V_7O_{30}$ or solid solution formed with some Bi and/or Fe ions. The presence of composite structure is confirmed by XRD results. The lattice parameters are calculated using X'perthighscore software. The peak values for x = 0 i.e. for pure $BiFeO_3$ are in close agreement with those reported earlier [22]. From the **Table 1**, it can be seen that there is a structural change in the crystal system with addition of $BiFeO_3$. When x = 1 i.e. in case of pure $Ba_5TbTi_3V_7O_{30}$ it is most symmetric i.e. in Cubic structure. With addition of $BiFeO_3$ there is a distortion in structure. The composite is most distorted (monoclinic structure) when x = 0.5 i.e. when there is 50 % of $BiFeO_3$ is added in the solution.
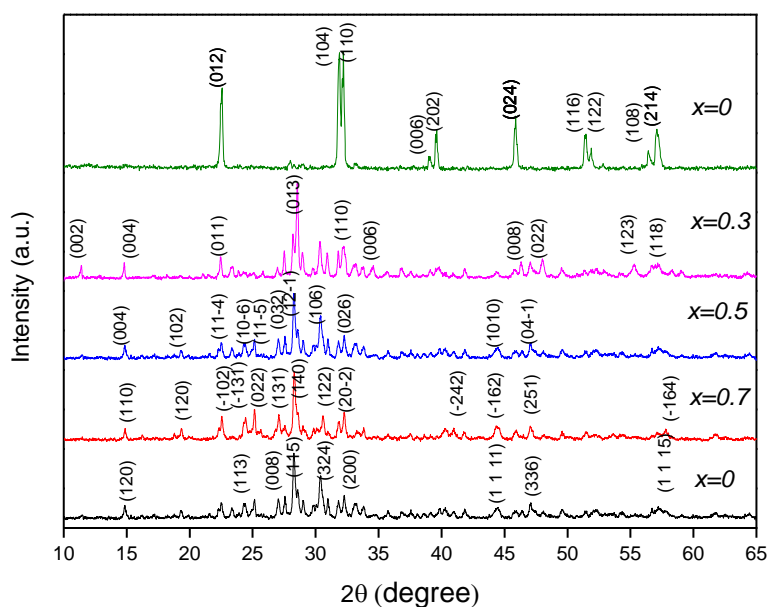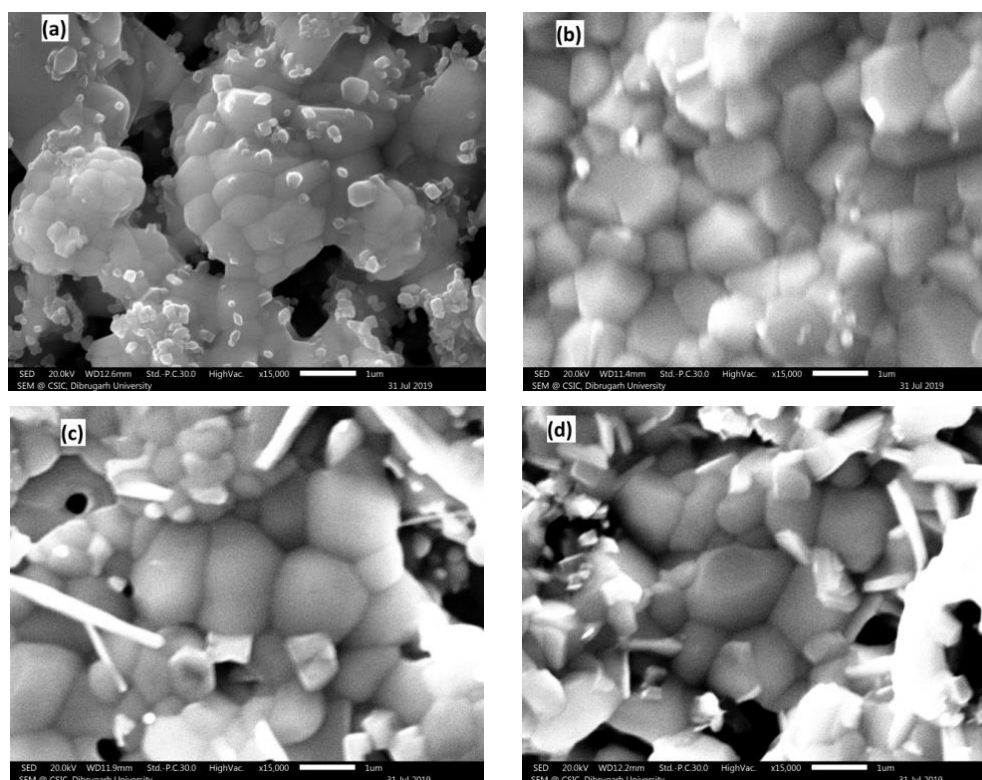

Figure 1 XRD pattern for $(1-x)BiFeO_3 - xBa_5TbTi_3V_7O_{30}$.

Table 1 Comparison of lattice parameters, a, b and c (in Å), particle size (P) Volume (in Å^3), Structure and SEM grain size (in μm).

(1-x)BiFeO$_3$ - xBa$_5$TbTi$_3$V$_7$O$_{30}$	a (in Å)	b (in Å)	c (in Å)	P (in Å)	V (in Å^3)	Structure	SEM grain size (in μm)
x = 0	5.63	5.63	5.63	5.5	124.59	Rhombohedral	~ 1.3
x = 0.3	3.92	3.92	15.57	3.5	239.39	Tetragonal	~ 1.36
x = 0.5	5.63	7.73	24.64	4.0	1046.63	Monoclinic	~ 1.8
x = 0.7	8.57	8.57	8.57	4.2	630.78	Orthorhombic	~ 1.13
x = 1	5.53	5.53	25.98	4.6	795.33	Orthorhombic	~ 0.89

The SEM micrographs of the sample (1-x)BiFeO$_3$- xBa$_5$TbTi$_3$V$_7$O$_{30}$ for x = 0.3, 0.5, 0.7 and 1 is shown in **Figure 2**. Growth of the grain is more or less complete. Linear intercept method is used to calculate the average grain sizes. It is found that with the increase of BiFeO$_3$there is remarkable change in average grain size. From **Table 1**, it can be seen that the increase in the grain size is not uniform. The range of grain size is found to be from 0.89 to 1.8 μm. The average grain size of pure Ba$_5$TbTi$_3$V$_7$O$_{30}$ (x = 1) is around 0.89 μm. The shape of the grain is elongated, angular and oval. As x increases the compactness also increases and the grains are most compact for x = 0.7. At x = 0.5, there is presence of porosity also there is appearance of columnar shape grains (it may be due to increase in the content of BiFeO$_3$). For x = 0.3, the shape is more of angular and cubicle. There is also increase in the porosity and the columnar shape grain becomes more distorted. It is found that the grain size is minimum when the sample is pure ferroelectric and the size of the grain is maximum when x = 0.5.

Figure 2 SEM micrographs of (1-x)BiFeO$_3$ - xBa$_5$TbTi$_3$V$_7$O$_{30}$ (a) x = 1 (b) x = 0.7 (c) x = 0.5 (d) x = 0.3.

