#### CHAPTER II

### SAMPLE PREPARATION AND EXPERIMENTAL SETUP

2.1 Introduction :-

It has been already discussed in section 1.7, the dissertation aims at synthesis and characterisation of the compensated off valecy substituted BaTiO<sub>3</sub> ceramics. A few points regarding the possibility of formation of solid solution chemistry of the synthesis and the solid state reaction are elaborated in this chapter.

2.2 The crystal structure and the Tolerance factor.

The most important piezoelectric cramics crystalline in the perovskite structure. This structure may be described as a simple cubic unit cell with a large cation (A) on the corners, a smaller cation (B) in the body centre and oxygens (0) in the centre of faces fig 2.1. The structure is network of corner linked oxygens octahedra, with the smaller cation filling the octahedra, holes and the large cation filling the dodecahedral holes.

A wide variety of cations can be substituted in the perovskite structure(55). The tolerance factor J given by th

relation.



Fig. 2.1 : THE UNIT CELL OF THE CUBIC PEROVSKITE TYPE STRUCTURE BaTIO3

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 $J = [R_A + R_0] / \sqrt{2} [R_B + R_0]$ 

& J describes ideal perovskite cubic structure where J=1  $R_A$ ,  $R_B$  and  $R_0$  indicate the ionic radius of large cation, small cation and anion respectively.

It is observed that for those compositions where J is slightly greater than one tend to be ferroelectric.

If J is less than one the structure favours to be posses tetragonally distorted (55).

We have modified this relation to calculate tolerance tactor for fractionally substituted solid solutions as

$$J = xJ_s + (1 - x) J_p$$
 ....(2.1)

Where x is the molar concentration,  $J_s$  and  $J_p$  are the tolerance factors for the substituted and parent species. The tolerance factors calculated for Ba  $Fe_{x/2} Sb_{x/2} Ti_{1-x}0_3$  and BaCr  $_{x/2} Sb_{x/2} Ti_{1-x} 0_3$  composition, selected for investigations are given in table 2.1 Further it is important to be noted that. J is 0.935 for BaTiO<sub>3</sub> and still it exhibits ferroelectric behaviour below 120°C. For PbTiO<sub>3</sub> J is 0.884 and it is ferroelectric below 490°k.

Table 2.1 shows that J increases as the level of

# Table 2.1

| Variation | Of Tolerance | Factor |
|-----------|--------------|--------|
| With      | Substitution |        |

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| Concentration |          | J        |
|---------------|----------|----------|
|               | FeSb     | CrSb     |
| X             | S Series | P Series |
| 0.025         | 0.935    | 0.95952  |
| 0.05          | 0.935    | 0.94360  |
| 0.1           | 0.936    | 0.9373   |
| 0.2           | 0.937    | 0.9396   |
| 0.4           | 0.939    | 1.05916  |

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at a elevated temperature decided by the phase diagram. We shall make an attempt to discuss the phase diagram of BaO and TiO<sub>2</sub> system, which happens to be the parent specie for the work carried out in the dissertation.

The phase diagram for the  $BaO-TiO_2$  system is as shown in fig.2.1 (56) The hexagonal form is more stable above  $1460^{\circ}c$ , the cubic form is stable below that temperature. However, ceramic containing the hexagonal phase are encountered either as a result of impurity action or disequilibrium.

On the Ti rich side of  $BaTiO_3$ , there is a region of solid solution of almost 3 mole % before Ba  $Ti_3O_7$  appears. This represents in the other terms a perovskite with A position vacancies and compensating oxygen vacancies. The incongruently melting compound Ba  $Ti_2O_5$  is unstable below 1210°c and is not usually encountered in solid state reaction.

The most common method of making Ba Tio<sub>3</sub> has been to react Ba CO<sub>3</sub> and TiO<sub>2</sub>. The reaction starts in air by the initial formation of Ba TiO<sub>3</sub> at BaCO<sub>3</sub>- TiO<sub>2</sub> grain boundaries, after which the process becomes diffusion controlled. As the reaction progresses Ba TiO<sub>3</sub> and BaCO<sub>3</sub> react to form Ba<sub>2</sub> TiO<sub>4</sub> until the complete BaCO<sub>3</sub> is used up. The remaining TiO<sub>2</sub> then reacts with. Ba<sub>2</sub> TiO<sub>4</sub> to form Ba TiO<sub>3</sub>. Formation of





substitution is increased. Therefore the material tends to reduce the tetragonal distortion.

Further, the structural modifications alone may not decide the ferroelctric behaviour. In addition to the structural modifications, the molecular field interactions between the cations and anions may play a dominant role in deciding the ferroelectric behaviour of the material.

## 2.3 Chemistry of BaTiO3 formation.

The required solid solutions could be synthesised either by co-precipation technique or by using ceramic synthesis procedure.

As far as co-precipation technique is concerned, one may land into the pure and stoichiometric products if kinetics of precipation is correctely known. Additionally the grain size achieved is very small. And to improve the grain size one has to adopt the ceramic process after the precipate is washed. Actually to prepare solid solutions with varying levels of substitutions, co-precipation is not a economical process.

The ceramic synthesis starts with selecting the carbonates or oxides of the constituent elements in stoichiometric proportion and then sintering this mixture  $Ba_2 TiO_4$  is inhibited below  $1100^{\circ}C$  or by the presence of  $CO_2$ atmosphere. It is emphasized that this is just approximate picture, since the reaction is hetrogeneous. Although complete reaction has been obtained below  $1200^{\circ}C$  in several hours (56).

