CHAPTER VIII

SUMMARY AND CONCLUSIONS

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In the last few years, great advances have been made in the field of ferroelectricity. As ferroelectrics are a cheap source of dielectric and piezoelectric devices, these materials are becoming useful and necessary for the latest microelectronics and quantum electronics technology. There has been an ever increasing amount of research and development, ranging from the most fundamental studies of the phenomenon to a wide variety of device and system applications. The ferroelectrics are strongly non-linear, and the non-linearity is fundamental to many of their applications.

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. Barium titanate exhibits the anomalous properties typical for ferroelectricity and is representative of the perovskite type oxides. A number of theories have been proposed to understand the phenomenon of ferroelectricity in barium titanate, hence it is most extensively studied. Barium titanate forms solid solutions with many of the compounds having perovskite structure viz. strontium titanate, calcium titanate, lead titanate etc. Its properties can be varied systematically over wide ranges. Such materials can be readily produced in a polycrystalline form which is fully adequate for many applications.
In the present work on the solid solutions of (Barium, strontium) Titanate and (Barium, Calcium) Titanate, studies on x-ray diffraction, dielectric hysteresis, coercive field, dielectric constant, dielectric amplifier, solid state battery formation, second harmonic generation and TANDEL effect were carried out and results have been presented in the chapters II to VII of this thesis.

Solid solutions of (Barium, strontium) titanate and (Barium, calcium) titanate were prepared by mixing the respective titanates in different molar proportions and heated in a globar furnace at high temperature, as reported by Sawaguchi: (1951). The solid solution system (Ba, Sr)TiO₃ has a cubic perovskite structure (Rushman et al 1946, McQuarrie, 1955), whereas solid solution system (Ba, Ca)TiO₃ has a tetragonal perovskite structure (Swanson and Fuyat, 1954) at room temperature. In present study an attempt has been made to determine the lattice structure parameters of polycrystalline (Ba, Sr)TiO₃ and (Ba, Ca)TiO₃. The pellets of these solid solutions were prepared under a pressure of 5 tons using a hydraulic press machine. These pellets after sintering were used for experimental purposes.

A modified form of Sawyer and Tower circuit (1930) was used to study the dielectric hysteresis loop and coercive field $E_c$ of (Ba$_x$-Sr$_{1-x}$)TiO$_3$ and (Ba$_x$-Ca$_{1-x}$)TiO$_3$. Hysteresis loop observed for (Ba$_x$-Sr$_{1-x}$)TiO$_3$ and (Ba$_x$-Ca$_{1-x}$)TiO$_3$ at
various temperatures are shown in figures 3.4 to 3.9 of chapter III. From these figures we can conclude that shape of the hysteresis loop is temperature dependent. It is rectangular at room temperature, however, as the temperature increases the shape of the loop gets disturbed. At Curie temperature the hysteresis loop vanishes totally. The study of shape of hysteresis loop enables to measure the coercive field at various temperatures. The temperature dependence of coercive field showed a curve typical of the first order transition.

Smolenskii and Rorgachev (1954) and Mitsui and Westphal (1961) have reported that dielectric constant of (Ba,Sr)TiO$_3$ and (Ba,Ca)TiO$_3$ is a function of temperature. The temperature dependence of dielectric constant of (Ba$_x$-Sr$_{1-x}$)TiO$_3$ and (Ba$_x$-Ca$_{1-x}$)TiO$_3$ was studied by us. The method of comparison of capacitance was used to evaluate the dielectric constant at various temperatures. The dielectric constant versus temperature curves show a peak at Curie temperature.

Dielectric amplifier using ferroelectric materials is an interesting and has promising applications. Vincent (1951) reported the use of barium titanate and certain combinations of strontium and barium titanates as dielectric amplifier. During our studies on the dielectric amplifier of ferroelectric solid solutions (Ba$_x$-Sr$_{1-x}$)TiO$_3$ and (Ba$_x$-Ca$_{1-x}$)TiO$_3$, power
amplification was obtained by changing the reactance of the capacitor of these solid solutions in an a-c power circuit by means of a control voltage applied independently to the plates of the capacitor. The highest power gain was observed near the Curie temperature of the respective solid solutions. The power gain increased proportionately with increasing d.c. bias voltage.

During the study of the effect of electric field on ferroelectricity of KNO₃ crystals, Ishibashi and co-workers (1964) reported the solid state battery formation of KNO₃ crystals. In order to study the battery formation in the solid solutions of (Baₓ-Sr₁₋ₓ)TiO₃ and (Baₓ-Ca₁₋ₓ)TiO₃, a d.c. electric field of about 1 kV/Cm was applied across the sample at high temperature and then switched-off. The current and electromotive force was observed across the sample. The emf with the same polarity as that of applied d.c. voltage disappears at low temperature but recovers on heating. The emf decays with time with a large value of decay constant. Momentary short circuiting of electrodes does not destroy the emf. At room temperature, a very small emf is observed and this emf increases on the addition of a drop of water to the sample. 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.

We have investigated the dependence of second harmonic voltage on d.c. bias for (Baₓ-Sr₁₋ₓ)TiO₃ and (Baₓ-Ca₁₋ₓ)TiO₃.
TANDELS (Thermoautostabilized, nonlinear dielectric element, Glanz et al 1963) at a frequency of 10 kHz. It was found that the critical peak voltage for various TANDELS at which TANDEL behaviour could be observed, were different. For low biasing d.c. fields, second harmonic voltage varies linearly with applied d.c. bias voltage. But for higher d.c. bias, second harmonic voltage decreases suddenly, indicating destabilization of the TANDELS. This is in agreement with the result of Mansingh and Prasad (1977) and Chavan and Patil (1980).

Dielectric hysteresis studies show that the solid solutions of $(\text{Ba}_x\text{-Sr}_{1-x})\text{TiO}_3$ and $(\text{Ba}_x\text{-Ca}_{1-x})\text{TiO}_3$ are ferroelectric. They show the ferroelectricity even at room temperature. The rectangular shape of hysteresis loop changes with increasing temperature and ultimately it vanishes at phase transition temperature. These solid solutions belongs to the family of perovskite type structure, the phase transition is displacive type. Coercive field is also a function of temperature, which disappears at transition temperature. Increasing concentration of Sr and Ca in the respective solid solutions decreases the coercive field.

Dielectric constant of the solid solutions $(\text{Ba}_x\text{-Sr}_{1-x})\text{TiO}_3$ and $(\text{Ba}_x\text{-Ca}_{1-x})\text{TiO}_3$ varies with temperature. It is maximum at Curie temperature. Dielectric constant also varies with Sr and Ca concentrations in the respective solid solutions.
The dielectric amplifier studies show that the device is a power amplifier and power gain varies with temperature as well as the concentration of Sr and Ca. The greatest gain is obtained near the Curie temperature. The power gain increases proportionately with increasing d.c. bias voltage at Curie temperature.

From the solid state battery formation studies, we arrive to the conclusion that the application of electric field of about 1 kV/cm to the material at high temperature produces some emf and current, which is the indication of formation of solid state battery. This battery gives the maximum emf and current at transition temperature. Response of the battery is satisfactory in the paraelectric state. Drastic change in emf and current for \( (\text{Ba}_x\text{Sr}_{1-x})\text{TiO}_3 \) and \( (\text{Ba}_x\text{Ca}_{1-x})\text{TiO}_3 \) define the Curie temperature of the respective samples.

The review of electrical second harmonic generation studies of \( (\text{Ba}_x\text{Sr}_{1-x})\text{TiO}_3 \) and \( (\text{Ba}_x\text{Ca}_{1-x})\text{TiO}_3 \) compel us to think that large second harmonics can be generated in the autostabilized state.
References:


