

Structural and Magnetic Properties of $(1-x)\text{Ba}_5\text{PrTi}_3\text{V}_7\text{O}_{30}-x\text{BiFeO}_3$

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ABSTRACT

Bismuth Ferrite (BiFeO_3) is a single phase Fe- based multiferroic having Perovskite structure. It shows both ferroelectric and ferromagnetism simultaneously in the single material. But the magnetic order is very low due to complex antiferromagnetic order yielding small remnant magnetization. However, Magnetic property could be improved if BiFeO_3 mixed with $\text{Ba}_5\text{PrTi}_3\text{V}_7\text{O}_{30}$ having TB-structure. Solid Solution $(1-x)\text{Ba}_5\text{PrTi}_3\text{V}_7\text{O}_{30}-x\text{BiFeO}_3$ is prepared by using Solid State Reaction technique for different values of x . Pellets are calcined at $\sim 750^\circ\text{C}$ then sintered at $\sim 800^\circ\text{C}$. Basic Crystal qualities and formation of single phase compound is confirmed by the XRD (X-Ray Diffractogram). The crystal structure is more or less constant i.e. Orthorhombic. However, further increase in x changes the crystal structure. For $x=0.7$ the system is Rhombohedral in structure. Grain morphology is being analysed by Scanning Electron Microscope (SEM: JOEL-IT300). Surface morphology shows that average grain size range from around $0.75\ \mu\text{m}$ to $2.10\ \mu\text{m}$. Average grain size is maximum for $x=0.3$ and minimum for $x=0$ (i.e. pure ferroelectric material). Magnetic measurement is done at a wide low temperature range (10-350K) by Physical Property Measurement System (PPMS: Quantum Design, San Diego, USA) Vibrating Sample Magnetometer (VSM). Hysteresis (M-H) loops are measured at room temperature (300K). It shows that the magnetization changes when the value of x changes. Remanence is maximum for $x=0.3$ and Coercivity is maximum for $x=0.7$. The material could be suitable to fabricate non volatile magnetic storage memory device.

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1. Introduction

Single phase multiferroics are usually Fe- or Mn- based oxides. Among all the multiferroic, Bismuth Ferrite (BiFeO_3) is the most popular one, because it can be easily manufactured in bulk and thin-film forms [1] and also it is the only material which demonstrates the multiferroic behaviour at room temperature. It shows both ferroelectric and (anti-)ferromagnetism coupling (coupling effect between electric and magnetization polarization might results into presence of both ferroelectric and ferromagnetic materials in a single material to generate coupling properties) between the two order parameters i.e. charge and spin respectively. It has Neel temperature ($\sim 643\ \text{K}$) [2], [3], [4] and Curie temperature ($\sim 1100\ \text{K}$) [5] which is above the room temperature. BiFeO_3 is a rhombohedral ferroelectric [6], ferroelastic in nature in the temperature range from low temperature to 810°C and has a remunerated antiferromagnet having cycloidal spin with Neel temperature of 370°C . However, its complex antiferromagnetic ordering yields small remnant magnetization.

Bismuth ferrite (BiFeO_3) is ferroelectric in nature with Fe^{3+} ions having magnetic properties and its Bi ion with lone pair electrons in the 6s orbital which moves away from the center-symmetric location

(surrounded by oxygens). BiFeO₃ has a non-centrosymmetric rhombohedrally distorted perovskite structure [7], [8] having space group R3c [9]. The mechanism is stereochemical activity of the Bi³⁺ 6s² lone pair; there is a transfer of a charge from 6s² to properly empty 6p orbitals. The presence of weak ferromagnetic is may be due to residual moment of the canted Fe³⁺ spin structure. Magnetic and electric coupling occurs because of lattice distortion of BiFeO₃ [10].