Dielectric studies

The variation of dielectric constant (ε_r) with temperature for $(1-x)BiFeO_3$ - $xBa_5TbTi_3V_7O_{30}$ at 1 kHz for the temperature range (RT- 673 K) are shown in **Figure 3**. At transition temperature (T_C) there is presence of the ferroelectric- paraelectric phase transition. From **Table 2**, it can be observed that with increase in x, transition temperature (T_C) decreases. Which may due to the reason that V^{5+} ionic radii is smaller than Fe^{3+} resulting into mismatch of ionic radii of Fe^{3+} and V^{5+} [13] and interaction of Bismuth ion of $BiFeO_3$ with different lattice site of $Ba_5TbTi_3V_7O_{30}$. However, for x = 0.7 having orthorhombic structure (confirmed from XRD), there is an anomaly, that there is increase in Transition temperature (T_C) and dielectric constant (ε_{max}) compared to its neighbors i.e. x = 0.5 (monoclinic structure), indicating transition temperature (T_C) and dielectric constant (ε_{max}) strongly depends upon the structural changes also.
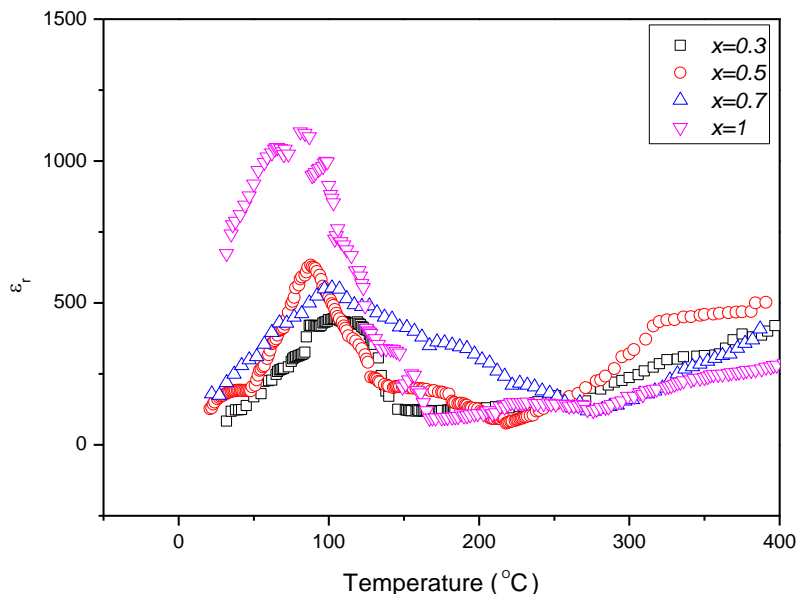

Figure 3 Variation of dielectric constant (ε_r) with temp for $(1-x)BiFeO_3$- $xBa_5TbTi_3V_7O_{30}$ at 1 kHz.

At higher temperature range, as the $BiFeO_3$ content increases the dielectric properties also increases, which may be because of the presence Fe multivalent states [18] in $BiFeO_3$ resulting into giant dielectric behavior.
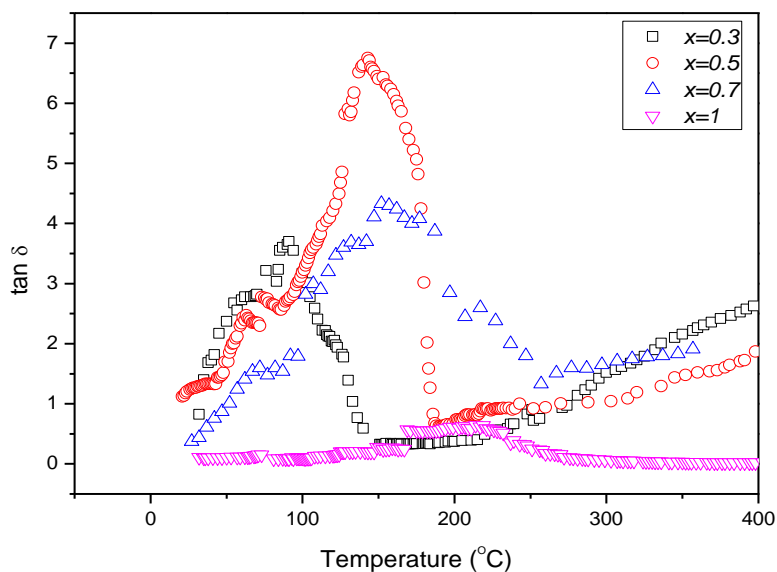

Figure 4 Variation of tan δ with temperature for $(1-x)BiFeO_3$ - $xBa_5TbTi_3V_7O_{30}$ at 1 kHz.

