

Study of Electrical and Magnetic Properties of Multiferroic Composite $(\text{BiFeO}_3)_x(\text{Ba}_5\text{RTi}_3\text{V}_7\text{O}_{30})_{1-x}$



Hage Doley, Anuradha Panigrahi and Pinaki Chakraborty

Abstract Polycrystalline Samples of the composite $(\text{BiFeO}_3)_x(\text{Ba}_5\text{RTi}_3\text{V}_2\text{O}_{30})_{1-x}$ (R—Rare Earth Element) is prepared by high-temperature Solid-State Reaction Technique. The formation of the material has been confirmed through XRD (X-ray Diffractometer) to ensure the single-phase formation. Dielectric characterization has been done by Impedance Analyser (HIOKI-IM3536) to study the variation of dielectric constant with frequency and temperature in a wide range to see the dielectric anomaly. Magnetization study is also done by Vibration Magnetometer for different values of x in the composite $(\text{BiFeO}_3)_x(\text{Ba}_5\text{RTi}_3\text{V}_2\text{O}_{30})_{1-x}$.

Keywords Dielectric · Impedance analyzer · Neel temperature magnetization XRD

1 Introduction

In 1957, Royen and Swares synthesized a material BiFeO_3 which is single-phase material exhibiting both ferroelectric and ferromagnetism in the same material popularly known as multiferroic (smart material) [1]. These materials can be used for fabrication of multifunctional electronics and communication devices such as multiple state memories (new-generation RAM), data storage media, [2] transducers, sensors, and spintronic devices. Among many multiferroic materials, BiFeO_3 is found to be the most significant because it exhibits its multiferroic properties at and above room temperature. It has a high paraelectric/ferroelectric transition temperature $T_c = 1100$ K [3] and a high Neel temperature $T_N = 643$ K. Unfortunately, this compound has high leakage current and low dielectric constant and high loss tangent. Due to

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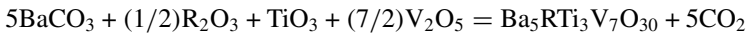
this limitation, it is not very suitable for device application. This problem can be solved by mixing pure ferroelectric material with this multiferroic BFO in a suitable proportion. A proper coupling can be established between the electric and magnetic order making it more suitable for use as a multiple state memories and data storage device. The ferroelectrics ($\text{Ba}_5\text{RTi}_3\text{V}_2\text{O}_{30}$) has a TB structure [4] which has many numbers of cationic sites, which provides a scope of interaction between different sites and favors a coupling between magnetic and ferroelectric order. So there is the scope of improving the property of BFO by adding BRTV in different proportion to make a solid solution $(\text{BiFeO}_3)_x(\text{Ba}_5\text{RTi}_3\text{V}_2\text{O}_{30})_{1-x}$. Some works have been done by us [5] making the composite $(\text{Ba}_5\text{HoTi}_3\text{V}_2\text{O}_{30})_{1-x}(\text{BiFeO}_3)_x$, which shows that in a particular composition the magnetic order appears suppressing the electric order in the ferroelectric BHTV. Now, we are planning to study how the magnetic order in BFO will be affected by adding BRTV and in certain composition (i.e., for which value of x) the composite is showing dielectric and magnetic order most effectively.

2 Methodology

2.1 Preparation of $\text{Ba}_5\text{RTi}_3\text{V}_2\text{O}_{30}$ ($R = \text{Rare Earth Element}$)

For the synthesis of ceramics sample for our investigation, solid-state reaction technique could be employed.

For the preparation of polycrystalline specimens of $\text{Ba}_5\text{RTi}_3\text{V}_7\text{O}_{30}$, ($R = \text{Ho, Pr, Tr, etc.}$). The stoichiometric amount is calculated by the reaction:



These stoichiometric compounds are ground in agate mortar by mixing with methanol then the mixture is calcined in a muffle furnace at a temperature of $\sim 750^\circ\text{C}$.

The calcined powder is further ground to fine form so that the size will be in nanoscale.

