

ELECTRICAL AND MAGNETIC PROPERTIES OF THE PRASEODYMIUM DOPED MULTIFERROIC COMPOSITES

Abstract

In this study Solid solution of $(\text{Ba}_5\text{PrTi}_3\text{V}_7\text{O}_{30})_{1-x}(\text{BiFeO}_3)_x$ for different values of x is fabricated using a high-temperature solid-state reaction technique. Basic crystal qualities are analyzed using XRD (X-Ray Diffraction). For $x = 0.5$, the crystal structure of the composite is Tetragonal. From SEM (SEM: JOEL-IT300) study it is found that there is an emergence of columnar shape grains as the content of BiFeO_3 increases in the composite. Electrical properties such as Dielectric constant and loss tangent at various frequencies (4Hz-1000Hz) and at wide temperature ranges (RT-500°C) are measured using an Impedance analyzer (HIOKI-IM3536). All the sample was found to have ferroelectric characters and as BiFeO_3 content increases the dielectric constant was found to decrease and the loss tangent increased. Magnetic measurement is done using PPMS (Physical Property Measurement System) Vibrating Sample Magnetometer (VSM) at a temperature range (of 10-350K). B-H hysteresis loop was detected at room temperature. It was found that the dielectric characteristic and magnetic property of solid solution improves when it is mixed with a ferroelectric material.

Keywords: Dielectric Constant, Loss tangent, Magnetization, VSM.

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I. INTRODUCTION

Multiferroic materials and/or magneto-electric materials have multiform properties in the single phase i.e., they may exhibit both magnetic and electric order in a single phase. The characteristics of having spontaneous electrical and magnetic order have a wide range of probable applications as sensors [1], spintronic devices, data storage media, actuators, dual storage devices (electrical and magnetic polarization can be used for storing data as RAM) and multiple state storage/memories. It has been found that the magnetically ordered state is good for storing data but controlling the states of magnetic fields for application is complicated. However, the electric voltage is much easier to be controlled at the microscopic level; hence device, where the magnetic state is being controlled electrically, has more utility. In such devices, electric voltages switch the ferroelectric state which in turn switches the magnetic state.

There exist only very few single-phase multiferroics at room temperature. It is because ferroelectric materials by nature are polarized and insulators whereas magnetic materials are mostly found to be conducting in nature. In addition to that leakages of impurities or atoms in material severely weaken the ferroelectric properties even if the material is an insulator.

Bismuth ferrite (BiFeO_3) is one such kind of multi-ferroelectric material. It has a non-centrosymmetric rhombohedral distorted perovskite structure [2,3] with an $R3c$ space group [4]. It exhibits complex magnetic behavior due to magnetic interactions among Fe^{3+} ion and its Bi ion mediated by oxygen surroundings.

S. Chandarak et al. [5] studied dielectric properties of ferroelectrics mixed with Bismuth Ferrite composite i.e. $(\text{BaTiO}_3)_x(\text{BiFeO}_3)_{1-x}$ and found that the dielectric characteristics significantly improve with the addition of BaTiO_3 ; the increase in values of dielectric constant is because of giant-dielectric characters which are due to the multivalent states effect of Fe ion and as BaTiO_3 content increases; ceramic density grain packing improves; also BaTiO_3 - BiFeO_3 ceramics shows giant-dielectric like property identical to that of BiFeO_3 .

Nalwa et al. studied the rare earth-doped Bismuth Ferrite and found that there is an increase in the remnant polarization in the rare earth BiFeO_3 sample but also associated with high conductivity [6].

In our earlier work, we mixed Tb-doped vanadate ferroelectrics with Bismuth Ferrite and found that there is an enhanced magnetization [7] in the composite along with a decrease in electrical conductivity [8] of the BiFeO_3 sample. In our present study, we aim to mix Pr-doped vanadate ferroelectrics with BiFeO_3 to fabricate a solid solution of $(\text{Ba}_5\text{PrTi}_3\text{V}_7\text{O}_{30})_{1-x}(\text{BiFeO}_3)_x$ composite for different values of x and study the electric and magnetic properties of the material.

