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# Study of structural effects on the dielectric and magnetic properties of alkaline earth metals doped SmTiO<sub>3</sub>

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#### Graphical abstract



#### Highlights

- Ba and Sr doped SmTiO<sub>3</sub> multiferroic materials were prepared by solid state route.
- P-XRD and SEM were studied for support the modification of structure by doping.
- Dielectric and magnetic studies were done for the multiferroic nature of SmTiO<sub>3</sub>.
- Observed ferroelectric and ferromagnetic results more support this phenomenon.

#### ABSTRACT

 $Sm_{1-x}Ae_xTiO_3$  (Ae = Ba, Sr & x = 0.5-0.25) synthesized using solid state route were subjected to structural, morphological, magnetic and dielectric permittivity measurements for the investigation of multiferroic nature of these compounds. The P-XRD studies revealed the formation of orthorhombic structured (*Pbnm*) single phase at room temperature. Magnetic measurements exhibit the antiferromagnetic (AFM) nature of  $Sm_{1-x}Ae_xTiO$ ; however, the Neel temperature reduces from 53 K for undoped  $SmTiO_3$  to 45 K and 40 K for Ba and Sr doped  $SmTiO_3$  respectively. The M *vs* H study also showed a faint AFM hysteresis at RT. Dielectric properties under various frequency ranges (100 Hz – 5 MHz) investigated between 100 and 400°C depicts a weak ferroelectric phase due to moderate structural distortion induced by chemical doping which in turn could be responsible for the distinctive magnetization and polarisation changes at room temperature.

*Keywords:* A. Multiferroics; B. Perovskite structure; C. Magnetization; D. Dielectric permittivity; D. Ferroelectric hysteresis.

#### **1. Introduction**

An idea behind the tuning of magnetisation, polarisation and strain factors of the multiferroic characteristic of materials is one among the vast interesting topics over the last few decades that have direct promising technological applications. The ability to regulate the electrical polarization by either an electric field or magnetic field and vice versa makes these magneto-electric (ME) multiferroic materials extensively feasible for application in data storage<sup>1</sup>, spin valves<sup>2</sup>, spintronics<sup>3</sup>, sensors<sup>4</sup> and microelectronic devices [1-4]. Apart from the naturally existing multiferroics like BiFeO<sub>3</sub> and Cr<sub>2</sub>O<sub>3</sub>, novel multiferroic composites with high magneto-electric coupling is of much interest and new multiferroic materials can be projected through various combinations. Usually, in case of perovskites (ABO<sub>3</sub>) the cations of a  $(ns)^2$  valence electron configuration occupying the A-site ensures stability of ferroelectrically distorted structures and the B-site atom mostly contributes to the magnetic exchange interactions. Since A-site is responsible for the stability of the central BO<sub>6</sub> in its centrosymmetric position, the prime concern lies in disturbing them by introducing cations of various sizes into the A-site. This would in turn alter the dielectric as well as the magnetic properties of perovskites.

Rare earth titanates (RTiO<sub>3</sub>) are an important class of materials, where the magnetic properties are extremely sensitive to the magnitude and details of the lattice distortion and hence have drawn considerable attention recently. The additional features of RTiO<sub>3</sub> are, they are isostructural and isoelectronic materials and have only one electron in the  $t_{2g}$ -shell of Tiatoms.<sup>5</sup> Also, the pertaining superexchange interactions in orthorhombically distorted Titanates, RTiO<sub>3</sub> has been theoretically contemplated in the report of a grand prospect in tuning its multiferroic property by Solovyev et al [5]. Generally, the magnetic order of Ti of the lanthanides (R=La, Sm) corresponds to G-type antiferromagnetism. This especially relates to the structural anomalies found above the Neel ordering studied using high-

resolution capacitance dilatometer by Komarek et al [6]. Kumari et al reported that BLTMNZ ceramic exhibits a diffuse type phase transition with maximum dielectric constant of 13187 was observed in x = 0.04 composition [7]. A first principles study of Y half-substituted LaTiO<sub>3</sub> revealed hybrid improper polarizations due to a strong inherent phase competition induced by disorder of substitution of Y in place of La [8]. Ionic radii of A-site cations in Ba<sub>1-x-y</sub>Sr<sub>x</sub>Ca<sub>y</sub>TiO<sub>3</sub> sufficiently acquired for the modification of TiO<sub>6</sub> octahedra distortion and T<sub>c</sub> values [9]. An enhancement of lattice distortion and ferroelectric polarisation were also observed in nano-aggregated rare earths Ce and La doped BaFeTiO<sub>3</sub> [10]. In this article, we report on the tuning of the magnetic and dielectric properties of SmTiO<sub>3</sub> by substitution of Ba and Sr alkaline-earth elements into the A site. These compounds were explored for their multiferroic properties by performing their dielectric, ferroelectric and ferromagnetic characterizations at room temperature. Furthermore, we noticed that an optimisation of structural parameters is highly prevailed for their intrinsic magnetic and dielectric properties while on the replacement of samarium by alkaline-earth elements in SmTiO<sub>3</sub> perovskite compound.

#### 2. Experimental details

 $Sm_{1-x}Ae_xTiO_3$ , where Ae (alkaline earth) = Ba, Sr were prepared by the conventional solid state route.  $Sm_2O_3$ ,  $BaCO_3$ ,  $SrCO_3$  and  $TiO_2$  (anatase phase) were weighed as per their stoichiometric ratio mixed with ethanol and then finely ground with Agate mortar. An extra 5% of  $Sm_2O_3$  was added to avoid the loss of rare earth Sm metal at high temperatures. The resultant powders were calcined at 900°C for 6 hours with two intermediate grinding followed by calcinations under H<sub>2</sub>+Ar atmosphere at 1100°C for 12 hours. Finally, the powder samples were mixed with 5% of PVA and pressurised into a compacted pellet for the electrical transport measurements.

The samples were characterized by X-Ray Diffractometer (Bruker D8 advance, CuK $\alpha$ -radiation, wavelength  $\lambda \sim 1.5415$  Å) for structural investigation and Field Emission Scanning Electron Microscope (Philips FEI Quanta-200f) with Energy-Dispersive X-ray spectroscopy studies for surface morphology and elemental composition analyses respectively. Vibrating Sample Magnetometer (LakeShore model-7407, USA) and HIOKI 3532-50 LCR controller (Japan) were used to study the magnetic characteristics, dielectric properties and ferroelectric hysteresis (P-E loop) respectively.

#### **3. Results and Discussion**

Fig. 1 shows the powder X-ray patterns of Sm<sub>0.5</sub>Ba<sub>0.5</sub>TiO<sub>3</sub>(a), Sm<sub>0.5</sub>Sr<sub>0.5</sub>TiO<sub>3</sub>(b) and Sm<sub>0.5</sub>Sr<sub>0.25</sub>Ba<sub>0.25</sub>TiO<sub>3</sub>(c). It showed a typical XRD pattern of polycrystalline perovskite structure. At room temperature, these compounds exhibit orthorhombic symmetry with space group of *Pbnm*. The refined lattice parameters using powder and unit cell softwares with the corresponding changes in volumes for Sm<sub>0.5</sub>Ba<sub>0.5</sub>TiO<sub>3</sub> (a = 5.2687 Å, b = 5.7781 Å, c = 7.779 Å and V = 229.4129 m<sup>3</sup>), Sm<sub>0.5</sub>Sr<sub>0.25</sub>Ba<sub>0.25</sub>TiO<sub>3</sub> (a = 5.3061 Å, b = 5.8023 Å, c = 7.6596 Å and V = 235.8208 m<sup>3</sup>) and Sm<sub>0.5</sub>Sr<sub>0.25</sub>Ba<sub>0.25</sub>TiO<sub>3</sub> (a = 5.3819 Å, b = 5.7862 Å, c = 7.5497 Å and V = 235.0989 m<sup>3</sup>) were compared to the XRD pattern of SmTiO<sub>3</sub> (JCPDS card number – 70-2295; a = 5.454 Å, b = 5.660 Å, c = 7.779 Å and V = 240.13 m<sup>3</sup>). The XRD measurements depicted the change in lattice parameter of SmTiO<sub>3</sub> after the Ba<sup>2+</sup> and Sr<sup>2+</sup> substitution, which confirms a successful addition of host elements. In XRD patterns, the peak splitting was much lower in comparison with the other reports [11].

The tolerance factor (*t*) of Sm<sub>1-x</sub>Ae<sub>x</sub>TiO<sub>3</sub> compounds (t ~ 0.81 for Sm<sub>0.5</sub>Ba<sub>0.5</sub>TiO<sub>3</sub>, ~ 0.76 for Sm<sub>0.5</sub>Sr<sub>0.5</sub>TiO<sub>3</sub> and ~ 0.78 for Sm<sub>0.5</sub>Sr<sub>0.25</sub>Ba<sub>0.25</sub>TiO<sub>3</sub>) were calculated using Goldschmidt formula, t = ((R<sub>a</sub> + R<sub>o</sub>) / $\sqrt{2}$ (R<sub>b</sub> + R<sub>o</sub>)), where R<sub>a</sub>, R<sub>b</sub> and R<sub>o</sub> are the ionic radii of

A, B cations and oxygen respectively [12]. The above calculated tolerance factor values suggests that the substitution of alkaline earth metal atoms into the A-site leads to deviation from the ideal condition (0.880 < t < 1.090) for highly symmetrical perovskite structure [13,14]. Similarly, the orthorhombic distortion factor was calculated using  $\varepsilon = (a-b)/(a+b)$  formula, (where, a and b are the lattice parameters for the equivalent orthorhombic perovskite structure) and were found to be 0.046, 0.044 and 0.036 for Sm<sub>0.5</sub>Ba<sub>0.5</sub>TiO<sub>3</sub>, Sm<sub>0.5</sub>Sr<sub>0.5</sub>TiO<sub>3</sub> and Sm<sub>0.5</sub>Sr<sub>0.25</sub>Ba<sub>0.25</sub>TiO<sub>3</sub> respectively. From the above study, it is clear that though doping of alkaline earth metals in SmTiO<sub>3</sub> results in the distortion of TiO<sub>6</sub> octahedra, yet the overall symmetry of the crystal system is unaffected.

The FESEM images (Fig. 2) show the microstructures of the synthesized polycrystalline samples. In our report, barium doped samarium multiferroic ceramics were mostly rod types with different lengths. Others show a mixture of agglomerated flake and spherical particle like morphologies. The EDX spectrum confirms the presence of respective elements in each sample. In Fig. 3 (a, b and c), it displays the variation of dielectric permittivity with respect to temperature (°C) and applied frequency (Hz) for all three compounds. The magnitude of the dielectric permittivity reduces from 31845 (100 Hz) to 48 (1 MHz) for Sm<sub>0.5</sub>Ba<sub>0.5</sub>TiO<sub>3</sub> and similarly from 2445 (100 Hz) to 71 (1 MHz) for Sm<sub>0.5</sub>Sr<sub>0.5</sub>TiO<sub>3</sub> and 664 (100 Hz) to 297 (1 MHz) for Sm<sub>0.5</sub>Ba<sub>0.25</sub>Sr<sub>0.25</sub>TiO<sub>3</sub> with respect to temperature, which is comparable to Ba doped EuTiO<sub>3</sub> compound [11]. The splitting of dielectric curves with an overlapping dielectric permittivity as a function of temperature might be attributed to either the defects in the polycrystalline form or possible charge disorientation induced by structural disorder due to chemical doping. In order to understand the mechanism of dielectric dispersion in terms of variation of temperature and frequency, the change in dielectric permittivity is plotted against the applied frequency in Fig. 3 (d). It is noted that, by varying frequency, the change in dielectric permittivity was linearly dependent

up to a certain range (~ 10000 Hz). Also, a drastic variation of dielectric permittivity seen at high frequency range is probably attributed to the enhancement of disorder dipole orientation occurred in Sm-Ti-O network. In addition, either a charge imbalance by chemical doping of  $A^{2+}$  (A = Ba, Sr) in Sm<sup>3+</sup> site or induced defects by the emergence of oxygen vacancies were also strong responsible factors for such discriminated dielectric property for these compounds [15,16].

