

Dielectric studies of polycrystalline (Sr,Fe)TiO₃ ceramics

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The characteristic properties of polycrystalline (Sr,Fe)TiO₃ ceramics have been studied through Mössbauer, EPR, IR and differential scanning calorimetry because perovskite type dielectrics have useful applications in electronic industry. In Fe-doped materials, the small concentration of Fe atoms provides active centres that can be probed through Mössbauer and EPR methods which are precise enough to detect small lattice structural perturbations and yield valuable information. The present work deals with their dielectric properties including dielectric relaxation time that is considered an important study from a theoretical angle. It is found that the two-state Debye relaxation model is inadequate. These ceramics tend to behave like relaxors with ferroelectric transition temperature in the range 200-250°C depending upon iron concentration.

Keywords: Ferroelectric ceramics, Relaxor, Dielectric relaxation

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1 Introduction

Dielectric materials PbTiO₃ and BaTiO₃ belonging to the tetragonal perovskite structural class, and their synthetic analogues with various substitutional atoms, have been widely studied because of their technological applications in electronic industry¹⁻⁴. In the same series, SrTiO₃ has cubic symmetry at room temperature with no ferroelectric property (it exhibits ferroelectric transition below 40K under strong electric field). Therefore, it was chosen as a reference material to study the effect of doping with a small fraction of iron which is an important transition metal element. Also, paramagnetic Fe(3+) can give EPR, IR and Mössbauer spectra which can be analyzed in a complimentary manner for a systematic study and such studies on polycrystalline Sr_{1-x}Fe_xTiO₃ ($x = 0.1, 0.2$ and 0.3) have already been reported^{5,6}. Recently, differential scanning calorimetry and XRD studies of these samples have also been reported through which structural phase change in the doped samples have been identified⁷. The series of studies on these Fe-doped ceramic samples have thrown light on the physical and lattice dynamical aspects of the perovskite type crystals.

The present work on the measurement of dielectric constant of these materials is important from the point of view of practical application. The synthesis and dielectric studies on iron-based ceramics of different types, usually referred³ as PFT (lead, iron, tantalum), PFN (Refs 3,8) (lead, iron, niobium), BFN (Refs 4,9) (barium, iron, niobium), have been reported in recent

years. In the light of its relaxor behaviour, the ferroelectric BFN (BaFe_{0.5}Nb_{0.5}O₃) ceramic has also been well studied for its semiconducting and electrical properties. This class of ceramic has drawn wide attention as it appears to provide an environmentally safe material with ambient dielectric properties and it has the potential to replace lead-based ceramics in electronic industry. It was, therefore, considered desirable to study the dielectric behaviour of Sr_{1-x}Fe_xTiO₃ and examine the result of Fe substitution. However, there is a basic difference between this system and those described above in respect of atomic substitution. In those materials (for example BFN), it is the tetravalent Ti which is totally substituted by a combination of other atoms, whereas in our case, it is the divalent Sr which has been partially substituted by Fe atoms. The charge imbalance is expected to give rise to structural distortion (lower than cubic) and produce a non-zero dielectric constant. This gives the basis for a detailed study of the dielectric constant of the ceramic under investigation.

2 Experimental Details

The polycrystalline Sr_{1-x}Fe_xTiO₃ ceramics were prepared through high temperature solid state reaction method. The starting materials were high grade SrCO₃, TiO₂ and Fe₂O₃ and these were thoroughly mixed in the right proportion for the chosen concentration of Fe in a given sample. The mixture was calcined at 1040°C for 8 hr in the normal supply

of oxygen and then gradually cooled over several hours. The lumps were thoroughly crushed in the powdered form and mixed with binder PVA (polyvinyl alcohol) and shaped as pellets under the pressure of $1.52 \times 10^7 \text{ kg m}^{-2}$. These pellets were sintered at 1050°C for ten hr and then cooled down to room temperature over a period of 4 hr. Such pellets and their powder were used for various experiments except for the measurement of dielectric constant. Almost after two years, a few of these pellets were polished to make both the faces flat and parallel, and then thinly coated with high purity air dry silver paste which was prepared by a thorough mixing of fine silver powder in the organic liquid amyle acetate. These pellets had the diameter of 2.54 cm and thickness of 2.39 mm and were used for dielectric measurements.

3 Results and Discussion

The SEM photograph given in Fig. 1 shows that the particle distribution in the sample is homogeneous and uniform with average grain size of about $5.1 \mu\text{m}$ as calculated by Jefferies Planimetric method. There were some patches present in the pellets. Capacitance

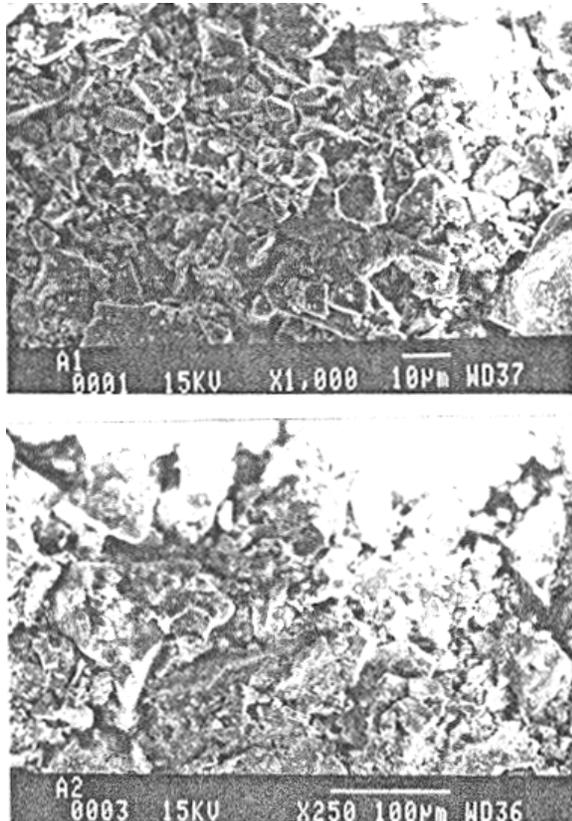


Fig. 1—SEM photographs of polycrystalline $(\text{Sr}_{1-x}\text{Fe}_x)\text{TiO}_3$ ceramics for $x=0.1$ and 0.2 , respectively

and loss tangent measurements were carried out in metal-insulator-metal (MIM) system using H10K1 3532-50 LCR HiTESTER. Dielectric constant (ϵ) was calculated by the relation $\epsilon = C/C_0$ where C and C_0 are the capacitance of the parallel plate condenser with and without the pellet. Here $C_0 = (0.08854 A/d) \text{ pF}$ where A is the area of the pellet and d is its thickness. The dielectric constant and loss tangent ($\tan\delta$), and their variation with frequency of the applied electric field and temperature, are the measured parameters.

The dielectric constant decreases with frequency and similarly the magnitude of loss tangent is reduced at higher frequencies. and room temperature for the sample with $x = 0.1$ as shown in Fig. 2. The dielectric constant and loss tangent ($\tan\delta$) decrease with the frequency of the electrical signal which is in general agreement with experimental data on ferroelectric materials^{10,11}. The variation of dielectric constant over the temperature range $32\text{--}250^\circ\text{C}$, at frequency 100 Hz shows little change up to 150°C followed by a sharp increase beyond 150°C that appears to achieve a maximum at around 250°C or at a higher value as shown in Fig. 3. This behaviour is shown by all samples, that is for $x = 0.1, 0.2$ and 0.3 . At higher frequencies of 1 kHz and 10 kHz, the variation is very little. It is found that the $x = 0.1$ sample has the largest value of dielectric constant of about 10,000 at 250°C whereas this value decreases to about 7500 – 7000 for $x = 0.2$ and 0.3 .

