#### CHAPTER IV

### DIELECTRIC PERMITTIVITY & DTA

### 4.1 Introduction and literature survey

The most commonly measured small signal electrical property is dielectric permittivity, ( $\varepsilon$ ), also often referred to as the dielectric constant. The dielectric constant in ferroelecric materials is rarely constant, but varies with applied field, frequency, stress and temperature and other parameters. Ferroelectrics are only a group of polar materials, & they include the mostl significant polar materials, both from a basic viewpoint and from an application's viewpoint. In some ferroelectrics, the temperature dependence of the dielectric constant above transition temperature is expressed by equation (1.1),

$$E = E0 + ----- ... (4-1)$$
  
T - Tc

Generally, the dielectric constant is the ratio of the capacitance of a capacitor filled with substance under test to that of empty capacitor. It is a dimensionless parameter called relative permittivity or dielectric constant.

The temperature dependence of small signal (reversible)

dielectric constant (E) of  $BaTiO_3$  was measured by Merz (65). Polar dielectric materials characteristically have much high values of (E in the range 100 - 10000) than non polar dielectric materials (E in the range 1-10). In addition most polar materials show a large increase in E at a temperature in the region of a crystalline phase transition temperature.

In paraelectric (cubic) phase i.e. above curie temperature (Tc) dielectric constant obeys the expression :

$$\epsilon = ---- T > Tc$$
 ...(4.2)  
T-Tc

Since equation (4.2) is electrical equivalent of Curie Weiss behaviour observed in ferromagnetic materials Tc in equation (4.2) is termed Curie Weiss temperature, which does not coincide with curie point Tc, and c is usually referred to as curie constant (Merz 66, Drougard and Young, 67). Curie point Tc is the temperature at which the large signal saturaction polarization (Spontaneous polarization) falls to zero.

The dielectric non-linearity is a significant characteristic of ferroelectrics. If the polarization created by an applied field E does not remain proportional to E as it increases, then an a.c. measurement of the permittivity will differ as the magnitude of the measuring voltage changes.

important small signal Another electrical property of polar dielectric material, especially from an application viewpoint, is dissipation factor. This is usually measured in terms of tans ( a dimensionless quantity), where tan  $\delta$  is the ratio of the imaginary part to the real part of E. Most polar dielectrics are very good insulators and hence have a low value of tan  $\delta$  typically in the range 0.01-0.3. Tan  $\delta$  like  $\epsilon$ , also shows anomalous increase at Tc. In polar dielectric materials  $\epsilon$  and tan  $\delta$ remain fairly constant over a wide range of frequencies. In single crystal materials a decrease or relaxation exhibited by E and tan  $\delta$  is only observed at frequencies as high as 10<sup>8</sup> to 10<sup>11</sup> Hz. The relaxation frequency varies significantly for different materials. Ceramics usually have a lower relaxation frequency than single crystal materials because of additional effects of the dispersion frequencies associated with multidomains.

The dielectric properties of BaTiO<sub>3</sub> single crystals were first investigated extensively by Merz (69). Subsequently, (68) and a number of other authors extended and Cross improved the resuts obtained by Merz. Robert (69) and Mason (70) have studied separately the dielectric properties of polarized ceramic BaTiO<sub>3</sub> and reported that dc bias causes a marked decrease of dielectric constant measured with small ac field. The high values of dielectric constant in BaTiO<sub>3</sub> have been computed by Marutake (71). The dielectric permittivity of BaTiO3 was measured versus applied electric field strength at various temperatures using pulse method by kalisz (72). Measurements of the dependence of dielectric constant on grain size of BaTiO<sub>3</sub> as a function of temperature were described by Miller (73). The dielectric behaviour of different particle size powders of barium titanate, potassium ferrocyanide trihydrate and ammonium suplhate has been studied by Mansingh et al (74). The results of variation of overall dielectric constant of BaTiO3 single crystals with applied ac electric field and crystal temperature were reported by Deshpande et al (75). The dielectric constant

 $\epsilon_c$  of poled tetragonal BaTiO<sub>3</sub> was measured in frequency range Ø.1 to 6 GHz by Clemens et al (76) Dielectric constant of ceramic BaTiO<sub>3</sub> under high dc biasing field of 5 to 20 KV/cm was measured by Yamashita et al (77).