II. MATERIALS AND METHODS

Solid state reaction technique is used to prepare a $(\text{Ba}_5\text{PrTi}_3\text{V}_7\text{O}_{30})_{1-x}(\text{BiFeO}_3)_x$ composite. The required material is mixed at appropriate proportion and calcined at

temperature $\sim 750\text{ }^\circ\text{C}$ (at a rate of $\sim 1\text{ }^\circ\text{C}/\text{min}$) for about 12 h. Polyvinyl Butyral is put in small amount as a binder into the processed powder then using die pressed by ~ 7 tons to fabricate a pellet having dimensions ~ 2 mm thickness and ~ 13 mm diameter. Samples are sintered at $\sim 800\text{ }^\circ\text{C}$ for 6 h and then cooled by $\sim 2\text{ }^\circ\text{C}/\text{min}$. Crystalline phase formation is analyzed by X-ray powder diffraction with Cu- K_α radiation ($\lambda = 1.5405\text{ \AA}$) within the Bragg's angles range ($10^\circ \leq \theta \leq 60^\circ$) having a rate of scanning $3^\circ/\text{min}$. The morphology of the sample is studied by SEM (JOEL-IT300). Processed samples are made electrodes by finely polishing and applying a paste of silver on the top and bottom surfaces. The dielectric characteristics are studied by HIOKI-IM3536 (Impedance Analyzer). Magnetic measurements were carried out with a vibrating sample magnetometer in Physical Property Measurement System (Quantum Design, San Diego, USA) at low temperatures (10-350K). Hysteresis (B-H) curves are measured at normal temperature (300K).

III. RESULTS AND DISCUSSION

1. Structural Studies: Using X'pert highscore software the lattice parameters are obtained. The crystal system is more Orthorhombic in nature as can be seen in Table 1. However, as x increases further there is a shift in the structure. When $x = 0.5$, (i.e., 50% of BiFeO_3) crystal structure of the sample is Tetragonal. The change in the structure of the addition of BiFeO_3 may be due to the distortion in oxygen octahedra caused by mechanical stress caused by the addition of BiFeO_3 . For $x = 0.7$, (i.e. 70% of BiFeO_3) the crystal structure of the solid solution is Rhombohedral which is similar in structure to $x = 1$ (i.e. pure BiFeO_3 is Rhombohedral) [9].

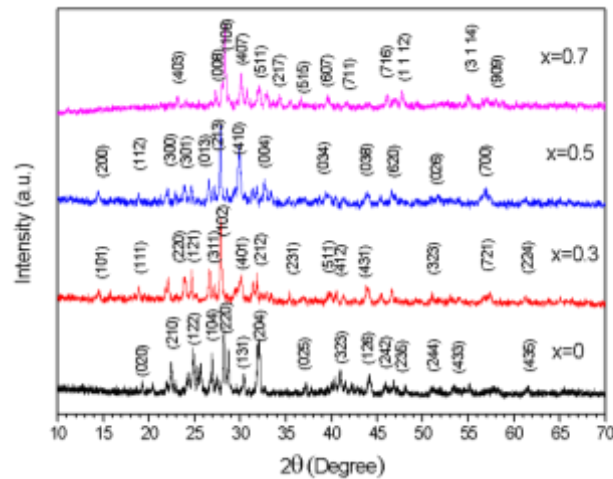


Figure 1: XRD pattern for $(\text{Ba}_5\text{PrTi}_3\text{V}_7\text{O}_{30})_{1-x}(\text{BiFeO}_3)_x$

Table 1: Lattice parameters (in \AA), volume (\AA^3), Structure and Grain Size (in μm) for $(\text{Ba}_5\text{PrTi}_3\text{V}_7\text{O}_{30})_{1-x}(\text{BiFeO}_3)_x$

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

2. **Micro Structural Studies:** SEM micrographs of $(\text{Ba}_5\text{PrTi}_3\text{V}_7\text{O}_{30})_{1-x}(\text{BiFeO}_3)_x$ for $x = 0, 0.3, 0.5$ and 0.7 is shown in Figure 2 (a-d). The grain growth is found to be more or less complete. The grain size is determined using the linear intercept method as shown in Table 1. It was found that as the BiFeO_3 content increases, columnar shape grains start appearing because of the loss of Bismuth Oxide (Bi_2O_3) when the temperature is high. The presence of porosity may be because of the presence of some impure phases of BiFeO_3 .