The powder is die pressed under a pressure of ~ 7 tons by hydraulic pressure to pallet form of size about 1 cm in diameter. The pallets are sintered at $\sim 800^\circ\text{C}$.

2.2 Preparation of BiFeO_3 (BFO)

Fe_2O_3 and Bi_2O_3 are mixed in a stoichiometric ratio and calcined at 700°C for 4 h to form BiFeO_3 .

2.3 Preparation of Solid Solution $(\text{BFO})_{1-x}(\text{BRTV})_x$

The calcined powder of BiFeO_3 and $\text{Ba}_5\text{RTi}_3\text{V}_2\text{O}_{30}$ with different proportions are mixed with a small amount of PVB (polyvinyl butyral) as a binder and the powder is die pressed under a pressure of ~ 7 tons by hydraulic pressure to pallet form of size about 1 cm in diameter. The pallets are sintered at 800°C for 6 h followed by cooling at $2^\circ\text{C}/\text{min}$.

Finally, the pallets are painted with silver paste to make it conducting on both sides then the electrical measurement is done.

3 Characterization

3.1 Structural Characterization

The structural characterisation of the calcined powder has been put into X-ray Diffractometer (XRD). The XRD results of BFO, BHTV and $(\text{BHTV})_{1-x}(\text{BFO})_x$ are shown in Fig. 1a-d.

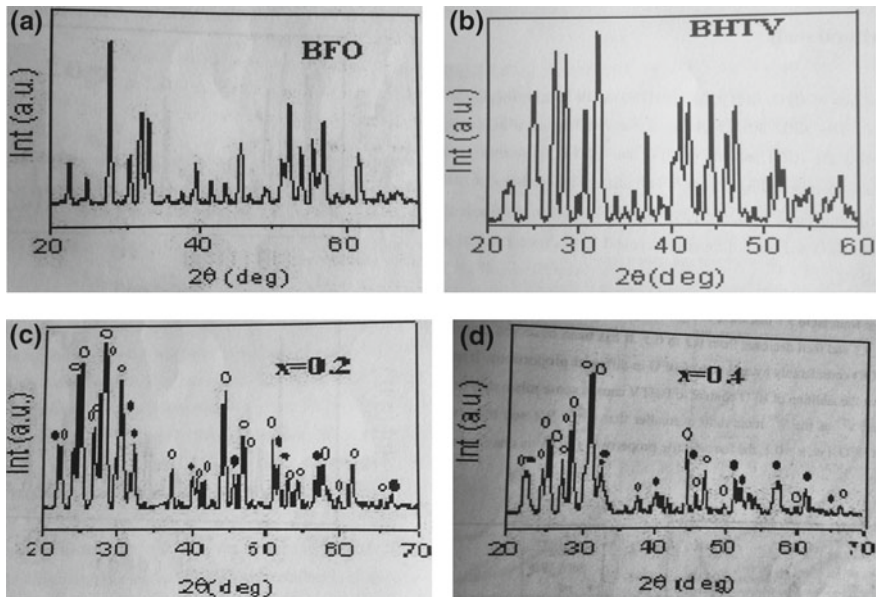


Fig. 1 a XRD for BFO. b XRD for BHTV. c XRD for $(\text{BHTV})_{1-x}(\text{BFO})_x$ for $x = 0.2$. d XRD for $(\text{BHTV})_{1-x}(\text{BFO})_x$ for $x = 0.4$

3.2 Electrical Characterization

Using a HIOKI model, dielectric constants and the loss factor ($\tan\delta$) could be measured for different frequencies at different temperatures. The transition temperature (T_c) is marked for different variations of x and see how T_c is changing for different x values. Here the result is reported for $R = \text{Ho}$.

3.3 Magnetic Characterization

Magnetic hysteresis is obtained by the Vibration magnetometer, the remnant magnetization is measured for different value of x in the solid solution.

4 Results and Discussions

Result of X-Ray Diffraction study

When the XRD profile is compared then it is seen that Fig. 1c, d contain separate reflection peaks corresponding to both BFO (indicated by symbol) and BHTV (indicated by symbol) thus it proves that the composite indeed a solid solution of BHTV and BFO and not a different compound.

Variation of (ϵ_r) with frequency

From Fig. 2, it can be seen that the value of relative dielectric constant (ϵ_r) decreases from ~ 64 to ~ 18 for frequencies increasing from 1 kHz to 1 MHz, which is a general feature of polar dielectric materials.

Variation of (ϵ_r) with temperature

From Fig. 3, it can be seen that with the rise of temperature the value of ϵ_r first increases reaches its peak value which is its transition temperature (T_c), and after slight decrease of dielectric constant (ϵ_r) it further increases (undermentioned frequencies).

From Table 1, it can be seen that for 1 kHz, dielectric constant, $\epsilon_{r\text{max}}$ is 2316 which is relatively very high in comparison to values at 10 and 100 kHz, it may be because it represents the grain boundary region. This dielectric anomaly at $T_c = 240^\circ\text{C}$ (513 K) corresponds to the ferroelectric–paraelectric phase transition. The presence of peaks in ϵ_r – T graph is an indicator for ferroelectric nature of the compound. There is another peak at 378°C for 10 kHz.

Hence, the dielectric constant may be due to the contribution from both dipole orientation and long-range migration of charge species. The second peak may be considered because of an ionic transition.

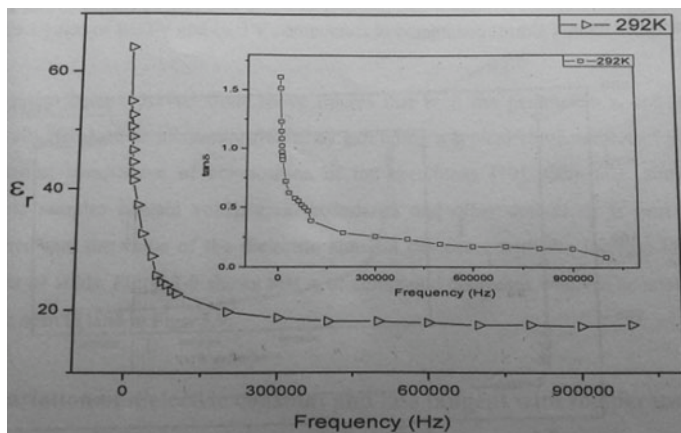


Fig. 2 Frequency variation of ϵ_r and $\tan\delta$ of BHTV (at room temp) $(\text{BiFeO}_3)_x(\text{Ba}_5\text{HoTi}_3\text{V}_2\text{O}_{30})_{1-x}$ for $x = 0$

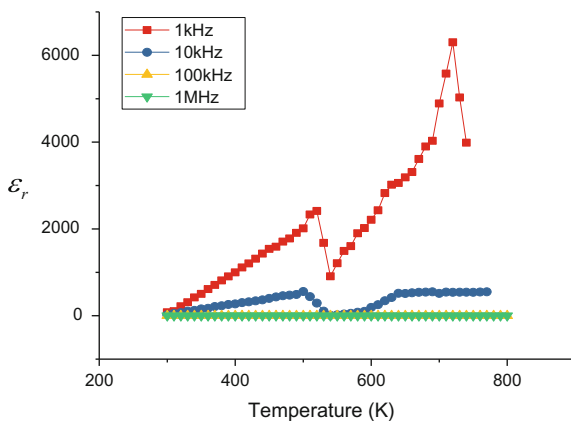


Fig. 3 Variation of ϵ_r with temperature (K) for BHTV at various frequencies. $(\text{BiFeO}_3)_x(\text{Ba}_5\text{HoTi}_3\text{V}_2\text{O}_{30})_{1-x}$ for $x = 0$

Dielectric study of $(\text{BHTV})_{1-x}(\text{BFO})_x$

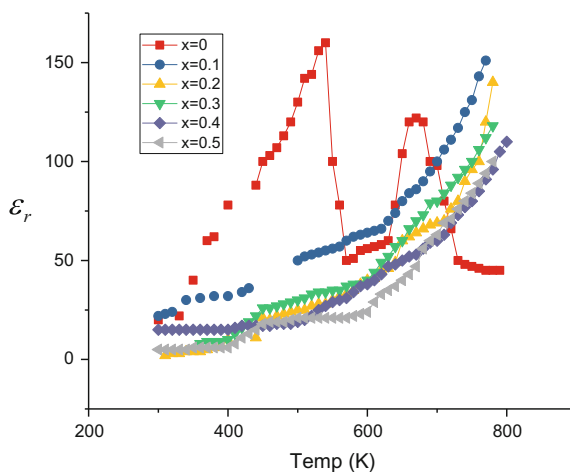
Figure 4 shows the dependency of dielectric constant (ϵ_r) with the temperature at frequency 100 kHz for $(\text{BHTV})_{1-x}(\text{BFO})_x$ with x ranging from 0 to 0.5 and temperatures ranging 300–800 K.

Table 2 shows the values of T_c and ϵ_r for $(\text{BHTV})_{1-x}(\text{BFO})_x$ ($x = 0, 0.1, 0.2, 0.3, 0.4, 0.5$). It is clear that T_c significantly increases when x changes from 0 to 0.3 and then decreases for 0.3 to 0.5.

The change in T_c is due to the addition of BFO into BHTV in different proportions, which might have caused a mismatch in the ionic radii of Fe^{3+} and V^{5+} as the V^{5+}

Table 1 Comparison of dielectric properties and T_c (K) of BHTV compounds at different frequencies

Compounds	$\text{Ba}_5\text{HoTi}_3\text{V}_7\text{O}_{30}$			
f (kHz)	1	10	100	1000
ϵ_{RT}	64	41	23	18
ϵ_{max}	2316	651	163	41
T_c (K)	513	501	500	498

Fig. 4 Variation of ϵ_r with temperature (K) for $(\text{BHTV})_{1-x}(\text{BFO})_x$ at 100 kHz frequency**Table 2** Comparison of dielectric properties and T_c (K) of $(\text{BHTV})_{1-x}(\text{BFO})_x$ compound for different values of x at frequency 100 kHz

Frequency	100 kHz	
$(\text{BHTV})_{1-x}(\text{BFO})_x$	T_c (K)	ϵ_r
$x = 0$	500	163
$x = 0.1$	603	48
$x = 0.2$	625	41
$x = 0.3$	631	42
$x = 0.4$	613	43
$x = 0.5$	538	48

ionic radii is smaller than Fe^{3+} . It was found that even with small amount of BFO, i.e., $x = 0.1$, there is considerable change in the ferroelectric property of BHTV.

The decrease of T_c for $x = 0.4$ and 0.5 indicates that there is a modification in ferroelectric property of BHTV by addition of BFO. Up to $x = 0.3$, the compound is predominately ferroelectric in nature.

There is an increase in Curie temperature till $x = 0.3$ and beyond $x = 0.3$ the solid solution is dominated by BFO (i.e., multiferroics), where Neel temperature (T_N) decreases because of the presence of BHTV. This mismatch may be caused by the

Fig. 5 Coercive field (T) versus Magnetization (M) for $(\text{BHTV})_{1-x}(\text{BFO})_x$ at $x = 0.1$

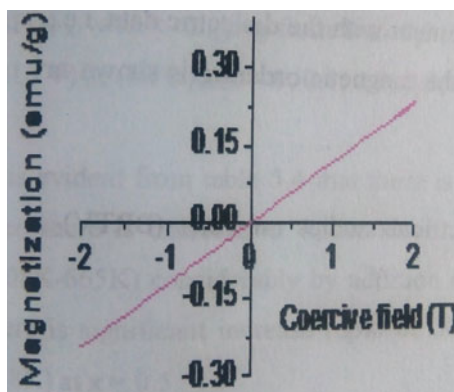
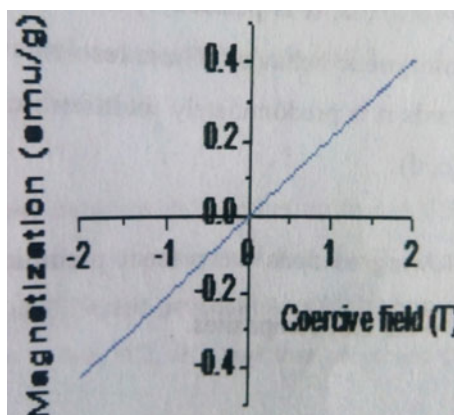


Fig. 6 Coercive field (T) versus Magnetization (M) for $(\text{BHTV})_{1-x}(\text{BFO})_x$ at $x = 0.2$



presence of different concentrations of BHTV and BFO, which introduces distortion in the oxygen octahedron of BHTV showing significant variation in T_c and ϵ_r . The oxygen octahedron undergoes distortion due to mechanical stresses caused by the increase in the percentage of BFO, resulting in the decrease of transition temperature since T_c depends upon the structural changes. Here, the little amount of BFO can make a complete solid solution which indicates that until $x = 0.3$ in composite falls in the morphotropic phase boundary (MPB) region. Even with the low concentration of BFO in solid solution, BFO dominates the behavior of the compound and it is substantiated by the magnetization behavior.

Magnetization study

The magnetization versus magnetic field has been studied by VSM and Fig. 5 show that for $x = 0.1$, it is perfectly paramagnetic. However, at $x = 0.4$, it starts showing ferromagnetic properties (Fig. 7). These results are in agreement with the dielectric data, i.e., $x > 0.3$ onwards it is predominately multiferroics (Figs. 6 and 8).

Fig. 7 Coercive field (T) versus Magnetization (M) for $(\text{BHTV})_{1-x}(\text{BFO})_x$ at $x = 0.4$

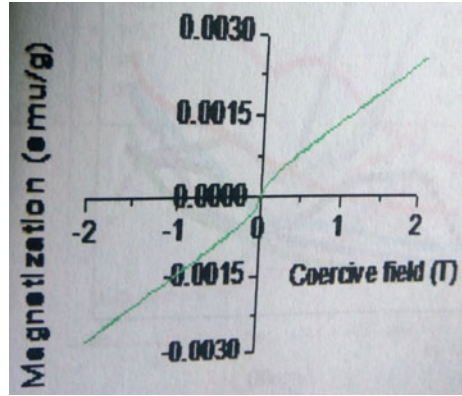
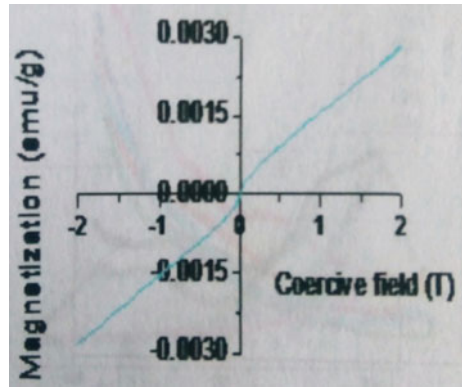


Fig. 8 Coercive field (T) versus Magnetization (M) for $(\text{BHTV})_{1-x}(\text{BFO})_x$ at $x = 0.5$



5 Conclusions

It has been observed that the transition temp T_c of BHTV changes considerably by the addition of BFO. T_c increases up to $x = 0.3$ and then decreases for $x = 0.4$ and $x = 0.5$. It may be due to the interaction of Bismuth ion with different lattice site of BHTV.

It is also seen that when multiferroic BiFeO_3 is mixed with ferroelectric materials $\text{Ba}_5\text{HoTi}_3\text{V}_2\text{O}_{30}$ to forming a solid solution $(\text{BiFeO}_3)_{1-x}(\text{Ba}_5\text{HoTi}_3\text{V}_2\text{O}_{30})_x$, then magnetic property starts appearing for certain composition (for $x = 0.4$) in BHTV. That means the composite is predominately paramagnetic at $x = 0.1$ and $x = 0.2$, but for $x = 0.4$ and 0.5 , it shows ferromagnetic behavior.

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