
CHAPTER - V

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During the last few years, ferroelectrics have been studied extensively in theory and in experiment. Ferroelectrics are a cheap source of dielectric and piezoelectric devices. These materials are becoming useful and vital component of the latest technology, microelectronics and quantum electronics. Because firstly they have large values of the absolute dielectric constant (permittivity) and secondly, their nonlinear optical properties can be used for the multiplication of optical frequencies and the deflection and modulation of laser and other light.

Ferroelectrics continue to arouse interest among the research workers as they hold promise in diverse new areas of technology and their understanding is not yet complete. The barium titanate ferroelectric belongs to the class of perovskite type oxides as the end members. A number of theories were given in order understand the phenomenon of ferroelectricity in barium titanate. Hence even at the present moment barium titanate is most extensively studied. Other perovskite type oxides as lead titanate, strontium titanate, calcium zirconate etc. show some similar properties in one way or the other. The properties of their solid solutions vary anonymously.

In the present work on the solid solutions of (lead, strontium) titanate and (lead, calcium) titanate, studies on dielectric hysteresis, solid state battery formation and second harmonic generation (TANDEL EFFECT) were carried out and results have been presented in the chapters II, III and IV respectively.

Solid solutions of (lead, strontium) titanate and (lead, calcium) titanate were prepared from their respective titanates by the method of heating the sample in a furnace at a high temperature as reported by Nomura and Sawada (1950) and Sawaguchi (1951). In order to prepare pellets a pressure of 5 tons was given by Brahma's pressure machine, these pellets after sintering were used for experimental purposes.

A modified form of Sawyer and Tower circuit (1930) was used for the study of dielectric hysteresis loop on the cathode ray oscilloscope. Since the hysteresis loop is a feature common to all ferroelectrics. For the solid solution system of (lead, strontium) titanate and (lead, calcium) titanate at various temperatures the photographs of hysteresis loop are shown in Fig. (2.4) and Fig. (2.5) of chapter II. From these photographs we can conclude that the shape of the hysteresis loop is temperature dependent. At room temperature the shape of the loop is rectangular. As the temperature increases the shape of the loop gets disturbed. In the vicinity of Curie temperature the near vanish of the loop is

observed. At Curie temperature it totally vanishes. Spontaneous polarization increases rapidly on crossing the Curie point and reaches a saturation value at low temperatures.

The effect of electric field on ferroelectricity of KNO_3 crystals was experimentally studied by Yutaka Takagi and others (1969) and reported the solid state battery formation of KNO_3 crystals.

In our present study, for the solid solution systems of $(\text{Pb}, \text{Sr})\text{TiO}_3$ and $(\text{Pb}, \text{Ca})\text{TiO}_3$, by fusing these materials with the application of a d.c. electric field of 1 KV/Cm at high temperature and then taken off, it was observed that some emf is generated which means solid state battery is formed. The graphical representation of emf against temperature in Fig. (3.2) and Fig. (3.3) of chapter III, clearly shows that emf is temperature dependent. Emf disappears at low temperatures but recovers when the sample is heated again. The emf decays with time but time constant is quite long. Even after the electrodes are short circuited the emf gradually recovers almost the same value as expected without any short circuitry. These facts especially a long decay constant and a recovery of emf we can conclude that some chemical reaction is taking place and a solid state battery is formed. The graphs show a drastic change in emf near Curie temperature.

The dependence of second harmonic voltage on d.c. bias was investigated for the solid solution $(\text{Pb,Sr})\text{TiO}_3$ and $(\text{Pb,Ca})\text{TiO}_3$ TANDELS (Thermoauto stabilized nonlinear dielectric elements; Glanc et al, 1963) at a frequency of 10 KHZ. For various TANDELS, it was found that the critical peak voltage at which TANDEL behaviour could be observed, were different. By observing the graphs of the second harmonic voltage response for these TANDELS as shown in Fig. (4.4) and Fig. (4.5) under chapter IV, we come to know that the second harmonic voltages generated are linear with the applied d.c. bias for low biasing fields, but for higher d.c. bias second harmonic voltage decreases suddenly indicating destabilization of the TANDELS. This is in agreement with the results of Mansingh and Eswar Prasad (1977) and Chavan and Patil (1980). Our results establish that $(\text{Pb,Sr})\text{TiO}_3$ and $(\text{Pb,Ca})\text{TiO}_3$ TANDEL elements provide the autostabilized state and this would make them interesting from the view point of various applications.

Dielectric hysteresis studies show that the solid solutions of (lead, strontium) titanate and (lead, calcium) titanate are ferroelectric. They show ferroelectricity even at room temperature. The shape of the hysteresis loop is rectangular. As the temperature increases the shape of the loop changes and vanishes at phase transition temperature. These solid solutions belongs to the family of perovskite type structure, the phase transition is displacive type.

The application of electric field (d.c.) to the solid solutions of (lead, strontium) titanate and (lead, calcium) titanate, the emf is generated which confirms that solid state battery is formed. The drastic change in emf at 487°C for $(\text{Pb}, \text{Sr})\text{TiO}_3$ and at 483°C for $(\text{Pb}, \text{Ca})\text{TiO}_3$ defines the phase transition temperature.

In the vicinity of Curie temperature, SHG studies of (lead, strontium) titanate and (lead, calcium) titanate compel us to say that large second harmonics can be generated in the autostabilized state.

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