Various Literature reports mixing BiFeO₃ having perovskite structure [11] with same structural family (having ferroelectrics properties) [12], [13], [14] to improve the ferroelectric properties of BiFeO₃ [15]. In our study we have tried to explore the possibility of mixing BiFeO₃ with Ba₅PrTi₃V₇O₃₀ of different structural family (TB-structure) [16], [17] and to see if there is any enhancement in the magnetic property in the system. The reason behind the selection of TB structure is that it has more open structure in comparison to that of perovskite structure, which might allow wide cation and anion substitution resulting into improved magnetic and ferroelectric properties.

2. Material and Method

(1-x)BiFeO₃-xBa₅PrTi₃V₇O₃₀ (x = 0, 0.3, 0.5, 0.7, 1) solid solution are developed using solid state reaction technique. The starting materials are mixed stoichiometrically and calcined at ~750 °C for around 12 h at rate of about 1 °C/min. The calcined powders are then mixed with a small amount of PVB (polyvinyl butyral) as a binder and then pressed as disks in a stainless steel die under an external pressure of ~7 tons to make pellets having 1-2 mm thickness and 12-13 mm diameter. Pellets are then sintered at ~800 °C for about 6 h followed by cooling at ~2°C/min. Formation of the crystalline phase are confirmed by X-ray diffractogram (Rigaku, Miniflex) with CuK α radiation of wavelength =1.5405 Å in the range of Bragg's angles 2 θ (10° < θ < 60°) with scanning rate of 3°/min. Surface morphologies are studied using Scanning electron microscope (SEM: JOEL-IT300). Both sides of sintered pallets are polished and electrode by applying silver paste. Dielectric properties are analyzed using Impedance Analyzer (HIOKI-IM3536). Magnetic measurement of the solid solution is carried out by using a Physical Property Measurement System (PPMS: Quantum Design, San Diego, USA) Vibrating Sample Magnetometer (VSM) at a wide temperature range of (10-350K). Hysteresis (M-H) loops are reported at room temperature (300K).

3. Result and Discussion

3.1 Structure

The lattice parameters are calculated by using X'perthighscore software. From the Table I, it can be seen that the crystal structure of the system remains more or less constant i.e. orthorhombic. However, with further addition BiFeO₃ there is change in crystal structure i.e. for x = 0.5, i.e. when the system contains 50% of BiFeO₃ in the solid solution the crystal structure of the system is Tetragonal. The structural change in the crystal system with addition BiFeO₃ is may be due to the reason that oxygen octahedron undergoes distortion due to mechanical stresses caused by the increase in the percentage of BiFeO₃. For x= 0.7, the system is Rhombohedral in structure which is in alignment towards x = 1 (i.e. pure BiFeO₃ is Rhombohedral) [18].