The variation of loss tangent (tan δ) with temperature for $(1-x)BiFeO_3-xBa_5TbTi_3V_7O_{30}$ at 1 kHz for the temperature range (RT- 673 K) are shown in **Figure 4**. From **Table 2**, it can be observed that with decrease in x there is increase in the value of dielectric loss (tan δ). High dielectric loss is may be because of the semiconducting nature of $BiFeO_3$ [7] and is maximum for x = 0.5. However, there is anomaly for x = 0.3, having moderate dielectric loss (tan δ), indicating dielectric loss may be also structural dependent.

Table 2 The Dielectric properties such as dielectric constant and dielectric loss are analyzed using Impedance Analyzer (HIOKI-IM3536).

Sample	ϵ_{RT}	ϵ_{max}	tan δ_{RT}	tan δ_{max}	$T_c(K)$
$0.7BiFeO_3-0.3Ba_5TbTi_3V_7O_{30}$	84	439	0.796	3.697	378
$0.5BiFeO_3-0.5Ba_5TbTi_3V_7O_{30}$	157	631	1.232	6.762	361
$0.3BiFeO_3-0.7Ba_5TbTi_3V_7O_{30}$	172	566	0.52	4.35	376
$Ba_5TbTi_3V_7O_{30}$	671	1,100	0.133	0.610	356

Magnetization studies

Figure 5 shows the variation of magnetic susceptibility of $(1-x)BiFeO_3 - xBa_5TbTi_3V_7O_{30}$ with temperature. For x = 0.3, 0.5, and 0.7, magnetic moment decreases as the temperature increases, which is an expected trend. It can be seen that with an increase in the value of x, there is increase in paramagnetic state in the system having a low spontaneous moment value. The presence of kink in the figure may indicate the appearance of weak ferromagnetism or antiferromagnetic nature. The ferromagnetism Curie temperature (T_C), for x = 0.7 ($T_C \sim$ 233.70 K), for x = 0.5 ($T_C \sim$ 233.27 K) and for x = 0.3 ($T_C \sim$ 230.9 K). However, for x = 0, i.e. for $BiFeO_3$, it was not possible to detect the spontaneous moment even at field upto 8kOe and temperature up to 100 K [23].

Further, reports shows that addition of $BiFeO_3$ in ferroelectric materials results in the onset of ferromagnetism. The addition of $Ba_5TbTi_3V_7O_{30}$ (TB-structure) in $BiFeO_3$ may results in distortion of perovskite layers of superstructure of pure $BiFeO_3$ [24] causing magnetic anisotropy and canting of spin structure of the compound resulting into local ferromagnetism or weak antiferromagnetism.
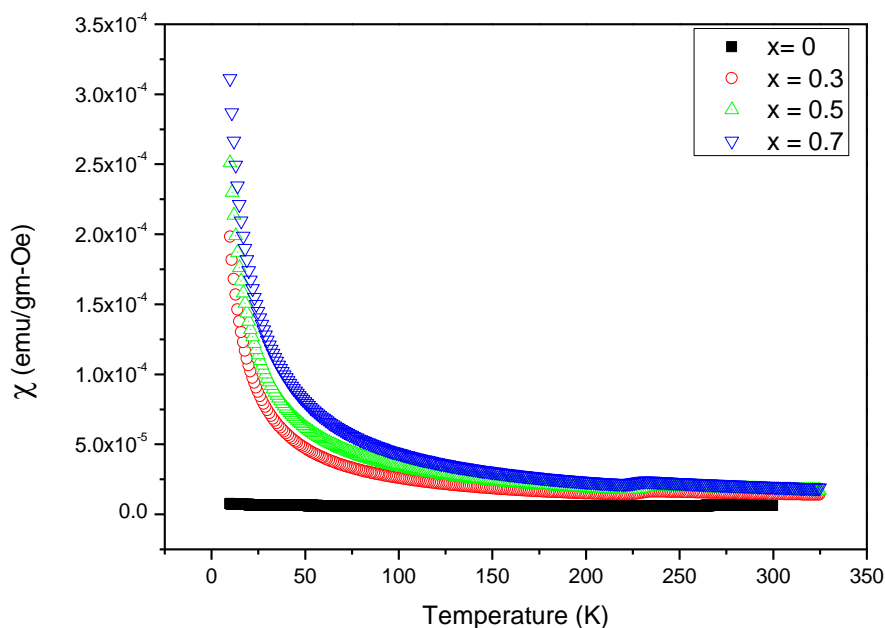

Figure 5 Variation of magnetic susceptibility (χ) with temperature for $(1-x)BiFeO_3 - xBa_5TbTi_3V_7O_{30}$.

Figure 6 shows the M-H hysteresis curve for pure $BiFeO_3$. It shows that the hysteresis curve does not saturate, also low value of coercive field (Hc ~ –65 Oe) as shown in **Table 3**, suggest anti-ferromagnetic nature with weak ferromagnetism [19]. The magnetization value is low and doesn't saturate even at high applied magnetic field which may be due to uncompensated antiferromagnetism property of the material. The presence of hysteresis loops is because of weak spontaneous moment [25] which may be due to canted antiferromagnetic order of Fe-O-Fe chains of spins.
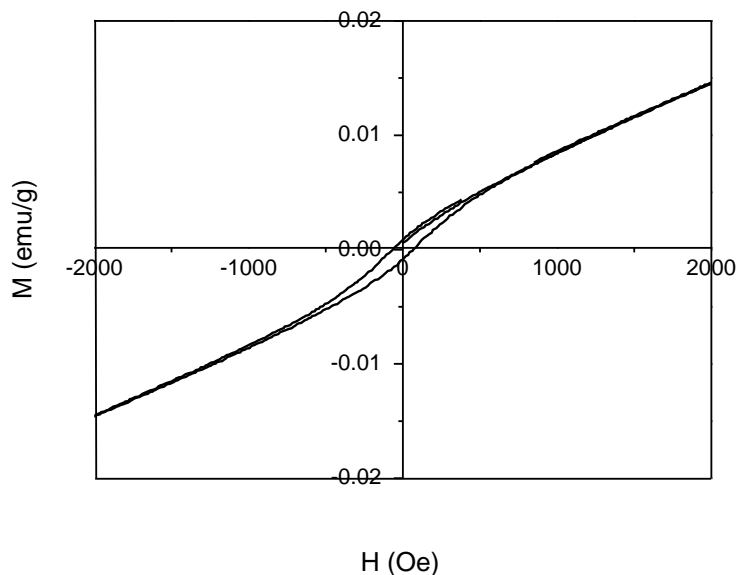

Figure 6 M-H hysteresis loops for $BiFeO_3$ at 300 K.

Table 3 The Magnetic properties are analysed out using Vibrating Sample Magnetometer (VSM). Hysteresis (M-H) loops are reported at room temperature (300 K).

Sample	H_c (Oe)	B_r (10^{-4} emu/g)
$BiFeO_3$	–65	8.5068
$0.7BiFeO_3$-$0.3Ba_5TbTi_3V_7O_{30}$	–1,206	180.57
$0.5BiFeO_3$-$0.5Ba_5TbTi_3V_7O_{30}$	–966	173.94
$0.3BiFeO_3$-$0.7Ba_5TbTi_3V_7O_{30}$	–612	139.99
$Ba_5TbTi_3V_7O_{30}$	0	0

