Mossbauer, EPR and IR studies of some Fe doped dielectric materials

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The PbTiO$_3$ and BaTiO$_3$ are well-known ferroelectrics of ABO$_3$ type perovskite structure with dielectric constants of about a few hundred. Several ceramics synthesised partially with other divalent, tetravalent and pentavalent atoms show high dielectric constants and are useful for electronic components and hence their characterisation is important. Mossbauer, EPR and IR methods can be quite effective provided these ceramics contain a small percentage of Fe which produces spectra depending upon its valence state and local symmetry. The spectra of such lead and strontium titanates show the presence of high spin Fe(III) valence state as indicated by $Q_S$, $I_S$ and $g$-values. The IR band at around 600 cm$^{-1}$ seems to originate from FeO$_6$ polyhedron besides the usual absorption band at around 410 cm$^{-1}$ coming from the TiO$_6$ polyhedron.

[Keywords: Ferroelectrics, PbTiO$_3$ and BaTiO$_3$, Dielectric materials, Ceramics]

1 Introduction

The PbTiO$_3$ and BaTiO$_3$ are widely studied ferroelectric crystals of ABO$_3$ type perovskite structure, at room temperature, with dielectric constants of about a few hundred. The dielectric constant usually follows the Curie-Weiss law $\varepsilon = B + A/(T-T_0)$ and accordingly, it shows a sharp peak around $T=T_0$ and quite often more than one transition temperature is shown by the experimental data. The standard explanation for permanent electric polarisation or ferroelectricity in these insulators is given in terms of their perovskite type crystal structure, which lacks the centre of symmetry. Their structure belongs basically to the bcc class, where divalent Pb or Ba ions occupy the corners and the tetravalent Ti occupies the body-centre of the cube which has undergone tetragonal distortion. There are three oxygen ions per molecule (or per unit cell located at face centres), which provide charge compensation and insulating property to the crystal, because bonding within the molecule effectively leads to inert shell configuration of all atoms. Such materials have important applications in making electrical components, capacitors, infrared sensors, piezoelectrics etc. and therefore, attempts have been made, in recent years, to synthesise materials with a high dielectric constant over a broad range of temperature.

A number of ceramic compounds have been synthesised by the solid-state reaction method, at high temperatures in the polycrystalline form, where either A type or B type ions have been partially or fully replaced by other suitable metallic ions. The important ones have been classified as (i) PMN (lead, magnesium, niobium) and (ii) PMN (lead, magnesium, niobium)$^{14}$ and (iii) BST (barium, strontium, titanium) series$^6$, etc. The category (i) includes ceramics like Pb(Mg$_{0.33}$Nb$_{0.67}$)O$_3$, Pb(Mg$_{0.33}$Zn$_{0.67}$)O and Pb(Mg$_{0.33}$Zn$_{0.67}$)O, for which the dielectric constant lies within 5000 to 8000 over the frequency range 1 to 10 kHz. These compounds behave as relaxors showing a broad peak in $\varepsilon$-$T$ curve. The category (ii) includes Pb(Mn$_{0.25}$Mg$_{0.75}$)O, for which the dielectric constant lies between 1400 to 1800 over the frequency range 1 to 10 kHz. The category (iii) includes many preparations like Ba$_{1-x}$Sr$_x$TiO$_3$ ($x = 0.1, 0.2, 0.3, 0.4, ...$) for which the maximum value of dielectric constant is about 1430 at the frequency 1 kHz. The materials falling under the first two categories have transition temperatures within -8 to 12 Celsius, whereas the last one has a transition temperature of about 64 Celsius. These preparations and measurements indicate quite clearly that, both dielectric constant and transition temperature of such materials can be suitably changed by a combination of metallic substitutions through successive experiments.
Since these ceramics may have important applications, it is desirable to characterise their physical properties/behaviour and have a better understanding of their working. However, this task is hampered by the fact that, it is difficult to grow their single crystals which have very high melting points and which are usually not soluble in a standard solvent. A polycrystalline material gives limited information about structural changes, small distortions, lattice vibrational effects, distribution of metallic ions over available sites, etc. which are pertinent to the basic understanding of materials. For example, it is usually assumed that, a divalent metallic ion like Mg, Sr or Zn occupies site A in the ceramic preparation, but it is hardly verifiable by a simple measurement of dielectric constant. Similarly, in the preparation of Pb(Mg0.33Nb0.67)O, one believes that Mg and Nb occupy B sites but no such evidence can be derived simply from the measurement of dielectric constants. Also, in these compounds, the metallic ions remain effectively in the inert state (closed electronic shell) which hardly respond to experiments involving magnetic, optical, IR and conductivity measurements and, therefore, one may have to use other microscopic probes. Mossbauer, EPR and IR methods can be quite effective, provided these ceramics contain a small percentage of Fe ions which produce spectra depending upon their valence state, local symmetry, electronic spin and vibrational modes. These measurements become possible because of the unpaired 3d electrons of the Fe ions and they are often used as physical probes into solids.