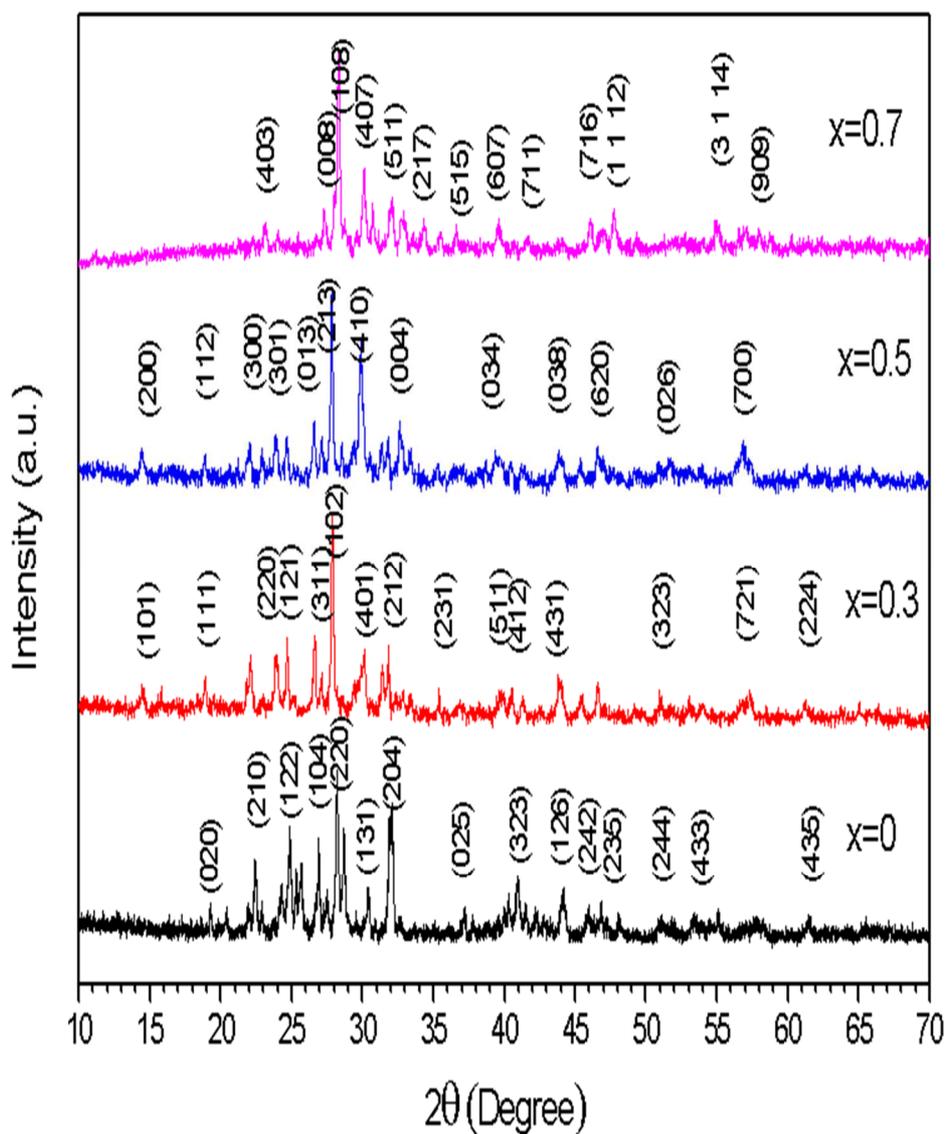


Figure 1. XRD pattern for $(1-x)\text{Ba}_5\text{PrTi}_3\text{V}_7\text{O}_{30-x}\text{BiFeO}_3$

Table 1. Comparison of lattice parameters (\AA), particle size (P) (in \AA) and volume (\AA^3) SEM (in μm).

	a	b	c	V	Structure	SEM grain size
$x=0.7$	12.54	6.58	6.58	1196.20	Rhombohedral	~ 2.10
$x=0.5$	12.10	12.10	11.09	1625.72	Tetragonal	~ 2.27
$x=0.3$	17.47	4.41	25.39	1957.56	Orthorhombic	~ 3.63
$x=0$	8.81	9.20	14.26	1157.41	Orthorhombic	~ 0.75

3.2 Microstructure

SEM micrographs of $(1-x)\text{Ba}_5\text{PrTi}_3\text{V}_7\text{O}_{30}-x\text{BiFeO}_3$ for $x=0, 0.3, 0.5$ and 0.7 is shown in Figure 2 (a-d). The grain growth is more or less complete. The average grain size is measured using linear intercept method and shown in Table I. With the increase of the BiFeO_3 content in the solid solution, there is the appearance of columnar shape grains. It may be due to the reason that there may be loss of Bi_2O_3 during high temperature processing resulting into porosity or it may be due to the small amount of impurity phases present in BiFeO_3 .