Various magnetic measurements as a function of applied magnetic field and temperature were carried out for all the prepared samples. The temperature dependent dc magnetic susceptibility plots of Sm<sub>0.5</sub>Ba<sub>0.5</sub>TiO<sub>3</sub>, Sm<sub>0.5</sub>Sr<sub>0.5</sub>TiO<sub>3</sub> and Sm<sub>0.5</sub>Ba<sub>0.25</sub>Sr<sub>0.25</sub>TiO<sub>3</sub> measured at 100 Oe are shown in Fig. 4 (a). The magnetic hysteresis loops at various fields of Sm0.5Ba0.5TiO<sub>3</sub>, Sm0.5Sr0.5TiO<sub>3</sub> and Sm0.5Ba0.25Sr0.25TiO<sub>3</sub> samples are also shown in Fig. 4 (b). It is known that, a pristine SmTiO<sub>3</sub> is an antiferromagnetic compound and their Neel transition temperature explicitly evolves at ~53 K [17]. Further, the substitution of Ba and Sr in the place of Sm had shifted their Neel transition temperature to 46.29 K, 42.59 K and 48.64 K for Sm<sub>0.5</sub>Ba<sub>0.5</sub>TiO<sub>3</sub>, Sm<sub>0.5</sub>Sr<sub>0.5</sub>TiO<sub>3</sub> and Sm<sub>0.5</sub>Ba<sub>0.25</sub>Sr<sub>0.25</sub>TiO<sub>3</sub> as shown in the inset of Fig. 4 (a). The observed Neel transition temperature  $T_N = 48.64$  K may be due to the crystal-field splitting and reduced thermal fluctuations as a result of Ba-Sr co-substitution in  $Sm_{1-x}TiO_3$  [5]. At room temperature (300 K), all the three compositions reveal their paramagnetic nature with a small hysteresis loop observed in-between the magnetization magnetic saturation values of Sm<sub>0.5</sub>Ba<sub>0.5</sub>TiO<sub>3</sub>, Sm<sub>0.5</sub>Sr<sub>0.5</sub>TiO<sub>3</sub> curves. The and  $Sm_{0.5}Ba_{0.25}Sr_{0.25}TiO_3 \ \ \text{samples} \ \ \text{are} \ \ 866.48 \ \ x \ \ 10^{-6} \ \ \text{emu/g}, \ \ 891.94 \ \ x \ \ 10^{-6} \ \ \text{emu/g} \ \ \text{and}$ 1682.80 x 10<sup>-6</sup> emu/g respectively. The coercivity values of Sm<sub>0.5</sub>Ba<sub>0.5</sub>TiO<sub>3</sub>, Sm<sub>0.5</sub>Sr<sub>0.5</sub>TiO<sub>3</sub> and Sm<sub>0.5</sub>Ba<sub>0.25</sub>Sr<sub>0.25</sub>TiO<sub>3</sub> samples are 118.54 Oe, 115.78 Oe and 141.89 Oe respectively (see Fig. 4 (d)). The maximum saturation ( $M_s$ ) value of 1682.80 x 10<sup>-6</sup> emu/g obtained from

 $Sm_{0.5}Ba_{0.25}Sr_{0.25}TiO_3$  might be originated due to the tilting of  $TiO_6$  octahedra, which induces a GdFeO<sub>3</sub>-type lattice distortion as evident from the X-ray diffraction pattern.

The effective magnetic moment ( $\mu_B$ ) were calculated for all the compounds using  $\chi^{-1}$  vs T plot and fitting of Curie - Weiss law ( $\chi = C/(T+\theta_p)$ ) were extracted from the respective temperature dependence of magnetic susceptibility curves. It is found that Sm<sub>0.5</sub>Ba<sub>0.5</sub>TiO<sub>3</sub> has Curie constant (C) and paramagnetic Curie temperature values of 0.38 emu.K/g.Oe and – 44 K. Similarly, Sm<sub>0.5</sub>Sr<sub>0.5</sub>TiO<sub>3</sub> and Sm<sub>0.5</sub>Ba<sub>0.25</sub>Sr<sub>0.25</sub>TiO<sub>3</sub> has 0.19 emu.K/g.Oe, – 32 K and 0.12 emu.K/g.Oe, – 29 K respectively. Negative values of  $\theta_p$  further imply that an existence of AFM exchange interaction below 50 K for these types of compounds. The effective magnetic moment decreases from 2  $\mu_B$  for SmTiO<sub>3</sub> to 1.7, 1.2 to 1.0  $\mu_B$  for Ba, Sr and Ba, Sr co- doped SmTiO<sub>3</sub> [18]. This reduction of  $\mu_B$  is due to a small magnetic spin disorder occurring over the samarium magnetic domain by the doping of non-magnetic Ba and Sr elements. Also, a small possibility of spin dilution in Sm<sup>3+</sup> with respect to Ba<sup>2+</sup> and Sr<sup>2+</sup> ions doping is evident. Another reason could be an induced structural defect over the octahedral site (O<sup>2-</sup>), which is conferred from the structural parameters in the XRD refinements [19].

