Ceramics Of $x(Pb_{0.9}Ti_{0.1}Fe_{12}O_{19})$- $_{1-x}(Pb_{1-x}gd_xtio_3)$ With Strain-Mediated Magneto-Dielectric and Magneto-Resistive Properties Where X = 0.50, 0.52, 0.54, 0.56, 0.58, and 0.60

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Abstract

Ceramics that are magneto-dielectric and magneto-resistive using mechanical mixing, Ti^{4+} and Gd^{3+} modified $PbFe_{12}O_{19}$ and $PbTiO_3$ composites have been created. The magneto-dielectric and magneto-resistive response of the constructed composited system $_x(Pb_{0.9}Ti_{0.1}Fe_{12}O_{19})$- $_{1-x}(Pb_{1-x}Gd_xTiO_3)$, where x = 0.50, 0.52, 0.54, 0.56, 0.58, and 0.60, has been described. While the magnetization vs. applied magnetic field curve indicates the presence of magnetic characteristics in produced composites, the polarization vs. applied electric field hysteresis supported ferroelectric properties. The presence of structural phases is confirmed by X-ray diffraction peaks at certain 2θ, which match to the structural phases of the different ceramic composite components. The presence of the magneto-electric effect in produced ceramic composites is directly manifested by changes in dielectric permittivity, dielectric loss, and resistance.

Keywords: Multiferroics, Magneto-Dielectric, Dielectric Relaxation

1. Introduction:

Magneto electric multiferroics are differentiated into single phase and composites on the basis of structure. In single phase, coupling between electric and magnetic order appears in single phase whereas in composites, this coupling arises due to individual contribution of electric and magnetic phase. The composite magneto electric materials are synthesized by mixing appropriate electric and magnetic phase which are formed individually. The co-existence of more than such ordering in materials made them important for various industrial applications such as data storage applications, sensors, actuators etc. The change in ferroelectric or ferroelastic properties under effect of magnetic field made these materials more important for many applications. This change in one of above mentioned ordering (Magnetic, ferroelectric or elastic) under effect of one of these known as magneto electric coupling. Materials with such kind of behavior made these materials important for many applications useful for mankind. The simultaneous co-occurrence of above mentioned ordering in materials made those materials important for various industrial applications such as information storage devices, sensing devices actuators whereas coupling in these ordering made more importance of such kind of materials in magnetically tuned electric sensor or electrically modified magnetic sensors etc. The magneto-electric coupling has been measured in terms of magneto-electric coupling coefficient. The change in dielectric properties under influence of magnetic field termed as Magneto-Dielectric Response (MDR). In which two different circles (Black and Green) represents ferroelectric ordering (Green Coloured) and other magnetic ordering (Black Coloured). The intersection of both these (Black & Green Coloured Circle) represent presence of both ferroelectric and magnetic termed simultaneously as multiferroism whereas effect of magnetic field on electrical properties of electric field on magnetic properties shown by orange circle shows presence of magneto-electric coupling in materials. In another part of figure, coupling between electric and magnetic ordering results in magneto-electricity whereas effect of magnetic field on position of atoms (Deformation) leads to magneto-elasticity. The change in position of atoms (Deformation) with electrical field termed as piezoelectricity. Such effect in multiferroic materials have attracted a great deal of attraction from scientific community owing to their potential for device applications.

2. Composites multiferroics (Mixed Ferrites and Ferroelectric Oxides)

Composite Multiferroics in which magnetic component (Magnetically Polarizable materials) and electric component (Electrically Polarizable)have been mixed together. Both these components have been synthesized individually before mixing for preparation of multiferroic

composite. Electrical component responsible for electrical properties (Ferroelectric Order) whereas magnetic component for magnetic properties (Magnetic Order). Few examples of multiferroic composites reported in past are $CoFe_2O_4$-$BaTiO_3$, $CoFe_2O_4$-$PbTiO_3$, $NiFe_2O_4$-$BaTiO_3$ etc.