In the present work, PbTiO₃ and SrTiO₃ have been chosen as host lattices and partially substituted Pb and Sr by a small atomic percentage of Fe. In other words, polycrystalline ceramics like PbₓFe₁₋ₓTiO₃ and SrₓFe₁₋ₓTiO₃, where x = 0.05, 0.1, 0.2, 0.3 etc, have been synthesized and are used for the Mossbauer, EPR and IR experiments, at room temperature. It is well known that, Mossbauer method works as a precise microscopic probe at Fe sites and even from a polycrystalline sample, the

![Mossbauer Spectrum](image)

**Fig. 1 — EPR spectrum of (Pb₀.₉Fe₀.₁)TiO₃ in x-band at 295 K. It gives g-values as 5.94 and 1.92**
necessary physical data can be obtained. The EPR and IR methods also work very well for polycrystalline samples. Choice of the host lattices is quite deliberate on physical grounds. The PbTiO₃ is a well-known ferroelectric crystal (cubic with tetragonal distortion) having transition temperature of 490 Celsius, whereas the SrTiO₃ is cubic at room temperature with no ferroelectric property (it becomes ferroelectric below 40 K under strong electric field) and it works as a reference lattice. Studies on both of these materials can show the distribution pattern of Fe in titanates on possible sites in a ceramic preparation, while the strontium titanate can also give information on how a small percentage of Fe changes its structural properties.

Fig. 2 — Mossbauer spectrum of (Sr₀.₃Fe₀.₇)TiO₃ at 295 K showing two quadrupole doublets with parameters given in Table I. The plot with dotted points is the observed spectrum superimposed with two individual doublets having different absorption areas

2 Methodology

The ceramic dielectric materials like Pbₓ, Feₓ, TiO₃ and Srₓ, Feₓ, TiO₃ were prepared through the standard solid state reaction technique. The starting compounds were high grade PbO, Fe₂O₃, TiO₂ and SrCO₃, and they were thoroughly mixed in the right proportion for the chosen concentration of Fe in a given sample. This Pb based mixture was heated in a porcelain crucible at 880 Celsius for 8 hr in the presence of normal supply of oxygen, and then cooled gradually to room temperature over a period of about 3 hr. The heating temperature was chosen at about 2/3rd of the average melting point of the constituents. The Sr based mixture was thus heated at 1040 Celsius. The lumps/aggregates were thoroughly crushed in the powdered form and mixed with the binder PVA (poly vinyl alcohol) and shaped as pellets under high pressure of 1.57x10⁷ kg m⁻² and sintered in the furnace at 900 and 1050 Celsius, respectively for about 10 hr, and then cooled down to room temperature over a period of 4 hr. In this way, each pellet had a diameter of 2.54 cm and thickness of 2.39 mm. From these polycrystalline pellets, small portions were carved out for experiments.

Fig. 3 — Mossbauer spectrum of (Sr₀.₃Fe₀.₇)TiO₃ at 77 K. It shows mostly one single absorption peak in the central region

Fig. 4 — IR spectrum of (Pb₀.₉₅Fe₀.₀₅)TiO₃ at 295 K. It shows two prominent absorption bands at 409.8 and 669.7 cm⁻¹
3 Results and Discussion

The Mossbauer, EPR and IR spectra of the polycrystalline samples were taken with the standard equipments at 295 K except for a few Mossbauer experiments at 77 K. The Mossbauer spectra provided the values of isomer shift (IS) and quadrupole splitting (QS) for the Fe ions, the EPR spectra gave the electronic g-values of Fe ions, and the IR spectra showed the vibrational absorption bands for TiO₆ and FeO₆ clusters. These values depend upon the concentration of Fe ions in the material, which suggest that, the crystal structure and its lattice vibrational properties are sensitive to the amount of iron. The Pbₓ, Fe, TiO₃ samples did not yield a good Mossbauer spectrum even for x = 0.2 and 0.3 because of very high absorption of 14.4 keV gamma radiation by heavy Pb and Ti atoms and the spectral statistics remained poor. Therefore, the values of IS and QS are at best approximate. The g-values are similar to those measured earlier. The results, wherever available, are given in Table 1. The typical EPR, Mossbauer and IR spectra are given in Figs 1 to 5.

The Mossbauer results on Srₓ, Fe, TiO₃ samples are interesting. One quadrupole doublet is observed for x = 0.1, while for x = 0.2 and 0.3 two quadrupole doublets are observed with unequal area ratio. This shows that, for a higher percentage the Fe ions get distributed both on A and B sites unequally. The 77 K data is worth attention in the sense that, for x = 0.3, it gives only one quadrupole doublet instead of two at 295 K, and for x = 0.2, the spectrum shows simply a single absorption peak. Though the spectra are still not sharp to claim the desired precision, the general trend undoubtedly shows that, that both IS and QS decrease significantly at 77 K. This suggests that, the lattice structure tends to become cubic at lower temperatures. This is contrary to what one finds for a pure SrTiO₃ crystal, where it remains cubic at T > 40 K and shows distortion at lower temperatures. It appears that, this material is susceptible to structural phase transitions. Also, the possible reduction in the IS value at 77 K is against the usual observation i.e. the IS decreases at higher temperatures because of the greater thermal energy or mean <v> of the Fe atoms, usually known as second-order Doppler shift. More experiments at low temperatures are required to confirm these results before a physical picture can be presented.

The IR absorption bands at around 410 and 600 cm⁻¹ are sharp in both Pb and Sr based ceramics as shown in Figs 4 and 5. While the former is assigned to TiO₆ polyhedron (11) (seen in pure samples), the latter seems to arise from the FeO₆ polyhedron of those unit cells in which Ti has been replaced by Fe. The strong IR band at around 1080 cm⁻¹ in Sr based samples indicates symmetry-related excitation of an additional vibrational mode (11). There are other visible, weak absorption bands possibly arising from similar reasons.

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References