The variation of $\tan\delta$ with temperature at electrical frequency 100 Hz given in Fig. 4 shows a peak around 200°C and its overall nature resembles with a broad Gaussian profile while the peak shifts towards higher temperatures at higher frequencies. This may be related to the phenomenon of dielectric

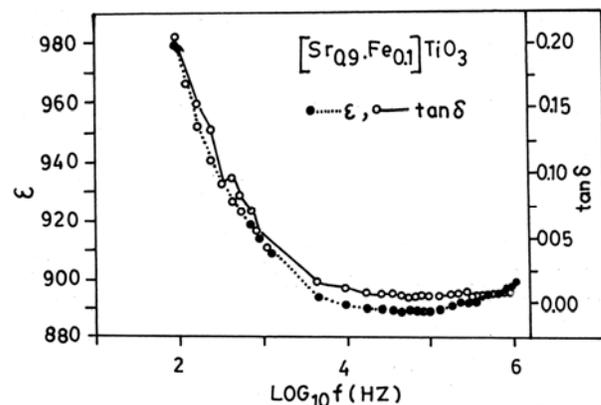


Fig. 2—Variation of dielectric constant (ϵ) and $\tan\delta$ at room temperature as a function of electrical frequency for the sample with $x=0.1$

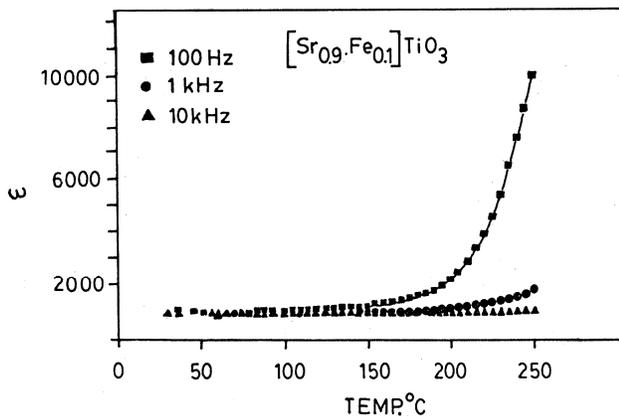


Fig. 3—Variation of dielectric constant (ϵ) with temperature for the sample with $x = 0.1$

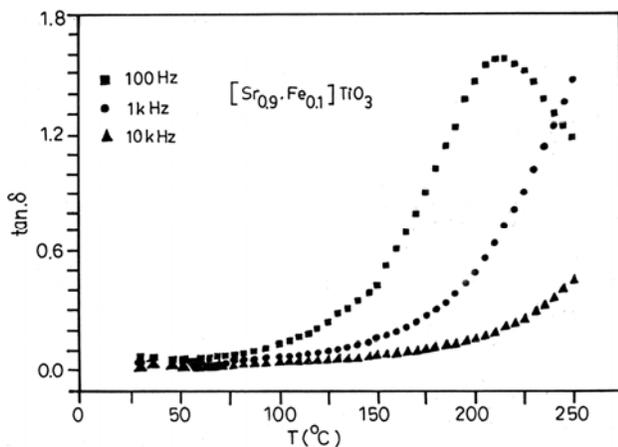


Fig.4—Variation of $\tan\delta$ with temperature for the sample with $x = 0.1$

relaxation¹². The relaxation time, which is related to the internal mechanism that couples electric polarization to lattice vibrations (or lattice distortions), may depend on temperature. The expression¹² for $\tan\delta$ is given by:

$$\tan\delta = [(\epsilon_0 - \epsilon_\infty) \omega\tau] / [\epsilon_0 + \epsilon_\infty \omega^2\tau^2] \quad \dots(1)$$

where ϵ_0 is the dielectric constant at low frequency ($\omega \rightarrow 0$), ϵ_∞ is the dielectric constant at very high frequency ($\omega \rightarrow \infty$) and τ is the relaxation time. At the peak (or maximum) of the curve $d(\tan\delta)/dT = 0$ and using the properties of the partial differential one may express it as $[d(\tan\delta)/d\tau] [d\tau/dT] = 0$.

The dielectric relaxation time represents the time taken by the electric polarization to make a transition between two (or more) quantum states of the lattice—in the same manner as magnetic relaxation happens due to transition between two magnetic states^{13,14}

(spin orientations). How can one visualize the two quantum states of a ferroelectric lattice? The simplest picture can be the two possible structures with different electric polarizations between which the crystal makes a transition or solids made of molecular groups which possess permanent dipole moments that can assume two directions (equilibrium positions) having same energy. Such a model is well represented by two similar potential wells (or configurational energy states) separated by a potential barrier E between which the dipoles can make transitions and their probability will depend on temperature. This represents a two-state Debye relaxation¹² for which $\tau = \tau_0 \exp(E/k_B T)$, but to calculate the value of the pre-exponential factor one may have to formulate the hamiltonian which connects the two states and then compute transition probability, etc. This is a non-trivial problem as has been shown in the case of magnetic relaxation¹⁴.

In general, $[d\tau/dT] \neq 0$ but one can have $[d(\tan\delta)/d\tau] = 0$ at $T = 200^\circ\text{C}$. This gives:

$$\tau = (\epsilon_0 / \epsilon_\infty)^{1/2} (1/\omega) \quad \dots (2)$$

The low frequency value of $\epsilon_0 \approx 10,000$ is the measured value for electrical signals of 100 Hz at $T = 200^\circ\text{C}$ in these ceramic samples. Experimental data at very high frequencies (say at MHz) are not available, but one can infer about them from the refractive index measurements at optical wavelengths and use the relation $\mu = (\epsilon)^{1/2}$, where μ is the refractive index of the material. The refractive index of SrTiO_3 for yellow light ($\lambda = 5893\text{\AA}$) has been measured as 2.40, that gives $\epsilon_\infty = 5.76$. Using these values in Eq. (2), one obtains that $\tau = 0.067$ sec (at $T = 200^\circ\text{C}$) which may be taken as its typical lowest value within an order of magnitude because both ϵ_0 and $(1/\omega)$ are expected to increase at lower frequencies.

4 Dielectric Relaxation

The study of relaxation time τ as a function of temperature can give valuable information about the dielectric relaxation mechanism inside the material. This has been attempted from the variation of $\tan\delta$ with temperature. At a given temperature, τ has been calculated from the corresponding value of $\tan\delta$ from the expression given in Eq. (1) and the typical τ - T curve for one of the samples has been shown in Fig. 5(a and b). The expression given in Eq. (1) gives a quadratic equation and two values of τ are obtained

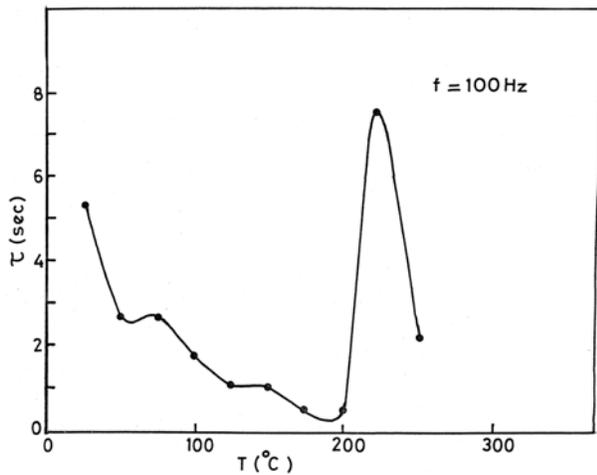


Fig. 5(a)—Variation of dielectric relaxation time (τ) with temperature at $f=100$ Hz for the sample with $x=0.1$

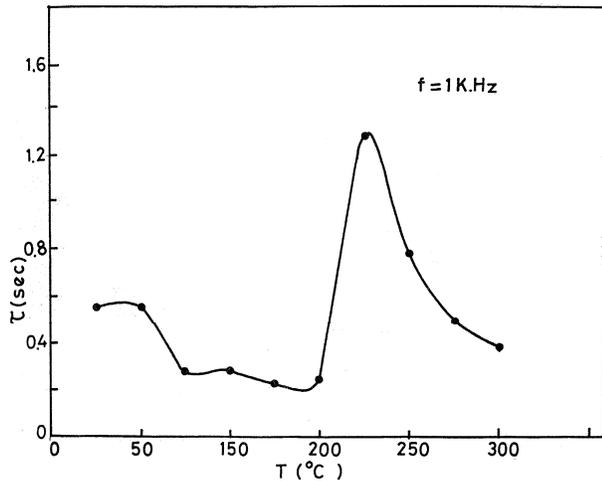


Fig. 5(b)—Variation of dielectric relaxation time (τ) with temperature at $f=1$ kHz for the sample with $x=0.1$

for a given $\tan\delta$. Figure 5(a and b) shows the variation for the larger value of τ whereas the second value is about four to six orders of magnitude smaller. The calculated values for one sample with $x = 0.1$ and at $f = 100$ Hz have been given in Table 1.