The references regarding the effect of complete or partial replacement of Ti on transition temperature are already mentioned in sec 1. In general it is very difficult to draw any systematic conclusion about the behaviour of dielectric constant because of compensated off valency substitution, as the search was not oriented in this direction. This happens to be the attempt of present investigations.

For this purpose, we have measured the dielecric constant of the solid solutions of  $BaFe_{x/2} Sb_{x/2} Ti_{1-x}O_3$  and Ba  $Cr_{x/2} Sb_{x/2} Ti_{1-x}O_3$ .

#### 4.2 Experimental

The method of measuring the dielectric constant is based on a comparison of capacity c" of a capacitor filled with the substance and the capacity c' of the empty capacitor.

C" The ratio  $--- = \epsilon$  the dielectric constant determination C'

of the value of the capacitance may in principle be accomplished by an LC resonant circuit as shown in fig 4.1 where  $\mathbf{C}_{\mathbf{S}}$  is calibrated varible capacitor and  $\mathbf{C}$  is capacitor in which the specimen may be placed. The experimental set up used for measurement of dielectric constant at various temperatures is discussed, sec. 2.6. The experimental set up consists of an electrically heated furnace with a temperature controller arrangement and digital capacitance meter. The VLCR-17, LCRQ meter is employed for the purpose. The instrument measures capacitor in the parallel equivalant form at 1 KHZ. The pellets of the above solid solutions, having thickness about (2 to 4 mm) are used. The two end faces of sintered pellet are placed in sample holder. The dielectric investigations here are based on the value of capacitance measured. The observed value of the capacitance is corrected for the parasitic capacitance of the sample mount, the relative dielectric constant is calculated

using the relation.

$$C = Eo Er \qquad \dots (4.3)$$

It is worthly to be noted that the instrumentation has



resolution of 0.25 °C for temperature, 1pF for capacitance and 0.01 for the measurement of tan  $\delta$ . The observations are recorded for every 2°C interval. While plotting the values of E, points where E remains constant are omitted for the sake of convenience of the presentation. Maximum temperature achievable through the furnace setup is at present limited to 688 °K.

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4.3 Result and discussion :-

a) The Fe Sb composition :

Fig 4.2 - 4.7 shows variation of  $\in$  as a function T for BaFe<sub>X/2</sub> Sb<sub>X/2</sub>Ti<sub>(1·x)</sub>0<sub>3</sub> composition for x=0, 0.025,0.05, 0.1, 0.2, 0.4. The x = 0 composition was purposely selected for the calibration. It is known that porosity of the sample, purity of the starting material and additional phases occuring in the sintered material play an important roll in deciding  $\in$  vs T behaviour. Therefore, x = 0 composition synthesised in the same sintering schedule shall be a correct specimen to compare the results to those of pure BaTi§ material.



Fig. 4.2 : Dielectric constant 'C' as a function of T for Ba  $TiO_3$ .

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 $(\mathbf{s})$ 

Fig. 4.4 : Dielectric constant \*E\* as function of T for Ba Fe.025<sup>Sb</sup>.025<sup>T1</sup>0.95<sup>0</sup>3.









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A few points, which are pecularties of the present investigations are as below.

1) Pure BaTiO<sub>3</sub> passes through a ferro to para electric transition at 133° C, while the remaining products of the series show a ferro to ferro electrical phase transition in the vicinity of the 133°C, the Tc for the BaTiO<sub>3</sub>. Occurance of additional paraelectric phases has been observed for the polymorphic compound

 $Pb_{0.995}[(2rg.6Sng.4)(1-x)Tix]g.99Ng.g103$  (78)

At present we donot wish to come to any exact conclusion. The reason is as below.

The information regarding the phase transition will be complete, if the saturation magnetisation and coersive field data, in the same temperature interval is available. At present we have not investigated these properties. As a supporting property the DTA of a few samples in the series, is performed. The results are discussed in the sec 4.4

2) The transition in the vicinity of BaTiQ is not prominant as compared to the one at higher temperature.