It is well known that, a ferroelectric component of BaTiO<sub>3</sub> (ABO<sub>3</sub> type) arises due to the transformation of Ti ion from the centre of the TiO<sub>6</sub> octahedra, by adding elements through chemical approaches, which in turn modifies the structural symmetry of the orthorhombic perovskite structure [20]. Also, the oxygen vacancies along with valence distribution from Ba<sup>2+</sup> or Ti<sup>4+</sup> ions are highly responsible for the maximum conductivity [21,22]. However, in practical point of view, there are some other factors like charge defects, non-stoichiometry and secondary phases specifically magnetically orientated phases, which highly affects the magnetic and electrical properties. Ferroelectric hysteresis loops (P vs E) observed for Ba, Sr and Ba, Sr co-doped SmTiO<sub>3</sub> materials are shown in Fig. 4 (c). It clearly

shows a well defined ferroelectric hysteresis loop at room temperature for these compounds. We have not found any saturated polarisation loops even at applied electric field of E ~ 2 kV/Cm. However, in that field range, a closed ferroelectric loop has been observed for all the samples indicating a strong polarisation effect in the presence of applied electric field. Moreover, we found that Sm<sub>0.5</sub>Ba<sub>0.5</sub>TiO<sub>3</sub> showed a saturation polarisation ( $P_s$ ) ~ 0.03 µc/Cm<sup>2</sup>, which is higher than other Sr ( $P_s \sim 0.012 \ \mu c/Cm^2$ ) and Ba, Sr co-doped ( $P_s \sim 0.017 \ \mu c/Cm^2$ ) SmTiO<sub>3</sub> polycrystalline compounds. From room temperature magnetic and ferroelectric hysteresis patterns, both compounds have the same mechanism as a function of applied magnetic and electric field. In detail, Ba and Sr doped SmTiO<sub>3</sub> revealed an enhanced  $M_s$  (emu/g) and  $P_s$  (µc/Cm<sup>2</sup>) values, but in the case of Ba and Sr co-doped SmTiO<sub>3</sub> it somewhat differs in both of its magnetisation and polarisation component.

In summary, we studied the multiferroic characteristics from magnetic and ferroelectric hysteresis studies for various alkaline earth metals (Ba and Sr) doped SmTiO<sub>3</sub> polycrystalline compounds prepared by the solid state reaction method. From that, we realised to have a similar behaviour over the loop changes while doping of  $Ba^{2+}$  and  $Sr^{2+}$  ions in the place of SmTiO<sub>3</sub> thus highly responsible for a moderate magnetisation and polarisation effect. Another most important criterion for multiferroic investigation is over the structural distortion by an internal pressure from SmTiO<sub>3</sub> perovskite symmetry by chemical doping could be responsible for other remarkable changes, which are clearly seen from our XRD refinements, dielectric permittivity, magnetic and electrical measurements.

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#### **Figure captions**

**Fig. 1.** Powder X- Ray Diffraction patterns collected at 300 K for (a) Ba, (b) Sr and (c) (Ba,Sr) co-doped SmTiO<sub>3</sub>.

**Fig. 2.** SEM micrographs (a,c,e) and EDX (b,d,f) spectrum of Sm<sub>0.5</sub>Ba<sub>0.5</sub>TiO<sub>3</sub>, Sm<sub>0.5</sub>Sr<sub>0.5</sub>TiO<sub>3</sub> and Sm<sub>0.5</sub>Ba<sub>0.25</sub>Sr<sub>0.25</sub>TiO<sub>3</sub> polycrystalline compounds.

**Fig. 3.** Variation of dielectric permittivity at different temperatures for (a)  $Sm_{0.5}Ba_{0.5}TiO_3$ , (b)  $Sm_{0.5}Sr_{0.5}TiO_3$  and (c)  $Sm_{0.5}Ba_{0.25}Sr_{0.25}TiO_3$  samples in the frequency range of 100 Hz to 5 MHz and (d) change of a dielectric permittivity as a function of frequency.

**Fig. 4.** (a) Temperature dependent magnetic susceptibility of  $Sm_{0.5}Ba_{0.5}TiO_3$ ,  $Sm_{0.5}Sr_{0.5}TiO_3$ and  $Sm_{0.5}Ba_{0.25}Sr_{0.25}TiO_3$  at 100 Oe (Inset reveals a low temperature Neel transitions). (b) Magnetic field dependence of magnetisation (M vs H hysteresis) at room temperature. Figure (c) and (d) shows ferroelectric and magnetic hysteresis patterns measured at room temperature.

Figure 1:



Figure 2:









