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## Magnetic and ferroelectric properties of Fe doped SrTiO<sub>3-δ</sub> films

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**Abstract.** Recent interest in SrTiO<sub>3</sub> stems from its wide applicability in microwave devices based on the tunable characteristics of dielectric constant in the microwave frequency range. It is obvious that for any such application, SrTiO<sub>3</sub> should have a ferroelectric Curie temperature ( $T_C$ ) close to room temperature or higher. By inducing strains by chemical substitutions, it was possible to obtain  $T_C$  as high as 200°C in SrTiO<sub>3</sub> modified with Fe<sup>4+</sup>. Hysteresis loops obtained confirms the presence of ferroelectric domains. Two apparent transitions, one at ~200 °C and another ~300 °C were seen in  $\epsilon'$ , which are replicated as sharp drops in resistivity curves. These temperatures far exceed the  $T_C$ s reported in the literature till now and could open new avenues for innumerable other applications for SrTiO<sub>3</sub>. The magnetic properties of Fe doped SrTiO<sub>3</sub> are also investigated. Low doping of Fe exhibits simple antiferromagnetic behaviour.

### 1.Introduction

SrTiO<sub>3</sub>, a quantum paraelectric or an incipient ferroelectric [1], whose phase transition to the ferroelectric state ( $T_C$ ) is quenched by the quantum fluctuations, allows non-linear properties only at low temperatures[2]. SrTiO<sub>3</sub> has long been labelled as a material for high frequency tunable devices, in particular in the microwave frequency range and any possible application needs a high temperature or at least a room temperature dielectric transition. Concerted efforts are in progress to induce ferroelectricity and increase the  $T_C$  close to room temperature either by chemical substitutions or by induced strains. SrTiO<sub>3</sub> doped with Mn and Pr showed polar behaviour with enhanced  $T_C$ . In the case of Pr-doped SrTiO<sub>3</sub>, room temperature ferroelectricity was seen [3], with spontaneous polarization decreasing as a function of increased Pr doping. In the Mn-substituted SrTiO<sub>3</sub> however, a broad dielectric transition with relaxor-like behaviour was seen with a transition maximum around 50 K [4]. In these two cases, instabilities and there by large amounts of strain created by the addition of the aliovalent with ionic radii close to that of the host ion has been exploited in realizing ferroelectricity. In a recent report Haeni *et al* [1], have shown that large strains similarly can be induced by other means, for example by depositing epitaxial layers of SrTiO<sub>3</sub> on single crystals of DyScO<sub>3</sub>, enhancing  $T_C$  by several hundreds of degrees.

Following the approach of inducing strains in the lattice by means of chemical substitutions to induce ferroelectricity, we were able to bring up the  $T_C$  above room temperature. Significantly enhanced  $T_C$  (up to 200 °C) was seen in a polycrystalline film of SrTiO<sub>3</sub> doped with 10 mole% of Fe, with strains modifying the crystal structure from a simple cubic (SrTiO<sub>3</sub>; space group Pm3-m,) to tetragonal (Fe-doped SrTiO<sub>3</sub>). Oxygen non-stoichiometry forces some of the Fe<sup>4+</sup> into Fe<sup>3+</sup> and in addition, presence of oxygen vacancies could induce considerable strain in the lattice, making the structural transformation possible. It is known that a distorted perovskite structure with tolerance factors <1 could induce spontaneous polarization.

SrFeO<sub>3-δ</sub>, which is a cubic perovskite when δ=0, with the structure transforming into a Brownmillerite orthorhombic phase when δ→ 0.5 [6]. The loss of oxygen, compounded by the disproportionation of Fe<sup>4+</sup> and Fe<sup>3+</sup> in the lattice together produces lowered crystal symmetry. In the orthorhombic state, in SrFeO<sub>2.5</sub>

oxygen vacancies were found to have been ordered with an oxygen missing in each alternate octahedra. Similarly, it is also possible to reduce the cubic symmetry in SrTiO<sub>3</sub> by means of reducing the stoichiometry of oxygen. This can be achieved by reducing SrTiO<sub>3</sub> or by the incorporation of aliovalent ion into the Ti<sup>4+</sup> site. We believe that the lowered symmetry achieved by means of doping an aliovalent ion, affected by the symmetry can induce dipole moment in SrTiO<sub>3</sub>. If the oxygen vacancy ordering also occurs in the reduced SrTiO<sub>3</sub> as seen in Brownmillerite SrFeO<sub>2.5</sub>, it can also cooperatively incorporate ordering in anion-cation pairs thus bringing in ferroelectricity.

As for the magnetic properties are concerned the other end of the series i.e., SrFeO<sub>3</sub> (with the complete replacement of Ti with Fe) is a helical antiferromagnet ( $T_N = 134$  K) and oxygen stoichiometry plays an important role in establishing the magnetic and transport properties in this system [5, 7]. SrFeO<sub>3- $\delta$</sub>  ( $\delta \sim 0$ ) is metallic at room temperature and at  $\delta \sim 0.15$  metal-insulator (MI) transition takes place with a large change in magneto resistance. As  $\delta \rightarrow 0.19$ , a charge ordered (CO) state appears around  $T_N$ . In an earlier paper we have identified compositions that lie on the boundary between MI and CO insulating states [7]. It is possible to dilute the helical structures in oxides by use of pressure, magnetic field and also by doping non magnetic ions. We have shown that by doping with a non magnetic ion such as Ti<sup>4+</sup> leads to a simple antiferromagnetic structure at lower Ti doping levels [7]. In this work the magnetic properties of the complete series of SrFe<sub>x</sub>Ti<sub>(1-x)</sub>O<sub>3- $\delta$</sub>  with x=0.2 to 0.9 have been carried out and it is shown that the ordering temperature decreases with decrease in Fe content.

## 2. Experimental

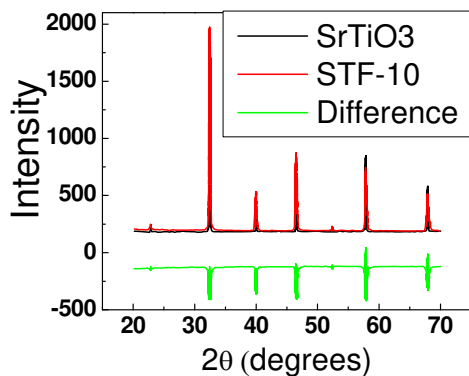
### 2.1 synthesis and characterization

In order to achieve the objectives of lowering its cubic symmetry and induce ferroelectricity in SrTiO<sub>3- $\delta$</sub> , 10 mole% of Fe was doped at the Ti<sup>4+</sup> site (hereafter called STF10). Polycrystalline films of 20  $\mu$ m thick were prepared using screen printing with STF10 sandwiched between two layers of screen printed Pt-electrodes on a sintered alumina substrate. Prior to the screen printing, STF10 powders were prepared by solid state reactions starting with stoichiometric powders of SrCO<sub>3</sub>, TiO<sub>2</sub>, and Fe<sub>2</sub>O<sub>3</sub>. The ball milled powders were heated at 1400 °C, before they were mixed with suitable inks for screen printing. The screen printed film was characterized using X-ray diffraction and has been identified as phase pure without any impurities. Dielectric measurements were done on a Solartron impedance analyzer (1260) in the temperature between 30 and 500 °C at frequency 1 kHz, 100 kHz, and 1 MHz at bias fields of 0, 10 and 20 V. Pyroelectric current was measured ramping the temperature at 10 °C/m in the temperature range 30-500 °C using a Keithley digital multimeter. Ferroelectric hysteresis loops were traced using the Radiant technology's RT66 test system in the Sawyer-Tower mode at various temperatures. The magnetic properties of different compositions of SrFe<sub>x</sub>Ti<sub>1-x</sub>O<sub>3- $\delta$</sub>  were investigated using a Physical Property measurement system.

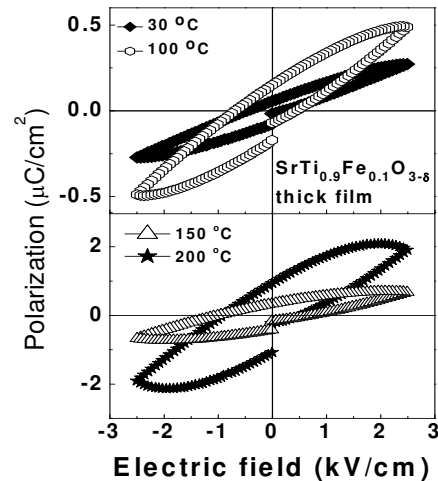
X-ray diffraction carried out on STF10 thick film screen printed over sintered alumina showed the polycrystalline nature of the film with no traces of impurity. The spectrum included peaks not only those of STF10 but also of Pt, which is used as an electrode, and alumina. This made analysis difficult and to circumvent this problem, instead X-ray diffraction patterns of the STF10 powders were obtained. These screen printed powders are expected not to show any drastic change either in structure or on composition as they were fired at low temperatures to evaporate the inks in the pastes.