3. Ferroelectric ordering

Ferroelectric materials and ferroelectricity are defined as those that display spontaneous electric polarisation even in the absence of an applied external electric field. Applying an electric field in the opposite direction will reverse the polarisation. Owing to their use in numerous technical applications, including sensors, micro actuators, dynamic random access memory (DRAM), and non-volatile ferroelectric random access memories (FRAM). Researchers are drawn to ferroelectric materials because of their unique properties. In Perovskite structure, huge cation is situated at A-site, smaller cation at body centre and oxygen at face centred location of unit cell. The emergence of ferroelectricity in these kinds of materials can be attributed to the off-center displacement of the B-site cation. The ferroelectric material experiences a phase transition above curie temperature, meaning that it changes from a non-centrosymmetric room temperature ferroelectric phase to a high temperature paraelectric phase with a centrosymmetric structure etc.

4. Ferromagnetic Ordering

Ferromagnetism is the fundamental property of a material that allows it to retain a net non-zero magnetic moment or magnetization even in the absence of an externally applied magnetic field. Materials that display this property are referred to as magnetic materials or magnetically ordered materials, since their magnetic domains align themselves in the direction of the magnetization and external field. The direction in which the domains align can be reversed by applying the field in the opposite way. These materials are also known as permanent magnets. These materials go through a phase transition from a magnetically ordered (non-zero magnetic moment) to a disordered (zero magnetic moment) state when temperature rises. Transition temperature, also referred to as critical temperature (TC) or Curie temperature, is the temperature at which magnetic material transitions from ferromagnetic to paramagnetic. Ferroelasticity are related to the possibility of switching the polarization, magnetization and strain between two symmetry-related or opposite values by means respectively of the suitable electric field, magnetic field, and mechanical stress. As a result, the corresponding ferroic property (ferroelectricity, ferromagnetism, and Ferro elasticity) is thermodynamically conjugated to each of these fields (electric field, magnetic field, and mechanical stress). The associated hysteresis, which macroscopically characterizes the dependency of the ferroic property on its corresponding conjugated field, is a feature of the highly non-linear switching process.

5. History & discovery

P. Curie predicted that crystals might have both ferroelectric and ferromagnetic properties at the same time in 1894. With discovery of Maxwell equations in the 19th century, real research on interaction between electricity and magnetism began. Nonetheless, it has long been believed that whereas, electrical behaviour mostly depends on electron charge, magnetism should cause by electron's spin. Pierre et al. proposed the basic idea that a crystal might exhibit both ferromagnetic and ferroelectric properties concurrently in 1922. For specific material classes, Landau and Lifshitz made a theoretical prediction about magneto electric coupling in 1959 [26]. Under symmetry considerations, Dzyaloshinsky (1959) demonstrated the magneto electric action in ant ferromagnetic material (Cr_2O_3) . Astrov conducted the first experimental observation of the M-E phenomenon for Cr_2O_3 in 1960 [28]. In 1994, while conducting research on ferromagnetism and ferroelectricity in boracite material, H. Schmid coined the term "multiferroicity". Chitra et al. [30] reported magneto dielectric effect in KNN-CFO composites. The maximum value of MD(%) effect has been reported is 5.3% for 40% CFO content whereas Rakhikrishna et al. reported MD(%) of 1.2% for 20% CFO concentration in lithium (Li) modified

KNN-CFO composite. Rakhikrishna et al has also reported magneto dielectric effect in NiFe2O4-KNN composite. The maximum value of MD(%) effect is 0.8 and 1.1% for 15 and 20% of nickel ferrite (NFO) concentration. Akshey et al reports decrease in dielectric constant with magnetic field is an direct proof of magneto dielectric (MD) effect present in prepared multiferroic ceramics and samples for x = 0.50 shows maximum magneto dielectric response (-2.86%) in comparison of other and this may be due to ferroelectric component which has been responsible for more strained grains with magneticfield.