The transition in the vicinity of  $BaTiO_3$  is now termed asT<sub>c1</sub> while the one at higher temperature is termed as T<sub>c2</sub>. The variation of  $T_{C1}$  and T and  $T_{C2}$  with composition is shown in fig 4.8 and 4.9. The  $T_{C1}$  passes through a minimum for x between 0.05 to 0.1. The variation of c/a recorded for this series also passes through a maximum for x = 0.025 ( sec 3.4 ) and then saturates for x > 0.1.

The  $T_{C2}$  on the other hand decreases monotonically with x. We have also tried to compared the  $\in$  just before the onset of the transition  $T_{C1}$  for the variation of x. This behaviour of  $\in$  as a function of x is shown in fig 4.10. The  $\in$  also passes through a minimum for x between 0.025 to 0.05. This behaviour is also concurrent with the observation of c/a as X from XRD (sec 3.4). The transition temperature of the FeSb system are recorded in table 4.1.

4.3.2 <u>The Cr Sb Composition</u>: fig 4.11 to 4.15 shows variation d E as a function of T for  $BaCr_{X/2}Sb_{X/2}Ti_{1-X} O_3$ 

The initial portion of the analysis for Fe Sb and Cr Sb systems is identical. A few generalised observations are noted below.

1) The data suggests that the series shows two transistions, one probably ferroelectric to ferroelectric and



concentration for Ba Fe<sub>x</sub>Sb<sub>x</sub>  $\frac{\text{Ti}}{2}$   $\frac{1}{2}$   $\frac{1}{2}$   $\frac{1}{3}$ 

Scale X axis : 1 cm = 0.025Y axis :  $1 \text{ cm} = 10^{\circ}\text{K}$ 660 640 620 600 0 580 560 540 520 500 0.1 0.2 0.3 0.4 . Conc. \_\_\_\_\_ Fig. 4.9 : The variation of second transition temperature with concentration for Ba  $\operatorname{Fe}_{\underline{x}} \operatorname{Sb}_{\underline{x}} \operatorname{Ti}_{(1-x)}^{O_3}$ .

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Fig. 4.13 : Dielectric constant '6' as a function of T for Ba Cr , nesh , net 10.3





another ferroelectric to paraelectric at temperature  $T_{c1}$  and  $T_{c2}$  respectively. The  $T_{c2}$  occurs above the range of investigation, but onset of this transition is clearly indicated in the data. The  $T_{c1}$  and  $T_{c2}$ , at onset of the transition, is given in the table 4.1, for all the compositions investigated.

2) The transition  $T_{c1}$  does not occurs in the vicinity, the  $T_c$  of BaTiO<sub>3</sub>, but it occurs at minimum 125°C above the  $T_c$ at 133°C.

The Tcl in this case is observed to increase monotonically For Fe Sb system the Tcl passes through a minimum.

The onset temperature  $Tc_2$  for CrSb system is closer to  $TC_1$  and passes a maximum for the substitution level of nearly 0.05.

Except for the exception of  $BaCr_{0.1}$  Sb<sub>0.1</sub> Ti<sub>0.8</sub> O<sub>3</sub>, The dieelectric constant passes through a maximum for x at 0.05. Similar variations are observed in the behaviour of c/a from XRD data, sec. 3.4.

As far as comparision of the observations on FeSb and CrSb system is concerned the following points are note worthy. 1) Both the systems show two transitions above R.T., the first transition is not prominant but the second one is prominant.

2) In case of Fe Sb systme  $Tc_1$  and the  $\epsilon$  pass through a minimum, while for Cr Sb systme the To and the  $\epsilon$  pass through a maximum as the substitution level is increased.

The variation of  $Tc_1$  and  $Tc_2$  with concentration is shown in fig. 4.16 and 4.17. The variation of  $\epsilon$  with concentraction for  $BaCr_{x/2}$   $Sb_{x/2}$   $Ti_{(1-x)}0_3$  is shown in fig 4.18.

