

Establishment of magneto-dielectric effect and magneto-resistance in composite of PLT and Ba-based *U*-type hexaferrite

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We are examining the behavior of a composite made of ferroelectrics with strong dielectric properties and ferrites with magnetic properties due to the rising need for materials for multipurpose devices. Many application avenues will be favored by the pairing of these materials' individual qualities with one another. Perovskite and *U*-type hexaferrite composite materials have been chosen for this study based on their magnetic and dielectric properties. The composites, $(1-x)$ PLT_{*x*}(Ba_{1-3*x*}Nd_{2*x*})₄Co₂Fe₃₆O₆₀ where $x = 0.52, 0.54, 0.56, 0.58$ are prepared by solid state reaction method and phase formation was examined. Consideration has been given to the magnetic, dielectric, and magneto-dielectric properties. This work has established the link between the electric and magnetic domains while applying electric and magnetic forces to the materials. The magneto-dielectric research revealed magneto-electric coupling in all of the samples. However, the sample shows the maximum coupling for $x = 0.54$ with MDR% values of 93.17%, which might be because this sample appears to have a high magneto-resistance (161%).

Keywords: Perovskite; *U*-type hexaferrite; magneto-dielectric effect; magneto-resistance response.

1. Introduction

Materials consisting of the ferrite and ferroelectric phases, also referred as multiferroic magnetoelectric (ME) composites, have subsequently gained a lot of attention due to their potential usage in multifunctional devices such as ME transducers, sensors and actuators.¹ The origins of spin-charge pairing in these phenomena have been investigated for a long time, but a recent surge in research on multiferroics² has piqued researchers' interest. van Suchtelen³ originally postulated the ME effect in composite substances as the consequence of the concept of product property, which is lacking in constituent phases.⁴ A magnetic field causes ferrite particles to alter form in composites of piezoelectric perovskite and spinal structural phase due to magneto-striction. This study covers a technique for obtaining a significant ME effect using a composite material composed of two phases: a perovskite phase known as PbLaTiO₃ (PLT) and a spinal *U*-type

hexaferrite phase known as (Ba_{1-3*x*}Nd_{2*x*})₄Co₂Fe₃₆O₆₀ (Ba-*U*). The method includes applying strain on piezoelectric particles, which results in electric polarization. The resulting ME effect is far more powerful than that of single-phase ME materials such as Cr₂O₃.⁵ High magneto-striction, high piezoelectric coefficient, high dielectric permeability, high poling strength, high molar percentage, no chemical reaction between the phases and high resistivity to prevent accumulation leakage are all prerequisites for achieving better ME effects in composites.⁶ PLT and Ba-*U* were chosen because they fit these requirements and can produce a substantial ME effect.

Because of its high dielectric value and piezoelectric capabilities, lead titanate (PT) has piqued the interest of academics. PT shows a ferroelectric phase at temperatures below 490°C,⁷ which is defined by a tetragonal crystal structure with space group P4mm. When the temperature rises above

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the Curie point, PT enters a paraelectric phase and its crystal structure changes to cubic with space group Pm3m.^{8,9} The transition from the ferroelectric to paraelectric phase, on the other hand, is accompanied by a large change in unit cell size, resulting in high internal stresses that can make PT unstable throughout the cooling process. To solve this issue, researchers have investigated strategies to lower the lattice anisotropy of PT by incorporating suitable dopants into the Pb sites, such as Ca²⁺, Ba²⁺, Cd²⁺, Sm³⁺, Gd³⁺, La³⁺ or Y³⁺ ions.^{10,11} Hard, thick ceramics with high mechanical strength can be produced using this method.

Doping PT with La³⁺ ions, for example, can lower the transition temperature to 438°C while preserving the piezoelectric characteristics. As a result, La-doped PT is a potential material for a variety of applications such as sensors, actuators and transducers.

Similarly, the (Ba_{1-3x}Nd_{2x})₄Co₂Fe₃₆O₆₀ is selected for this investigation because of its magneto-strictive and resistive materials.^{12,13} The primary prerequisite for composites to display high ME production is a substantial degree of magneto-striction. In particular, for addressing the fundamental connection between magnetic characteristics and their crystal chemistry and structure, spinel ferrites have sparked a great deal of interest in fundamental physics. Due to their high electric resistivity, high magnetic permeability, low dielectric loss, good chemical stability, low coercivities and high Curie temperature, which also depends on the compositions and heat treatment of the samples, Ba-hexaferrites are among the most adaptable and reasonable materials used in both high- and low-frequency devices.

According to a review of the literature, no research has been conducted on the synthesis as well as comprehensive analysis of a ferro-electromagnetic composite made of PLT and Ba-hexaferrite. Therefore, we decided to work on (1-x)-PLT_x(Ba_{1-3x}Nd_{2x})₄Co₂Fe₃₆O₆₀ where $x = 0.52, 0.54, 0.56, 0.58$ (abbreviated as (1-x) PLT_x Ba-U) composite made by solid state reaction method. In this work, we studied the structural, microstructural, magnetic and magneto-dielectric properties of the composites.

2. Experimental

Composites were prepared by solid state reaction method using a single sintering process. The raw materials in the form of oxides were used for the perovskite as well as hexaferrite formation. The raw materials for both phases were mixed separately for 24 h in stoichiometric proportion using ball mill in acetone medium. After mixing, the mixed powders were dried and calcined at appropriate temperatures. For both phases, the preliminary structural analysis was carried out using X-ray diffraction (XRD) techniques to confirm the corresponding phases. The tetragonal and hexagonal phases were confirmed from XRD for both the perovskite and ferrite parts, respectively. Thereafter, the calcined powders were mixed in the proposed ratio to form a series of composite

materials with the help of normal ball mill for 12 h. The binder polyvinyl alcohol (PVA) mixing was done followed by the pressing powder in the form of pellets with the use of hydraulic press. The sintering was done at the final stage at 1200°C.^{14,15}

The study outlines the procedures and instruments used to conduct a study on the structural, microstructural, magnetic, dielectric and magneto-dielectric properties of various samples. XRD and field emission scanning electron microscope (FESEM) are two analytical procedures used to assess the samples' structural and microstructural properties, respectively. XRD is a powerful technique for determining the crystallographic properties of materials, whereas FESEM allows researchers to obtain high-resolution photographs of the sample surface at the microscale level.

The vibrating sample magnetometer (VSM) is a device used to measure the magnetic characteristics of samples. This apparatus vibrates the samples with an oscillating magnetic field and detects the magnetic response.

The dielectric and magneto-dielectric properties of the samples were investigated at various frequencies using a Keysight impedance analyzer. This instrument examines a sample's impedance as a function of frequency, providing information about the sample's electrical properties. The ability of a material to store electrical energy is described by dielectric qualities, whereas magneto-dielectric properties define the interaction of magnetic and electrical properties.

Overall, the combination of these approaches enabled a thorough analysis of the samples' structural, magnetic and electrical properties at various scales and frequencies.

3. Results

3.1. Structural properties

Figure 1 displays the XRD patterns of composites made of 0.48PLT-0.52Ba-U and the parent material PLT and Ba-hexaferrite. The XRD refinement for PLT material has been done using crystallography open database (COD) ID 1521255.¹⁶ Whereas, hexaferrite peaks have been assigned using information from the work of Singh.¹⁵ It is clear from the figure that in the composites the reflection peaks from both phases are present without an impurity peak. The diffraction pattern for all the samples with composition $x = 0.52, 0.54, 0.56, 0.58$ are given in Fig. 2. For all the samples, in the absence of any additional impurity phase peak, it demonstrates the presence of both the ferroelectric and hexaferrite phases. To establish the hexagonal spinel structure in the ferrite phase¹⁵ and the presence of the tetragonal ferroelectric phase PLT,⁷ all the peaks were identified and indexed with appropriate indices.

It is generally known that a (1 1 34) reflection is more intense in a hexaferrite structure, and that a (1 1 0) reflection is more intense in a tetragonal perovskite structure, or ferroelectric structure. The composite samples show these two distinct

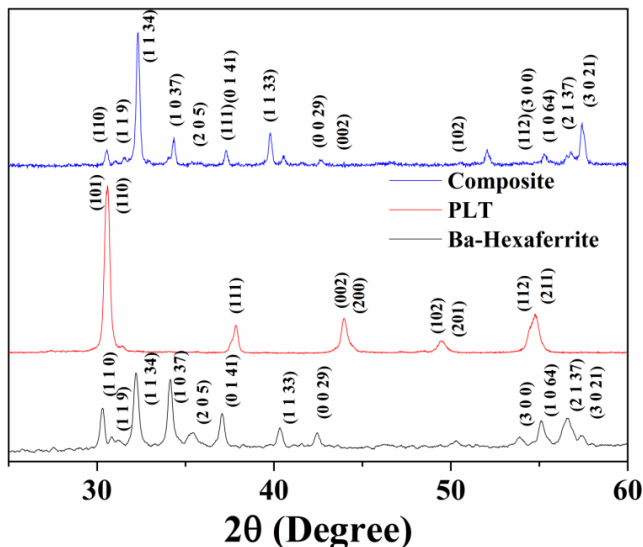


Fig. 1. XRD patterns of composites made of 0.48PLT–0.52Ba–U and the parent material PLT and Ba–U.

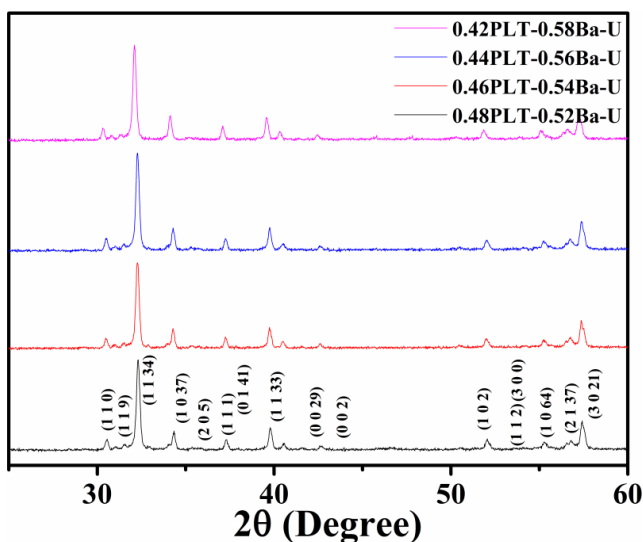


Fig. 2. XRD pattern for 0.48PLT–0.52Ba–U, 0.46PLT–0.54Ba–U, 0.44PLT–0.56Ba–U and 0.42PLT–0.58Ba–U.

groups of reflections. The absence of unexplained peaks indicates that no chemical reactions between the hexaferrite and ferroelectric phases during the final sintering have taken place. It was discovered that as the hexaferrite phase’s composition increased, so did the intensity and number of its peaks, whereas the ferroelectric phase’s intensity remained almost constant. The quantity of corresponding phases present in the composites determines the intensity and number of diffraction peaks.

3.2. Magnetic properties

The room temperature magnetization versus field profile (M–H loops) of all the prepared samples is shown in Fig. 3.

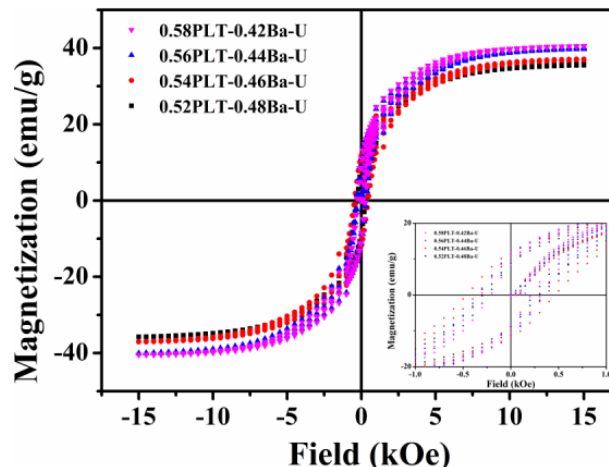


Fig. 3. The room temperature magnetization versus field profile (M–H loops).

Table 1. The values of remnant polarization, saturation polarization and coercive field.

Sample	Remnant polarization (emu/g)	Saturation magnetization (emu/g)	Coercive field (kOe)
0.52PLT–0.48Ba–U	8.17	35.36	0.28
0.54PLT–0.46Ba–U	9.64	36.82	0.32
0.56PLT–0.44Ba–U	10.72	39.02	0.30
0.58PLT–0.42Ba–U	11.20	40.94	0.32

It is clearly seen from the figure that the saturation magnetization for all the samples is in increasing order from $x = 0.52$ to $x = 0.58$. This is due to the increasing content of hexaferrite phase. The value of saturation magnetization, coercive field and remnant magnetization for all the samples are listed in Table 1. The value of the saturation magnetization (M_s) increases from 35.36 emu/g for $x = 0.52$ to 40.74 emu/g for $x = 0.58$. The unit cell of a *U*-type hexaferrite exhibits a sequence of stacking blocks as $SRS^*R^*S^*T$ in which the large cations of Ba^{2+} attain the position in oxygen lattice, whereas, Co^{2+} and Fe^{3+} cations are distributed on five different crystallographic sites; three octahedral sites, one tetrahedral site and one trigonal-bipyramidal site.^{17,18} Moreover, the opposite spins are coupled together through exchange interaction via O^{2-} ions.¹⁷ Due to the superexchange interaction between $Fe^{3+}-O-Fe^{3+}$ leads to magnetization value.^{17–19}

3.3. Magneto-dielectric coupling

As indicated in Fig. 4, the validity of ME coupling in all samples was determined using ϵ' versus frequency measurements with different magnetic fields (0, 0.5, 1 and 1.5 T). The samples show ME coupling only for all the samples as there is

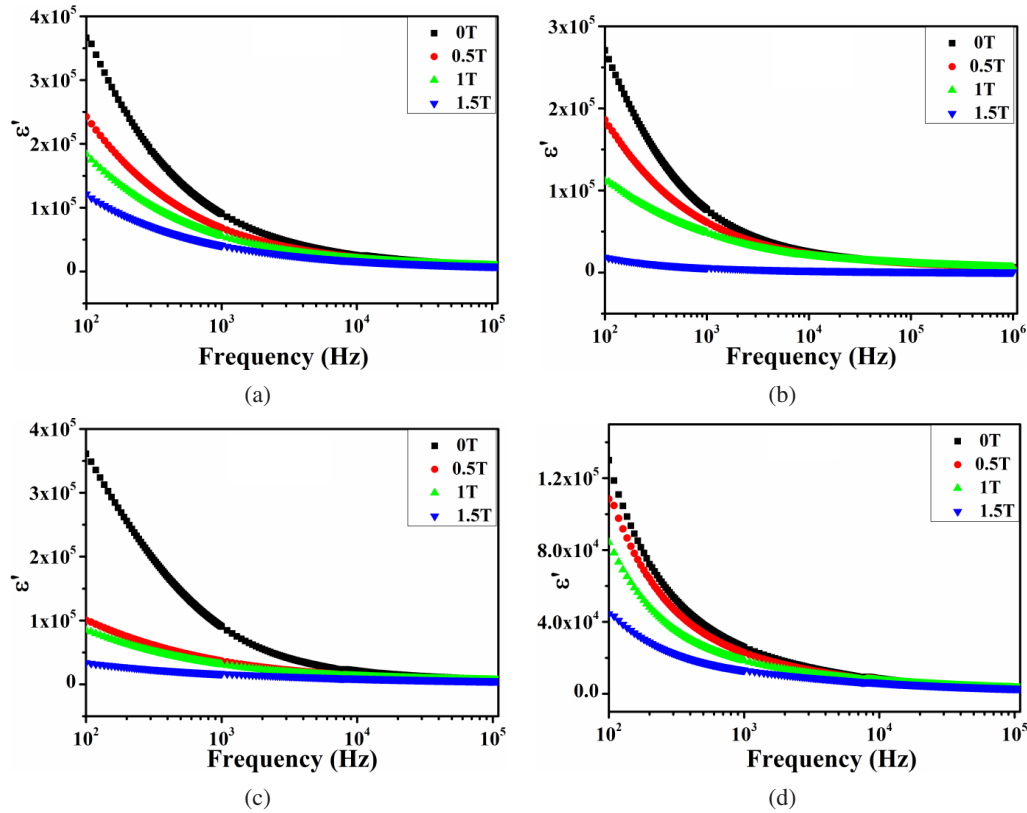


Fig. 4. ϵ' versus Frequency profiles at different magnetic field values for (a) 0.52PLT–0.48Ba–U, (b) 0.54PLT–0.46Ba–U, (c) 0.56PLT–0.44Ba–U and (d) 0.58PLT–0.42Ba–U.

Table 2. The value of MDR% for all the samples at fixed frequency 100 Hz and at room temperature.

Field (T)	x = 0.52		x = 0.54		x = 0.56		x = 0.58	
	ϵ'	MDR (%)	ϵ'	MDR (%)	ϵ'	MDR (%)	ϵ'	MDR (%)
0	366,343	0	270,790	0	361,229	0	130,025	0
0.5	355,834	33.83	254,220	31.28	100,391	72.20	125,356	16.60
1	279,635	49.88	240,873	64.45	85,160	76.42	123,094	35.17
1.5	257,769	72.39	211,230	93.17	33,654	90.68	115,241	65.77

variation in the value of ϵ' with change in the magnetic field. A visible decrease in the value of ϵ' has been observed in the figure.

This decrement in the value of ϵ' also indicates a negative magneto-dielectric response (MDR) in the samples. The application of a magnetic field causes the ferrite particles to change form due to magneto-striction in hexaferrite phase. The strain is then transferred to the ferroelectric particles, producing an electric polarization. Therefore, The simultaneous generation of stress in magnetic and ferroelectric domains by an externally applied magnetic field is responsible for the change in dielectric permittivity of the material.^{20,21} The MDR can be calculated as follows:

$$\text{MDR Response} = \frac{\epsilon'(H) - \epsilon'(0)}{\epsilon'(0)} \times 100\%, \quad (3)$$

where $\epsilon'(H)$ and $\epsilon'(0)$ represent the dielectric constant with and without magnetic field, respectively. The value of MDR% for all the samples at fixed frequency 100 Hz and at room temperature is given in Table 2 and Fig. 5. From the response value, it is found that $x = 0.54$ shows maximum magneto-dielectric effect. These results indicated that the sample 0.54PLT–0.46Ba–U exhibits maximum coupling in magnetic domains of Ba–U hexaferrite and electric domain of PLT phases. Further increase in the hexaferrite phase leads to weakness in the coupling. Figure 5 displays the trend of MDR at different field values and at fixed frequency 100 Hz.

3.4. Magneto-resistance response

Since the sample 0.54PLT–0.46Ba–U has shown maximum coupling in magnetic domains of Ba–U hexaferrite and electric

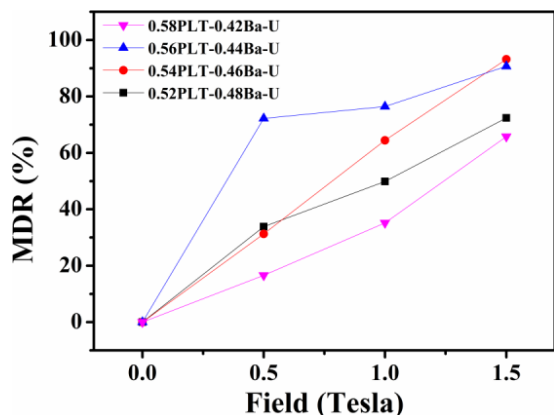


Fig. 5. The trend of MDR at different field values and at fixed frequency 100 Hz.