6. Objective

- To prepared composite was examined for both elemental confirmation, elemental distribution as well as and microstructural analysis.
- To prepared composites characterized for room temperature dielectric properties (ε', ε'' or □ac vs. Frequency)

7. Synthesis and Characterization of Prepared multiferroic Composites

The characterization and synthesis approaches (Auto-Combustion and Conventional Solid State Reaction Route) have been addressed in this chapter. Field emission scanning electron microscopy (FESEM) and X-ray diffraction (XRD) were used to characterize structural and micro structural examinations. Elemental mapping is used to analyze uniform distribution of different metal ions; energy dispersive X-ray spectroscopy (EDS) has confirmed presence of elements according to stoichiometric proportion. An impedance analyzer and a vibrating sample magnetometer were used to assess the magneto-dielectric characteristics, while a vibrating sample magnetometer was used to measure the room temperature magnetic. Archimedes' principle-based setup was used to measure the prepared sample's density. Dependent dielectric spectroscopy and impedance analysis have been used to measure the room temperature dielectric characteristics.

7.1 Sample Preparation:

The synthesis of samples has been prepared by using traditional solid state reaction technique and auto combustion. The ferroelectric component (Gd^{3+} modified $PbTiO_3$) was synthesized via solid state reaction route, whereas magnetic component (Ti^{4+} modified Ba M type hexaferrite) was created utilizing auto-combustion approach.

7.2 Characterization

Different characterization approaches have been used to characterize for various properties of synthesized substances. These techniques are included below.

- X-ray diffraction data used to study structural phase formation.
- Field Emission Scanning Microscopy used for Microstructural Analysis
- Magnetic Ordering: Vibrating Sample Magnetometer
- Dielectric Spectroscopy: Impedance Analyzer interfaced with computer

7.3 **Selection of Materials**

$PbTiO_3$ has been chosen as a ferroelectric perovskites due to its maximum dielectric and ferroelectric properties as compared to ferroelectric materials reported earlier, while Ba M type hexaferrite has been selected as the magnetic component from the literature review due to its highest magnetic moment among spinel ferrites used in the past for the synthesis of multiferroic composites. Ba M type hexaferrite can have its magnetic and dielectric properties tailored by utilizing Ti^{4+}, whereas $PbTiO_3$ can be modified with rare earth ion (Nd and La) lower the ferroelectric transition temperature of $PbTiO_3$.

8. **Result & Discussion**

Diffraction data 2θ vs. Intensity (a.u.) has been studied using either JCPDS cards that explore specific crystal structure properties (d-spacing, Lattice parameters, etc.) according to structural phase or reported diffraction data of related crystal structures to study crystal phases present in composite samples. Using JCPDS cards of the hexagonal phases of M-type ferrite and the tetragonal phases of PbTiO3, all diffraction peaks were examined and indexed based on their crystal plane. The diffraction peaks listed on JCPDS card no. 78-0299, which represents the

tetragonal structural phase (Space Group No. 99 and symbol P 4 mm), and 79-1411, which represents the hexagonal structural phase of SrFe12O19, which is thought to be M-type hexaferrite (Space Group P63/mmc No. 194), have been used to index all of the diffraction peaks. When there are no unindexed diffraction peaks, ceramic composites contain both structural phases in the specified space group. To facilitate easy differentiation, each phase's diffraction peaks are colored differently. Green-colored diffraction peaks correlate to the hexagonal phase of M-type hexaferrite, whereas red-colored peaks show the presence of the tetragonal phase. The average crystallite size and unit cell volume of both tetragonal and hexagonal crystal structures have been shown to grow when ferrite concentration rises due to diffraction peaks that are significantly pushed towards a higher diffraction angle (2θ). The following formula has been used to determine the lattice parameter of the produced composites:

$$\frac{1}{d^2} = \frac{4}{3}\left[\frac{h^2}{a^2} + \frac{hk}{a^2} + \frac{k^2}{c^2}\right] + l/c2 \text{.....(Eq. 1)}$$

$1/d^2_{hkl}=(h^2+k^2)/a^2 + l^2/c^2$.....(Eq. 2)

Whereas volume of unit cell has been calculated using relation

$$V=(abc).sin\beta$$

It has been clearly visualized from Table 1 that with increasing '*x*' from *x* = 0.50 to 0.60, cell volume of hexagonal unit cell increases from 802.87 Å^{3}to 823.18 Å^3 where tetragonal unit cell volume decreases from 73.51Å^3 to 72.69 Å^3 indicates that as content of hexaferrite increases in composite stoichiometry, unit cell volume of both unit cell changes manifestation of change in strain as well as dislocation density.

Table 1: Crystallographic Signatures (Lattice Parameters (a & c), Crystallite Size (D) vs. Composition (*x*) of $_{1-x}${$Pb_{0.74}Pr_{0.25}$)O3}-$_x${$Pb_{0.9}Ti_{0.1}Fe_{12}O_{19}$}Magneto-Dielectric Ceramic Composites where *x* = 0.50, 0.52, 0.54, 0.56, 0.58 & 0.60

Composition↓ Crystal Phase→	Hexagonal				Tetragonal			
Crystal Parameter	a(Å)	c(Å)	D (nm)	V(Å^3)	a(Å)	c(Å)	D (nm)	V(Å^3)
x= 0.50	5.883	23.198	55.4	802.87	3.892	4.853	57.7	73.51
x= 0.60	5.859	23.980	37.4	823.18	3.878	4.834	23.4	72.69

The strain and dislocation density has been calculated using formula and tabulated given as Eq 3 & 4 in Table 2 given below

ε = βcosθ/….(Eq. 3)

δ = 1/Average Crystallite Size (D)…..(Eq.4)

Table 2: Crystallographic Signatures (Strain (ε), Dislocation Density (δ) vs. Composition (*x*) of $_{1-x}${$Pb_{0.74}Pr_{0.25}$) O3}-$_x${$Pb_{0.9}Ti_{0.1}Fe_{12}O_{19}$} Magneto-Dielectric Ceramic Composites where *x* = 0.50, 0.52, 0.54, 0.56, 0.58 & 0.60

Composition↓ Crystal Phase→	Hexagonal		Tetragonal [13]	
	ε	δ (m^{-3})	ε	δ (m^{-3})
x = 0.50	0.00093	0.00032	0.0014	0.00030
x = 0.60	0.00064	0.00071	0.00062	0.0018

Table 2 unequivocally shows that greater strain is induced in composites with the same weight proportionate to the stoichiometry of composites due to the significant difference in the size of the unit cell volume (Tetragonal vs. Hexagonal), which correlates to the dislocation density. Surface morphology such as extent of porosity, grain growth and grain size has studied from micrographs collected using FESEM. The micrographs of prepared magneto-dielectric ceramic composites of $_x(Pb_{0.9}Ti_{0.1}Fe_{12}O_{19})$-$_{1-x}(Pb_{1-x}Gd_xTiO_3)$ where *x* = 0.50, 0.52, 0.54, 0.56, 0.58 & 0.60. Micrographs exhibit grains of different size, non-uniformly distributed and of hexagonal, circular and plate like shapes clearly visualized. The hexagonal and plate like grains corresponds to hexagonal structure whereas circular grains represent ferroelectric perovskite phase. The hexagonal; shape of the prepared samples causes a decrease of grain boundary and

surface energy. Micrographs also point towards agglomeration of smaller grains due to magnetic interaction between the individual grains of the prepared samples. The extent of cross-linked grains shows grain growth.

9. Conclusion

The obtained magneto-dielectric ceramic composites' crystal structures were analyzed, and it was discovered that they were perovskite tetragonal and hexagonal of magnetic ferrite without any secondary phase. Magnetic hysteresis makes it abundantly evident that as the proportion of ferrite in composites changes, ferromagnetic behavior takes precedence over ferroelectric response, leading to an increase in conductivity and dielectric loss. The magneto dielectric effect, which is ascribed to strain-mediated stress with applied magnetic field in composites, is confirmed by the shift in dielectric constant with magnetic field. It has been discovered that the greatest magneto dielectric response value indicates a negative magneto dielectric effect.

10. References

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