These observations indicate that quite different type of ionic or electronic interactions, are responsible for the origin of ferroelectricity in these systmes. In fact both  $Fe^{3+}$  and  $Cr^{3+}$  are the elements from the transition metal series, having almost the same ionic radius. Still the effect they lead in modification of the behaviour of the dielectric constant is characteristically different. For further classification of the phenomenon the investigations are requied on  $V^{3+}Sb^{5+}$  or similar substitutions as enlisted in table (1.1).











## 4.4 The Differential Thermal Analysis (DTA).

In this technique temperature difference between the specimen and thermally inert referance material is continuously recorded as a function of furnace temeprature DTA and TGA are complementary to each other , but range of measurement of DTA is quite larger.

As regards apparatus and methodology any DTA unit comparises of a sample holder with thermo couple assembly a furnace assembly, a flow control system a preamplifier and recorder a furnace power programmer and a controller. In the operating DTA, one insert a very thin thermocouple into disposal sample tube (2mm diameter can hold Ø.1-10 mg of sample). A duplicate tube contains a reference material such as alumina, alumadum powder, quratz sand or it may be empty. Two tubes are put in sample block, side by side and heated or cooled at a uniform programme rate. The DTA is a All respects of technique should dynamic method. be standarised to obtain reproducible results. First the material should be fine (100 mesh ). plot  $\Delta T$  is The function of T is an indication of energy gain or loses in the

specimen under investigations. If endothermic change occurs the specimen temperature lags behind reference temperature while for exothermic change the specimen leads the reference temperature.

A differential scanning calorimeter (DSC) is a device which records the difference in electric power required to keep a test sample and referance material of equal temperature as they are heated or cooled at rates up to The important applications of DTA concern with 80°C/min. the Clays ceramics, minerals, study of change in composition of clays, study of thermal stabilites of compounds, e.t.c. Then identification of newly formed inorganic compounds, study of solid phase reactions, phase transformations, inversion in single compounds reaction kinetics study of thermal and oxidative degradation are a few more applications.

#### 4.5 The Result And Discussion

The DTAs for the samples  $BaFe_{X/2}sb_{X/2}$  Ti  $_{1-x}$  O<sub>3</sub> at x=0.025, 0.1 and 0.4 and Ba Cr  $_{X/2}sb_{X/2}$  Ti $_{1-x}$  O<sub>3</sub> at x = 0.025, 0.1 and 0.4 were sent to Regional Sophesticated Instrumentation centre. I.I.T, powai, Bombay. Assuming the delay in receiving the data, the samples were sent for the

Differential Thermal Anlysis, before the investigations dielectric constant were performed.

Being a very costly analytical tool the range of investgation was limited to 300°c , hoping the transitions to occures before this temperature. Unfortunately the prominant transition TC2 occures for temperatures more than 300°c (table 4.1) . Therefore, no potential information could be derived from this observation. The transitions Tc<sub>1</sub> being less prominant and of second order might not have got a signature in the DTA. The DTA is being insensitive to the second order transitions in similar compositions (53).

# TABLE 4.1

# <u>Curie Temperatures Of Solid Solutions Of</u>

## Different Molar Proportions

Solid Solutions				Transition Temperature	
				Tc <sub>l</sub> •k	Tc <sub>2</sub> °k
Ba(Fe Sb)0.0	125 TiØ.97	503	>	390	658
Ba(Fe Sb)g.g	25 Ti0.95	Ó 3	>	354	
Ba(Fe Sb)g.g	5 Ti0.9	03	>	342	584
Ba(Fe Sb)Ø.1	TiØ.8	03	>	348	560
Ba(Fe Sb)Ø.2	2 Ti0.6	03	>	406	516
Ba(Cr Sb)Ø.]	125 TiØ.975	03	>	516	610
Ba(Cr Sb)0.6	025 Ti0.95	03	>		626
Ba(Cr Sb)Ø.(	05 Ti0.9	03	>	534	608
Ba(Cr Sb)g.	1 TiØ.8	03	>	550	608
Ba(Cr Sb)g.	2 TiØ.6	03	>	572	592
Ba TiO3			>	426	
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