Figure 7 shows the M-H hysteresis loops for the composite $(1-x)BiFeO_3$ - $xBa_5TbTi_3V_7O_{30}$ (for x = 0.3, 0.5, 0.7 and 1) at 300 K. It is being observed that even at very high applied magnetic field, there is no saturation of magnetization, indicating typical antiferromagnetic nature. The narrow loop of hysteresis curve suggests that magnetization is induced one and has canted antiferromagnetic order spins. The increases of $Ba_5TbTi_3V_7O_{30}$ in composite $BiFeO_3$ increases the spontaneous magnetic moment which may be due to statistical redistribution of ions Ti^{3+} and Fe^{3+} in the octahedral resulting into bulk magnetization and hence ferromagnetism [26]. For x = 0.3, there is maximum magnetization i.e. H_c ~ –1,206 Oe and B_r ~ 180.57×10^{-4} emu/g, thus the hysteresis loop is most developed. However, with further increase in x there is decrease in hysteresis loop area i.e. decrease in magnetization indicating system moves towards paramagnetic state having lower spontaneous moment. And for x = 1 ($Ba_5TbTi_3V_7O_{30}$) sample is pure paramagnetic in nature.
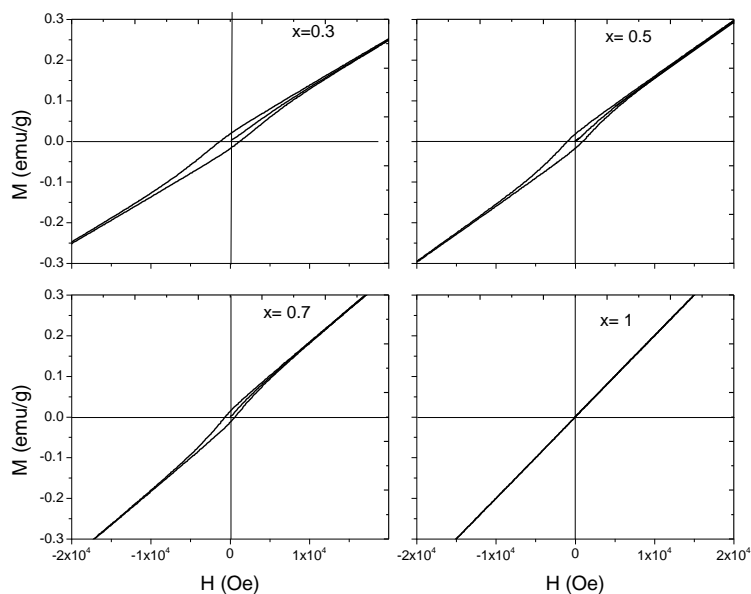
Figure 7 M-H hysteresis loops for $(1-x)BiFeO_3 - xBa_5TbTi_3V_7O_{30}$ at 300 K.

Conclusions

Ceramic composites $(1-x)BiFeO_3 - xBa_5TbTi_3V_7O_{30}$ having different x values is being prepared by high temperature solid state reaction method. XRD analysis shows that there is formation of composite phase consisting of $BiFeO_3$ and $Ba_5TbTi_3V_7O_{30}$. SEM study shows that there is increase in average grain size by increase in $Ba_5TbTi_3V_7O_{30}$ content in the composite. Dielectric studies show that dielectric constant increases with increase in the value of x i.e. by adding $Ba_5TbTi_3V_7O_{30}$ to $BiFeO_3$. Magnetic measurement shows that the remnant magnetization is maximum for x = 0.3.

Pure $BiFeO_3$ (x = 0) is antiferromagnetic and for x = 1 (pure $Ba_5TbTi_3V_7O_{30}$) is paramagnetic. Thus, it is concluded for x = 0.3 i.e. $0.7BiFeO_3 - 0.3Ba_5TbTi_3V_7O_{30}$, the composite has most effective magneto-electric coupling having moderate dielectric constant, and highest magnetization. So, the composite material $0.7BiFeO_3 - 0.3Ba_5TbTi_3V_7O_{30}$ could be considered as a very good multiferroic which can be used for construction of the nonvolatile dual storage memory devices exploring both the ferroelectric and ferromagnetic properties.

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