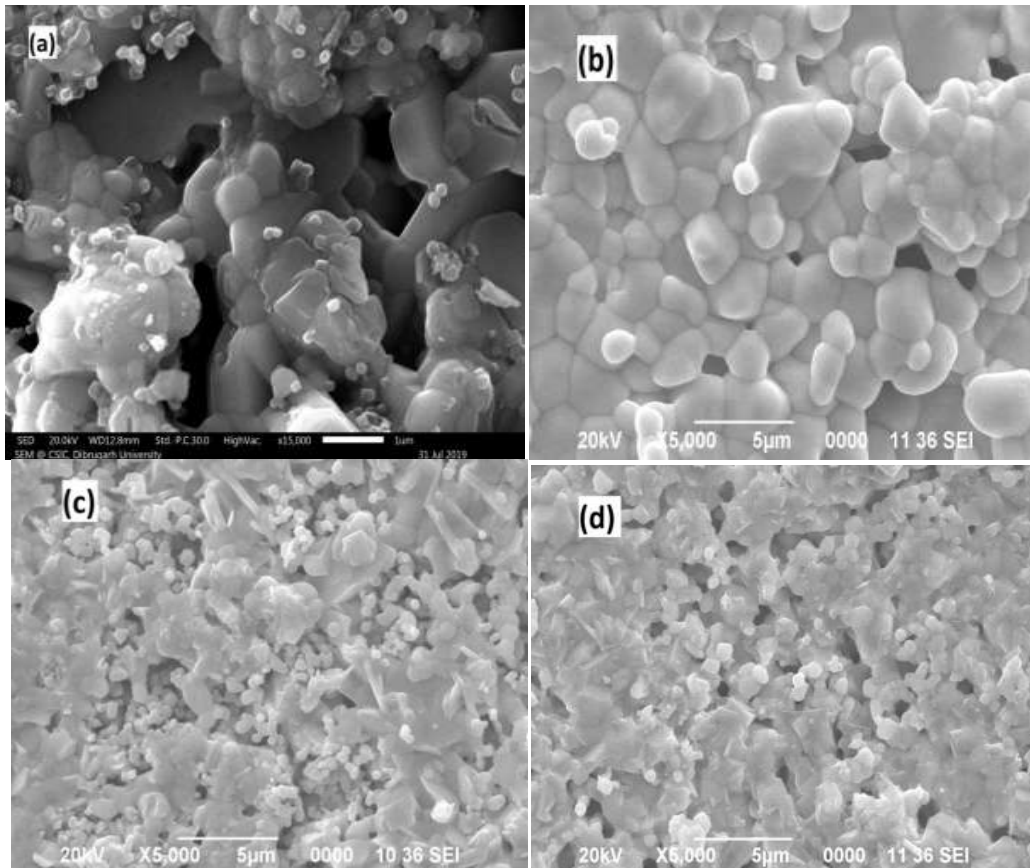


Figure 2: SEM images of $(\text{Ba}_5\text{PrTi}_3\text{V}_7\text{O}_{30})_{1-x}(\text{BiFeO}_3)_x$ for $x = 0, 0.3, 0.5, 0.7$

3. **Dielectric Studies:** From Figure 3, it can be seen that for $(\text{Ba}_5\text{PrTi}_3\text{V}_7\text{O}_{30})_{1-x}(\text{BiFeO}_3)_x$ at normal temp, in the frequency range from 4Hz to 10kHz, the ϵ_r decreases with an increase in frequency which is as expected of any characteristic dielectric materials. It was found that with an increase in the content of BiFeO_3 the value of the dielectric constant decreases for any given value of frequency. It may be due to the presence of conducting metallic ions such as Fe ion in the composite resulting in an increase in conductivity and hence a decrease in dielectric constant.