'Figure 1' shows the X-ray diffraction spectrum of powders of sintered STF10 powders which were screen printed on sintered alumina and fired at temperatures low enough to bring in the required adhesion without modifying the sample phase. The pattern shows a clean SrTiO<sub>3</sub> phase without impurities, with slight increase in the volume of the unit cell. Significantly, there are a number of peaks which show clear splits, indicating the transformation of the cubic perovskite structure of SrTiO<sub>3</sub> into a lower symmetry. This lowered symmetry, due to the addition of Fe- at the Ti- site could induce non-centrosymmetry, which is responsible for the realization of ferroelectricity in a number of perovskite oxide materials. Two reasons that could result in the lowered symmetry are (1) the addition of Fe<sup>4+</sup>, which induces strains in the

lattice due to the slight mismatch in the ionic radius and (2) the strains that are possible by the deposition of STF10 on the sintered alumina. Even though the significance of the strains due to the latter could be small when compared to the epitaxial films, their contribution to the lowered symmetry cannot be ignored. Tests to measure dielectric and ferroelectric properties were carried out in order to check the presence of ferroelectricity in STF10, due to the lowered sym



**Figure 1.** XRD pattern of SrTiO<sub>3</sub>, STF10 recorded using CuK<sub>α</sub> wavelength. The difference in intensity of these two patterns is shown.



SrTi<sub>0.9</sub>Fe<sub>0.1</sub>O<sub>3-δ</sub> thick film measured at different temperatures.

### 3 Results and Discussion

Hysteresis loops traced for STF10 thick films at different temperatures are shown in ‘figure 2’. Polarization shows a degree of saturation around 2.5 kV/cm with clear irreversibility, tracing a hysteresis loop. Attaining a complete saturation is marred by the experimental limitations. Nevertheless the trend of polarization reaching saturation is a clear indication of the presence of ferroelectric domains, even though without a significant degree of polarization as compared to ‘classical’ ferroelectrics like BaTiO<sub>3</sub> or PbTiO<sub>3</sub>. With the increase in temperature ( $T > 30$  °C), the hysteresis loops broaden and the spontaneous polarization increases. This is in contrast to ‘classical’ ferroelectrics, where the spontaneous polarization does not show an increase and exhibits a first order transition as a function of temperature as temperature reaches the Curie point ( $T_C$ ). In the present case however, polarization keeps increasing as the temperature is increased above 30 °C and does not reduce to zero even at temperatures higher than 150 °C. Further increase in temperature results in higher conductivity with higher dielectric loss factor, leaving a hysteresis loop that is larger in size. This is evident from the hysteresis traced at 200 °C, which shows a loop almost that of a lossy dielectric, but with largely reduced saturation. Polarization increases as a function of temperature continuously until experimental limitations curb further measurement ( $T > 200$  °C). To confirm the presence of high  $T_C$ , dielectric, resistivity, and pyroelectric responses were carried out as a function of temperature.

The oxygen non-stoichiometry and the mobility of the oxygen vacancies play an important role in the conductivity mechanism of these types of perovskites [8]. At high temperatures, the conductivity is dominated by the oxygen vacancy motion. The oxygen vacancies may get polarized and retain the polarization after the electric field is turned off. At high fields it was observed that oxygen vacancies cannot cross the grain-boundaries saturating the polarization. The polarization observed in this particular case may be due to the couple dipole moment between the cation and anion vacancy [9].

‘Figure 3’ (a) shows the variation of dielectric constant ( $\epsilon'$ ) and loss factor ( $\tan \delta$ ) as a function of temperature measured at 1 kHz under zero dc bias and 10 V bias. At zero bias, the dielectric constant increases with increasing temperature showing two slope changes, one around 200 °C and another around 350 °C, which are indicative of ferroelectric  $T_C$ s.