The τ - T curves for different samples or different frequencies show a similar nature but are shifted on the temperature scale by 20 to 30°C on either side. This indicates a significant change in lattice properties with respect to Fe concentration.

The τ - T curve gives the appearance of resonance or Gaussian profile that is not supported by Debye type two-step relaxation process. It also indicates the role of phonons. A simple expression may be given by:

$$\tau = \tau_0 \exp[(E-E_p)/k_B T] \quad \dots (3)$$

Table 1—Variation of relaxation time τ for sample $x=0.1$ and $f=100$ Hz

T ($^{\circ}\text{C}$)	$\tan\delta$	ϵ_0	τ (s)	τ (s)
25	0.05	975	5.36	8×10^{-5}
50	0.10	975	2.68	1×10^{-4}
75	0.10	975	2.68	1×10^{-4}
100	0.15	975	1.78	2×10^{-5}
125	0.25	975	1.07	4×10^{-5}
150	0.40	1500	1.03	6×10^{-6}
175	0.90	1625	0.51	1.2×10^{-3}
200	1.40	2500	0.49	2.2×10^{-6}
220	1.60	4375	7.54	2.6×10^{-6}
250	1.25	10,000	2.21	1.9×10^{-7}

where E is the potential barrier and E_p is the energy of phonons. The emission/absorption of phonons of different energies relative to potential barrier could give rise to a variety of relaxation times and this is manifested in this simple expression. The role of phonons becomes apparent for uniaxial dipoles (dipoles moments with two orientations) having potential (configurational) energy $E = -E_0 \cos^2\theta$, where θ is the angle between the dipole moment and the symmetry axis of the crystal. This gives two potential wells with energy minima at $\theta = 0, \pi$ and energy maximum at $\theta = \pi/2$. The transition from one potential well to the other (reversing the dipole's orientation) requires crossing over the potential barrier of magnitude E_0 and it is to be phonon assisted. This brings into picture phonons and their energy spectrum.

The three regions corresponding to $E \gg E_p$, $E \approx E_p$ and $E < E_p$ are obvious in expression given in Eq. (3). In the first case, it approximates to Debye-type $\tau = \tau_0 \exp(E/k_B T)$ that may be valid at low temperatures when energetic phonons are hardly available in the crystal. In the second case, the relaxation time assumes a peak value at moderate temperatures, and finally in the third case the relaxation time decreases at high temperatures. This description resembles qualitatively with the nature of the τ - T curves given in Fig. 5(a and b). Thus, the phonon spectrum of the lattice is expected to decide the effective relaxation time. At working temperatures one may expect a combination of the three cases and so a simple theory of relaxation may be inadequate.

In any detailed analysis of the relaxation process one may have to calculate the transition probability between the low energy quantum states (say, ϕ_1 and

ϕ_2) of the lattice via the virtual excited state (ϕ_3), and it may be given by the Orbach¹⁵ type approach for magnetic relaxation as:

$$P_{1 \rightarrow 2} = \int (2\pi/\hbar) \{[\langle \phi_1 | V' | \phi_3 \rangle \langle \phi_3 | V' | \phi_2 \rangle] / [(E_0 - \omega\hbar) + i\Gamma/2]^2\} \rho(\omega\hbar) d\omega \quad \dots (4)$$

where V' is the perturbing interaction hamiltonian that connects the two lattice states, $\rho(\omega\hbar)$ is the phonon density of states and the integration extends over the entire phonon spectrum. Considering the complex nature of the denominator the expression reduces into the form:

$$P_{1 \rightarrow 2} = \int (2\pi/\hbar) \{[\langle \phi_1 | V' | \phi_3 \rangle \langle \phi_3 | V' | \phi_2 \rangle]^2 / [(E_0 - \omega\hbar)^2 + (\Gamma/2)^2]\} \rho(\omega\hbar) d\omega \quad \dots (5)$$

A similar expression appears for the reverse transition probability $P_{2 \rightarrow 1}$ and the relaxation rate (inverse of relaxation time) is given by the sum of two transition probabilities. For a detailed calculation, one has to construct lattice states (ϕ 's) in terms of phonon occupation numbers and V' will be given in terms of phonon annihilation and creation operators which represent temperature dependent molecular vibrations (displacements) in the crystal.

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