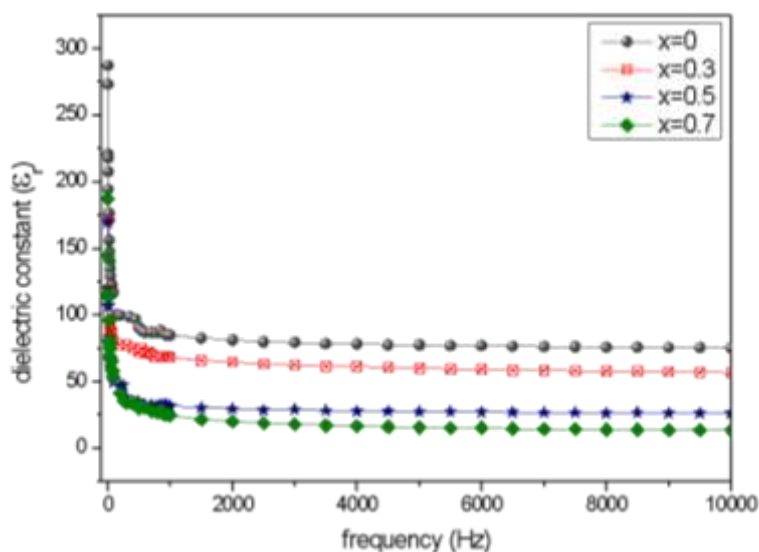


Figure 3: Frequency variation of ϵ_r for $(\text{Ba}_5\text{PrTi}_3\text{V}_7\text{O}_{30})_{1-x}(\text{BiFeO}_3)_x$ in RT.

From Figure 4 it can be seen that for $(\text{Ba}_5\text{PrTi}_3\text{V}_7\text{O}_{30})_{1-x}(\text{BiFeO}_3)_x$ at normal temp. at the frequency range from 4Hz to 10kHz, there is a decrease in tangent loss ($\tan\delta$) which is also expected for characteristic dielectric materials. With the increase in the content of BiFeO_3 tangent loss also increases for any given value of frequency which may be because of the presence of Fe ions in BiFeO_3 resulting in semiconducting nature.

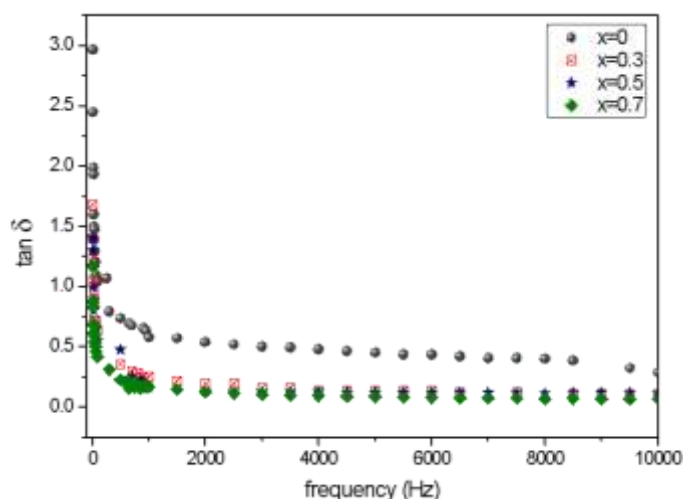


Figure 4: Frequency variation of $\tan\delta$ of $(\text{Ba}_5\text{PrTi}_3\text{V}_7\text{O}_{30})_{1-x}(\text{BiFeO}_3)_x$ at RT.

For $(\text{Ba}_5\text{PrTi}_3\text{V}_7\text{O}_{30})_{1-x}(\text{BiFeO}_3)_x$ at temperature range (RT- 500°C) for a particular frequency of 1kHz with the rise in temperature the value of dielectric constant also increases and after attaining the peak (at transition temperature T_C) it decreases as shown in Figure 5. It may be because of the contribution of dipole orientation of charges and long-range migration effect. With further increases in temperature, it is found that the

relative dielectric constant rises rapidly. It may be due to the reason that at high temperatures there is the creation and dominance of space charge polarization.