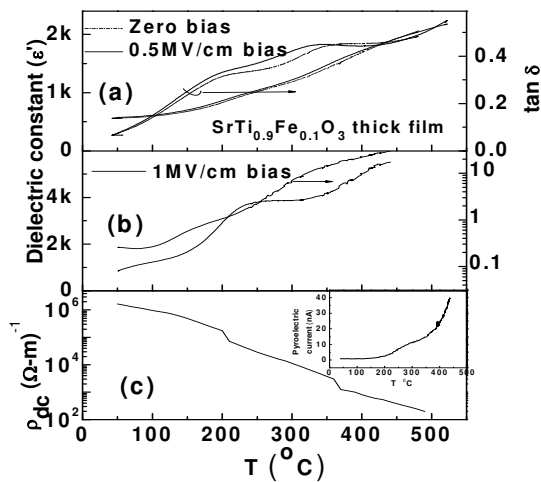


Figure 3. Dielectric constant and loss tangent versus temperature for  $\text{SrTi}_{0.9}\text{Fe}_{0.1}\text{O}_3$  thick film. (a) Zero bias (dotted line), 0.5 MV/cm bias (thick line), 1 MV/cm bias (thin line). (b) 1 MV/cm bias. (c) Conductivity and pyroelectric current (inset) with temperature.

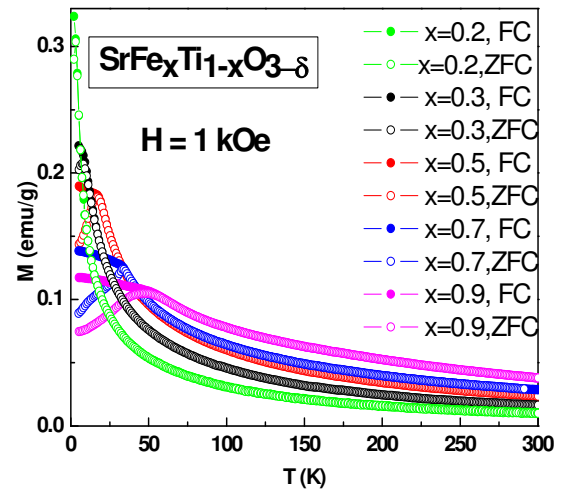


Figure 4.  $M(H)$  versus  $T$ . Filled circle FC and open circle ZFC, at constant field of 1 kOe for  $\text{SrFe}_x\text{Ti}_{1-x}\text{O}_{3-\delta}$  with  $x=0.2, 0.3, 0.5, 0.7, 0.9$

Even though the magnitude of the transitions is not very significant in  $\epsilon'$  vs  $T$ , the two peaks are clearly seen in the dielectric loss.

The transitions are broad, which is indicative of a diffused dielectric transition usually seen in perovskite systems known as ‘relaxors’ that have an inhomogeneous distribution of B-site cation and nano-domains. Increasing values of  $\tan \delta$  conform with the increase in the area under the hysteresis loop, which is directly proportional to the conductivity. At high temperatures the loss tangent is high ( $\sim 0.45$ ), indicative of high conductivity complementing the large area under hysteresis.

With increasing dc bias (0.5 MV/cm), the temperature dependence of the dielectric constant shows up relatively prominent slope changes around the  $T_{CS}$ . Dielectric loss on the other hand shows two clearly resolved peaks with slightly lowered Curie temperatures. Increase in the bias voltage to 1 MV/cm produces a significant change in the dielectric constant curve, with increased  $\tan \delta$  values. Increasing the bias field makes the domains strongly align towards the field direction. Dielectric loss shows broad peaks corresponding to those seen at zero and 0.5 MV/cm bias fields.

‘Figure 4’ shows the zero-field cooled (ZFC) and field cooled (FC) dc magnetization of different compositions of polycrystalline  $\text{SrFe}_x\text{Ti}_{1-x}\text{O}_{3-\delta}$  samples. With decreasing Fe content  $T_N$  shifts to lower temperatures. ZFC and FC show sharper maxima and decrease in bifurcation with increase in  $\text{Ti}^{4+}$  indicating the decrease in frustration. This is also evident from the low hysteresis loop which shows a non linear behaviour indicating the collinear antiferromagnetic structure.

It is shown that by inducing strain through chemical substitution,  $\text{Fe}^{4+}$  doped  $\text{SrTiO}_{3-\delta}$  films exhibit ferroelectric properties with a high temperature transition ( $T > 200^\circ\text{C}$ ).

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