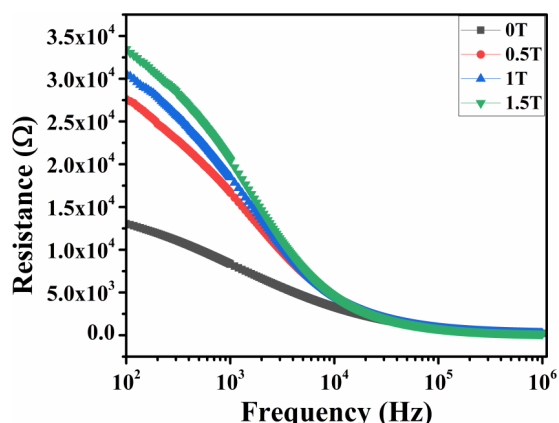


Fig. 6. P versus frequency profiles at different magnetic field values for 0.54PLT–0.46Ba–U.

domain of PLT phases, therefore, this sample is further studied for magneto-resistance behavior. The data for resistance value with respect to the frequency at varying magnetic field values has been taken and plotted as shown in Fig. 6. This figure clearly reveals that a large magneto-resistance response has been exhibited by the sample. The value of resistance in the sample changes drastically with the variation in magnetic field strength at low frequency region. The values obtained for the resistance and magneto-resistance response (MRR%)

Table 3. The value of MRR% for all the samples at fixed frequency 100 Hz and at room temperature.

Field (T)	$x = 0.54$	
	R (Ω)	MRR (%)
0	12,780	0
0.5	27,437	114
1	30,663	139
1.5	33,362	161

at different field strengths are listed in Table 3. It is obvious from the table that a quite high MRR% appears on varying the magnetic strength, and this strong magneto-resistance can lead to the powerful magneto-dielectric effects²² as obtained in the last section.

4. Discussion

The XRD studies confirm the presence of both hexaferrite and perovskite phase for all the samples. The intensity of reflection peaks from hexaferrite phase increases with the increases in hexaferrite content. The data from VSM informed that the magnetization in all the composite samples increases with increase in hexaferrite phase concentration, which is basically caused by the Fe^{3+} content in daughter samples. The magneto-dielectric effect was studied from the dielectric constant versus frequency data at different magnetic field strength values. It has been observed that the sample with $x = 0.54$ exhibited the maximum MDR%, which is direct co-related with the coupling of magnetic domains of hexaferrite phase and electric domains of perovskite phase. Further increases in hexaferrite phase causes lowering in this coupling result in the lesser value of MDR%. The strong magneto-dielectric effect may be originated from the high magneto-resistance phenomenon in $x = 0.54$ sample.

5. Conclusion

The composites of perovskite PLT and U -type Ba-hexaferrite have been prepared with solid state reaction route. The preliminary XRD results confirm the pure phases of perovskite as well as hexaferrite material. Moreover, the final results acquired from the XRD data gave indication that both phases are present in composite samples. The magnetization value increases with the rise in hexaferrite phase concentration which is co-related to the Fe^{3+} content. The value of saturation magnetization increases from 35.36 emu/g to 40.94 emu/g for $x = 0.52$ to 0.58, respectively. The magneto-dielectric study confirms that all the samples exhibited magneto-electric coupling. However, the maximum coupling is shown by the sample for $x = 0.54$ and 0.56, and MDR% value is 93.17% and 90.68%, respectively. Moreover, the same sample has exhibited the highest magneto-resistance response of 161% at 100 Hz.

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