At transition temperature pure ferroelectric material (i.e., $\text{Ba}_5\text{PrTi}_3\text{V}_7\text{O}_{30}$) has a dielectric constant (ϵ_{max}) ~ 377 which decreases with the addition of semiconducting nature material i.e., BiFeO_3 . At room temperature, the dielectric constant of the pure ferroelectric is more than any of the other mixed composites. However, at a much higher temperature, the relative dielectric constant keeps on increasing at an exponential rate whereas, for pure ferroelectric material, it decreases. The exponential increase of dielectric constant at high temperatures may be due to the breaking up of Fe-O-Fe chains due to thermal agitation.

Also, the introduction of $\text{Ba}_5\text{PrTi}_3\text{V}_7\text{O}_{30}$ having orthorhombic TB phase into Rhombohedral perovskite phase BiFeO_3 results in stabilization of perovskite phase and formation of morphotropic phase boundary (MPB) causing a decrease in the electrical conductivity of BiFeO_3 and hence a good ferroelectric material.

Thus, the dielectric characteristic of BiFeO_3 is enhanced when it is mixed with a ferroelectric material such as $\text{Ba}_5\text{PrTi}_3\text{V}_7\text{O}_{30}$.

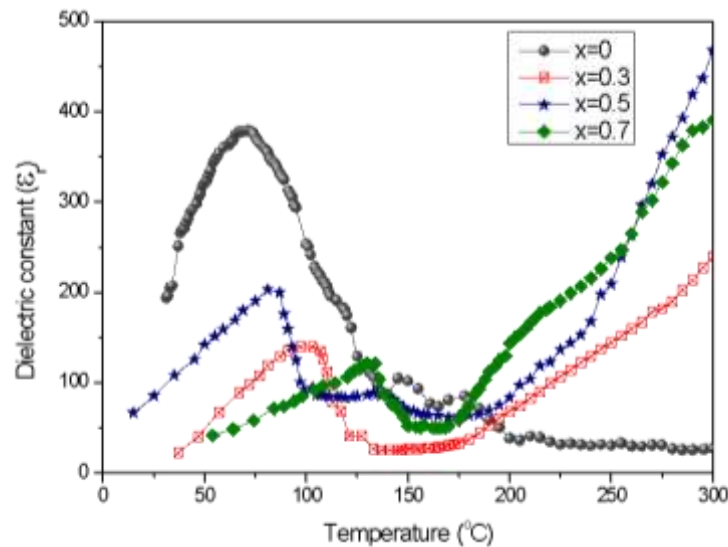


Figure 5: Variation of ϵ_r with temp for $(\text{Ba}_5\text{PrTi}_3\text{V}_7\text{O}_{30})_{1-x}(\text{BiFeO}_3)_x$ at 1kHz.

For $(\text{Ba}_5\text{PrTi}_3\text{V}_7\text{O}_{30})_{1-x}(\text{BiFeO}_3)_x$ at 1kHz in the temperature range ($RT- 500^\circ\text{C}$) it can be seen from Figure 6 that with an increase in temperature there is very little change in loss tangent ($\tan \delta$) for pure ferroelectric whereas for a mixed composite loss tangent ($\tan \delta$) rises sharply with increase in temperature.

A sharp rise in temperature at high temperatures with the addition of BiFeO_3 may be due to the predominance of Fe ions resulting from the breaking of the Fe-O-Fe bond resulting in cascading conductivity effect and hence a high loss tangent ($\tan \delta$).

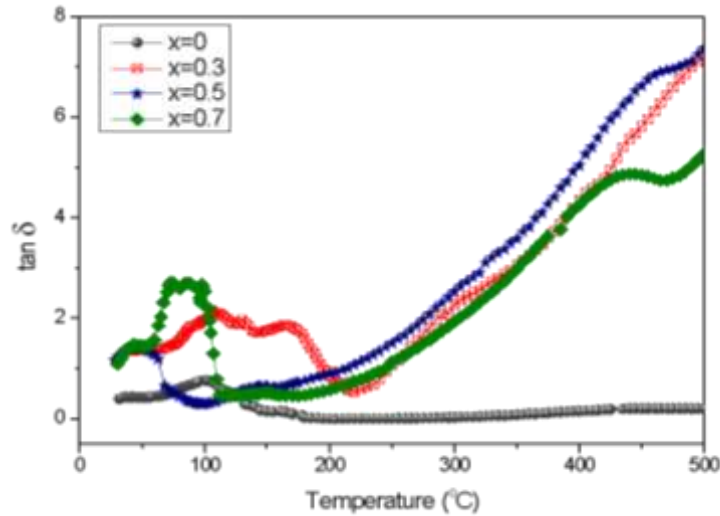


Figure 6: Plot of $\tan \delta$ vs temperature for $(\text{Ba}_5\text{PrTi}_3\text{V}_7\text{O}_{30})_{1-x}(\text{BiFeO}_3)_x$.

Table 2 Dielectric properties for $(\text{Ba}_5\text{PrTi}_3\text{V}_7\text{O}_{30})_{1-x}(\text{BiFeO}_3)_x$ at 1kHz.

$(\text{Ba}_5\text{PrTi}_3\text{V}_7\text{O}_{30})_{1-x}(\text{BiFeO}_3)_x$	ϵ_{RT}	ϵ_{max}	$\tan \delta_{RT}$	$\tan \delta_{max}$	$T_c(^{\circ}\text{C})$
x= 0	194	377	0.38	0.76	70
x=0.3	86	205	1.07	1.39	84
x= 0.5	22	141	0.59	2.19	99
x= 0.7	31	121	1.02	2.74	129

- 4. Magnetization Studies:** From B-H hysteresis curves of BiFeO_3 as shown in Figure 7 it can be seen that there is no saturation of Magnetization even on application of a high magnetic field indicating characteristic anti-ferromagnetic behaviour [10]. It can be seen from Table 3 that BiFeO_3 has low $B_r \sim 8.5068 \times 10^{-4}$ emu/g and $H_c \sim -65$ Oe suggesting weak ferromagnetic nature [11]. The occurrence of a hysteresis loop may be due to canted Fe-O-Fe chains ensuing weak spontaneous magnetic moments. Non-saturation of magnetization and low magnetic moment may be because of uncompensated anti ferromagnetic character.

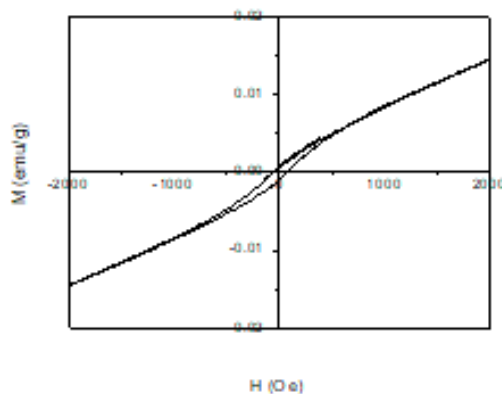


Figure 7: B-H hysteresis curves for BiFeO_3 at Normal Temperature.

From the B-H hysteresis curve of $(\text{Ba}_5\text{PrTi}_3\text{V}_7\text{O}_{30})_{1-x}(\text{BiFeO}_3)_x$ for $x = 0, 0.3, 0.5$ and 0.7 at the normal temperature as shown in Figure 8. As BiFeO_3 is introduced into the solid solution the loop starts appearing. Coercivity ($H_c = -1206$ Oe) maximum for $x=0.7$ and Retentivity ($B_r = 118.4 \times 10^{-4}$ emu/g) was found to be maximum for $x=0.3$ as can be seen from Table 3. When the Rhombohedral perovskite structured BiFeO_3 is mixed with the Orthorhombic TB- structured $\text{Ba}_5\text{PrTi}_3\text{V}_7\text{O}_{30}$ there is mechanical stress resulting in distortion of anti ferromagnetic order of Fe-O-Fe chains of BiFeO_3 and introduction of diamagnetic Ti^{4+} into sites of perovskite phase of BiFeO_3 results into dilution of the concentration of paramagnetic Fe^{3+} ions causing the development of weak ferromagnetism. Pure $\text{Ba}_5\text{PrTi}_3\text{V}_7\text{O}_{30}$ (i.e., $x = 0$), has paramagnetic characteristics.

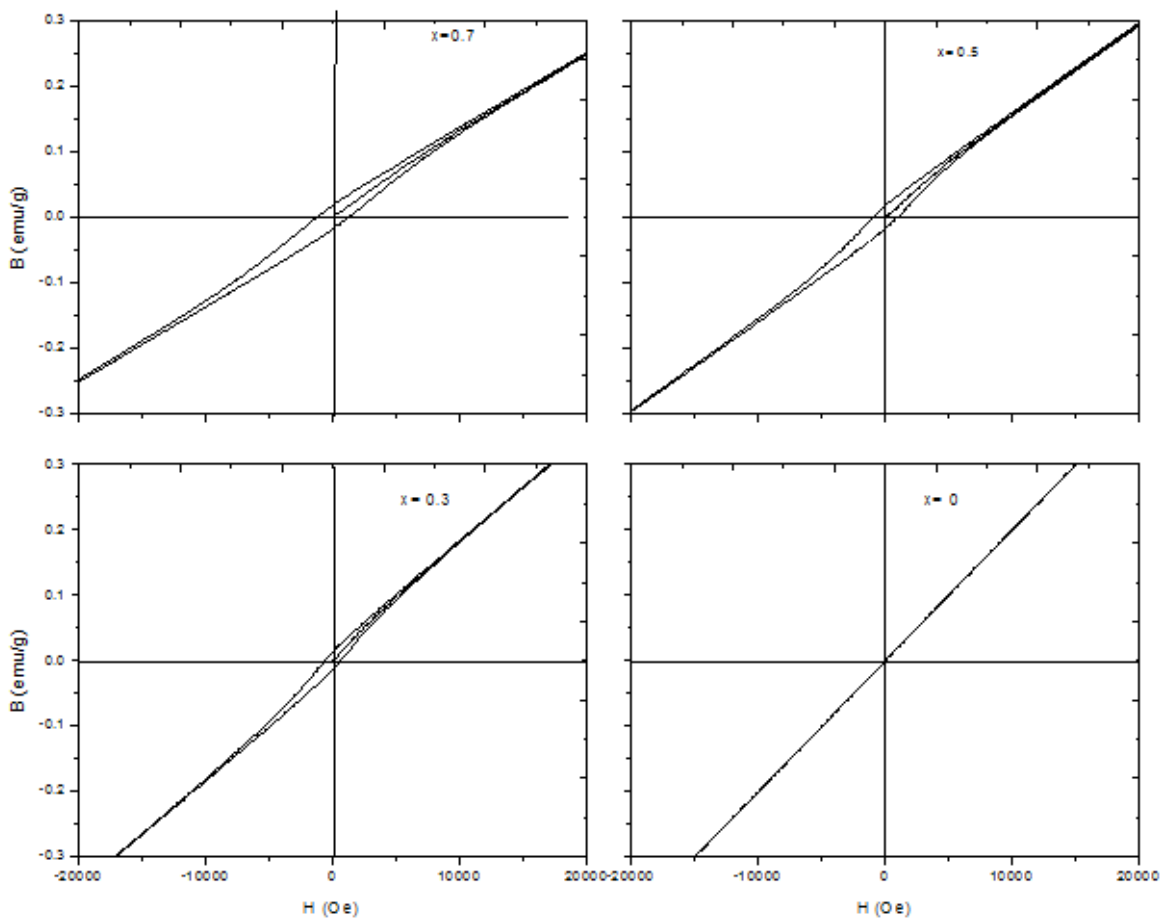


Figure 8: B-H hysteresis curves for $(\text{Ba}_5\text{PrTi}_3\text{V}_7\text{O}_{30})_{1-x}(\text{BiFeO}_3)_x$ at normal temperature.

Table 3: Magnetic parameters obtained for $(\text{Ba}_5\text{PrTi}_3\text{V}_7\text{O}_{30})_{1-x}(\text{BiFeO}_3)_x$ at RT.

$(\text{Ba}_5\text{PrTi}_3\text{V}_7\text{O}_{30})_{1-x}(\text{BiFeO}_3)_x$	H_c (Oe)	$B_r(10^{-4}$ emu/g)
x=0.3	-964.596	118.4
x=0.5	-1223.92	1.4918
x=0.7	-1527	18.00
x=1	-65	8.5068

IV. CONCLUSION

The introduction of $\text{Ba}_5\text{PrTi}_3\text{V}_7\text{O}_{30}$ into BiFeO_3 introduces a change in crystal systems which might have stabilized the perovskite phase and resulted in the formation of morphotropic phase boundary (MPB) causing a change in the electric properties of BiFeO_3 (electric conductivity decreases hence better ferroelectric material). The magnetic properties also improve with enhanced remnant magnetization which might be due to dilution in the concentration of paramagnetic Fe^{3+} ions and breaking of anti ferromagnetic order resulting in weak ferromagnetic material.

Thus, the dielectric characteristic and magnetic property of BiFeO_3 improve when it is mixed with a ferroelectric material i.e., $\text{Ba}_5\text{PrTi}_3\text{V}_7\text{O}_{30}$.

REFERENCES

- [1] Eerenstein W, Mathur ND, Scott JF. Multiferroic and magnetoelectric materials. *nature*. 2006 Aug;442(7104):759-65.
- [2] Andres J, Simões AZ, Aguiar EC, Gonzalez AH, Longo E, Varela JA. Strain behavior of lanthanum modified BiFeO_3 thin films prepared via soft chemical method.
- [3] Kubel F, Schmid H. Structure of a ferroelectric and ferroelastic monodomain crystal of the perovskite BiFeO_3 . *Acta Crystallographica Section B: Structural Science*. 1990 Dec 1;46(6):698-702.
- [4] Michel C, Moreau JM, Achenbach GD, Gerson R, James WJ. The atomic structure of BiFeO_3 . *Solid State Communications*. 1969 May 1;7(9):701-4.
- [5] Chandarak S, Ngamjarrojana A, Srilomsak S, Laoratanakul P, Rujirawat S, Yimnirun R. Dielectric properties of BaTiO_3 -modified BiFeO_3 ceramics. *Ferroelectrics*. 2010 Nov 2;410(1):75-81.
- [6] Nalwa KS, Garg A, Upadhyaya A. Effect of samarium doping on the properties of solid-state synthesized multiferroic bismuth ferrite. *Materials Letters*. 2008 Mar 15;62(6-7):878-81.
- [7] Doley H, Swain PK, Panigrahi A, Tado GT. Structural and ferroelectric properties in the solid solution $(\text{Ba}_5\text{TbTi}_3\text{V}_7\text{O}_{30})_x (\text{BiFeO}_3)_{1-x}$. *Ferroelectrics*. 2020 Nov 17;568(1):104-11.
- [8] Doley H, Swain PK, Panigrahi A. Modulating the magnetic properties of BiFeO_3 by addition of $\text{Ba}_5\text{TbTi}_3\text{V}_7\text{O}_{30}$. *Processing and Application of Ceramics*. 2020;14(4):277-81.
- [9] Moreau JM, Michel C, Gerson R, James WJ. Ferroelectric BiFeO_3 X-ray and neutron diffraction study. *Journal of Physics and Chemistry of Solids*. 1971 Jan 1;32(6):1315-20.
- [10] Rout J, Choudhary RN, Sharma HB, Shannigrahi SR. Effect of co-substitutions (Ca–Mn) on structural, electrical and magnetic characteristics of bismuth ferrite. *Ceramics International*. 2015 Aug 1;41(7):9078-87.
- [11] Rout J, Choudhary RN, Shannigrahi SR, Sharma HB. Structural, Electrical, and Magnetic Properties of Mechanosynthesized $(1-x) \text{BiFeO}_3-x\text{BaMnO}_3$ ($0 \leq x \leq 0.15$) Multiferroic System. *Journal of Electronic Materials*. 2015 Oct;44(10):3811-8.