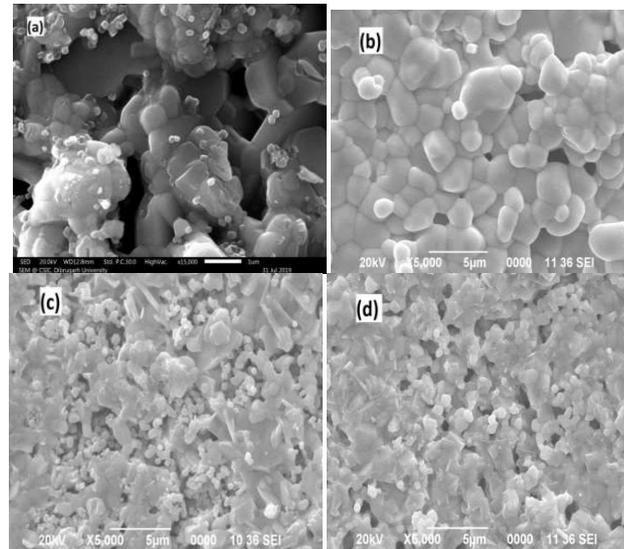


Figure 2. SEM micrographs of $(1-x)\text{Ba}_5\text{PrTi}_3\text{V}_7\text{O}_{30}-x\text{BiFeO}_3$ (a) $x=0$ (b) $x=0.3$ (c) $x=0.5$ (d) $x=0.7$

3.3 Magnetization Study

Figure 3 shows the hysteresis curves for BiFeO_3 (i.e. $x=1$ in the solid solution). The curve does not saturate even at high applied magnetic field indicating typical anti-ferromagnetic behaviour [19]. From Table II it can be seen that the Hysteresis loop of BiFeO_3 has low value of $H_c \sim -65$ Oe and $B_r \sim 8.5068 \times 10^{-4}$ emu/g signifying weak ferromagnetic nature [20]. The occurrence of hysteresis loops is due to canting of Fe-O-Fe Chains (antiferromagnetic order) causing weak spontaneous moment. Low value of magnetic moment and non-saturation of magnetization even at external high magnetic field is may be due to the uncompensated antiferromagnetism.

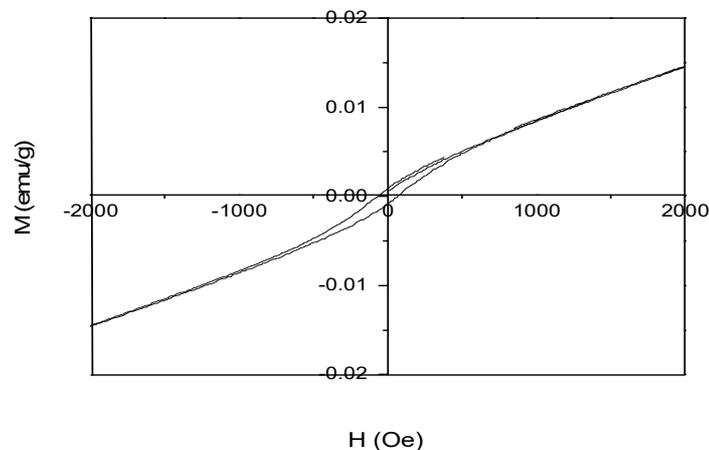


Figure 3. M-H hysteresis loops for BiFeO_3 at Room Temperature.

Figure 4 shows the Hysteresis loop of $(1-x)\text{Ba}_5\text{PrTi}_3\text{V}_7\text{O}_{30}-x\text{BiFeO}_3$ for $x = 0, 0.3, 0.5$ and 0.7 at the room temperature. It can be seen that as the BiFeO_3 content in the solid solution is increased the loop starts appearing. From Table II it can be seen that the Remanence ($M_r = 118.4 \times 10^{-4}$ emu/g) is maximum for $x=0.3$ i.e. $0.7\text{Ba}_5\text{TbTi}_3\text{V}_7\text{O}_{30}-0.3\text{BiFeO}_3$ and Coercivity ($H_c = -1206$ Oe) is maximum for $x=0.7$ i.e. $0.3\text{Ba}_5\text{TbTi}_3\text{V}_7\text{O}_{30}-0.7\text{BiFeO}_3$. Literature reports that mixing of BiFeO_3 of perovskite structure with different ferroelectrics with same structural family improves the ferroelectrics and magnetic property. When we mixed BiFeO_3 with $\text{Ba}_5\text{PrTi}_3\text{V}_7\text{O}_{30}$ of TB-structural family having Orthorhombic structure (From Table II) there is enhance magnetic property which may be due to distortion of perovskite structure resulting into breaking of antiferromagnetism order of BiFeO_3 .

For $x = 0$, i.e. (Pure $\text{Ba}_5\text{PrTi}_3\text{V}_7\text{O}_{30}$) the system has negligible magnetization and for practical purpose could be considered as pure paramagnetic in nature.

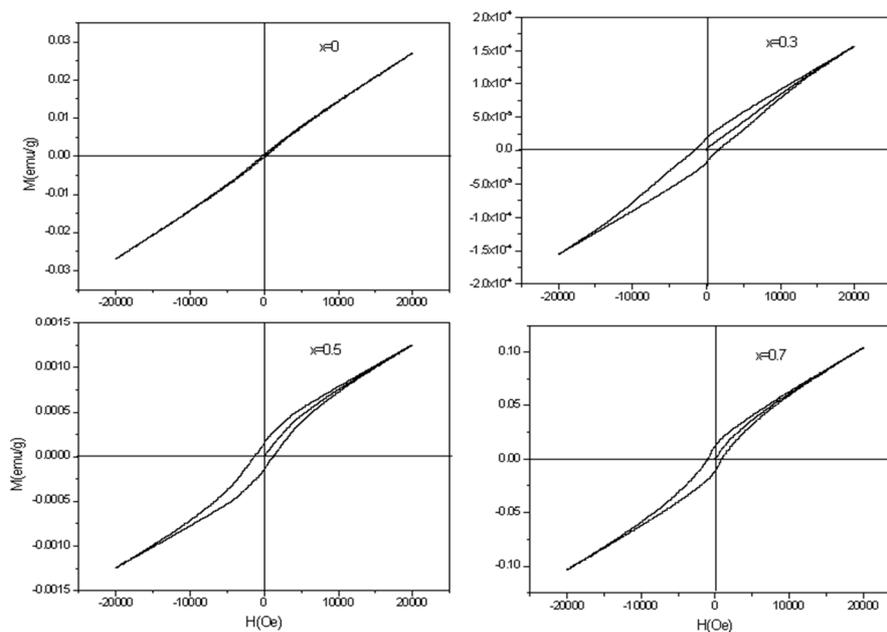


Figure 4. M-H hysteresis loops for $x\text{BiFeO}_3-(1-x)\text{Ba}_5\text{PrTi}_3\text{V}_7\text{O}_{30}$ at Room Temperature.

Table 2. The values of the parameters obtained at Room Temperature

	H_c (Oe)	$M_r(10^{-4}\text{emu/g})$
$x=1$	-65	8.50
$x=0.7$	-1527	18.00
$x=0.5$	-1223.92	1.49
$x=0.3$	-964.59	118.4

4. Conclusion

When Perovskite Structure (i.e. BiFeO_3) is mixed with TB-structure (i.e. $\text{Ba}_5\text{PrTi}_3\text{V}_7\text{O}_{30}$) it was found that there is enhance magnetic property in the system which may be due to distortion of perovskite structure resulting into breaking of antiferromagnetism order of BiFeO_3 . Remanence ($M_r = 118.4 \times 10^{-4}$ emu/g) is maximum for $x=0.3$ i.e. $0.7\text{Ba}_5\text{TbTi}_3\text{V}_7\text{O}_{30}-0.3\text{BiFeO}_3$ and Coercivity ($H_c = -1206$ Oe) is maximum for $x=0.7$ i.e. $0.3\text{Ba}_5\text{TbTi}_3\text{V}_7\text{O}_{30}-0.7\text{BiFeO}_3$. The material could be suitable for construction of the non volatile magnetic storage memory device.

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