## 2.4 <u>Reaction for the substituted compounds</u>

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As discussed in section (1.7) we have selected the compositions where 2 Ti<sup>4</sup> + atoms in Ba TiO<sub>3</sub>, are replaced by the combinations 1) Fe<sup>3+</sup> and sb<sup>5+</sup> and 2) Cr<sup>3+</sup> and sb<sup>5+</sup>. The solid state reactions corresponding to these compositions are given below

1) Ba 
$$CO_3 + \frac{x}{4}$$
 (Fe<sub>2</sub>O<sub>3</sub> + Sb<sub>2</sub>O<sub>3</sub>) + (1-X) (Ti O<sub>2</sub>)  
+  $\frac{x}{4}$  ·  $O_2 \xrightarrow{->} Ba$  Fe X/2 Sb X/2 Ti<sub>1-X</sub> O<sub>3</sub> + CO<sub>2</sub>  
2) Ba CO<sub>3</sub> +  $\frac{x}{4}$  (Cr<sub>2</sub>O<sub>3</sub> + Sb<sub>2</sub>O<sub>3</sub>) + (1-X) (Ti O<sub>2</sub>)  
+  $\frac{x}{4}$  ·  $O_2 \xrightarrow{->} Ba$  Cr X/2 Sb X/2 Ti<sub>1-X</sub> O<sub>3</sub> + CO<sub>2</sub>

Both these are oxidation reactions as the commercial antimony oxide is available in 3+ oxidation state. Owing to this fact the reactions are performed in the free air. The weights of the constituent oxides and carborates are selected in the stoichiometric proportion such that the product weight is nearly 10 gms. The weight of oxides and carborates selected for each composition are given in table 2.2, for reference.

#### 2.5 Preparation Of The Samples:

In the present work we aim to prepare feroelectric BaTiO<sub>3</sub> and their solid solutions with different molar concentration in the ceramic form. Ferroelectric ceramics have the advantage of being a great deal easier to prepare than their single crystal counter parts. In many cases they show ferroelectric properties approaching quite closely to those of single crystal so that useful preliminary information on the bulk ferroelectric behaviour of the material may be obtained. In addition it is possible to prepare a wide range of ceramic compositions and adjust the characterstics of the material for different applications.

The problem of preparation of ceramic ferroelectric was dealt in the third international conference held at Edinburg, Scotland on 10 th September, 1973. A hard ceramic can be easily prepared by a way of standard sintering procedure at high temperatures and shape of the ceramic body can be easily

# TABLE 2.2

The Weights Oxi

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Oxides and Carbonates Selected

BaCO3 =7.896gm For all Combinations

| Concentration | Oxides  | in gms  |        |
|---------------|---------|---------|--------|
| x             | Fe203   | Sb203   | Tio2   |
| 0             | 0       | 0       | 3.196  |
| 0.025         | 0.03992 | 0.07286 | 3.116  |
| 0.05          | 0.07985 | 0.1457  | 3.0362 |
| 0.1           | 0.1597  | 0.2914  | 2.8764 |
| 0.2           | 0.3144  | 0.5830  | 2.5568 |
| 0.4           | 0.6387  | 1.166   | 1.9176 |
|               |         |         |        |

Fe Sb Series

Cr Sh Series

| Concentration | Oxides | in gms  |        |
|---------------|--------|---------|--------|
| X             | Cr2O3  | Sb203   | Tio?   |
| 0.025         | 0.038  | 0.07287 | 3.116  |
| 0.05          | 0.076  | 0.1457  | 3.0362 |
| 0.1           | 0.152  | 0.2914  | 2.8764 |
| 0.2           | 0.304  | 0.583   | 2.5568 |
| 0.4           | 0.608  | 1.166   | 1.9176 |
|               |        |         |        |

modified to suit a member of practical requirements. Under the suitable conditions, the ceramic body can be polarised in any given direction by the application of strong d.c. field. These ceramics can then be used as electromechanical transducers in a number of applicaions. It should be noted that most of the results obtained with ceramic samples must be corrected for porosity before they can be considered representative of the material investigated. It is evident for example, that the dielectric constant actually measured on ceratic specimen will be a function of the number shapes and dielectric constant of pores Correction for ? have been worked out and tested experimentally by Rushman et al (57), Roberts (58) has shown for the cases of BaTiO3 and  $PbZrO_3$ , that the curie constant is also a function of porosity.

## 2.6 Experimental Setup

#### a) The Constant Temperature Zone Furnace

Basic requirement of the experimental setups for the measurement of Electrical permittivity  $\varepsilon = \varepsilon' + j \varepsilon''$  and the Electrical Resistivity (rho) and or conductivity 6 is a constant gradient furance, capable of providing adequate space for the sample holder. As far as the perovskite

family of ferroelectrics is concerned the temperature range of measurements is limited to about 600°c, as all the known ferroelectric solid solutions posses transition temperatures below nearly 490°c for PbTiO3 (59).

The requirements of constant temperature zone across the sample is stringent in these measurements. Unsteady temperature gradients across the sample may lead to the pyroelectric polarisation or generation of the thermo emf. These effects are predominant at the transition temperatures and may lead to unreliable measurands.

For the measurements of pyroelectric effect or seebeck co-efficient controlled temperature gradients are introduced across the sample, using an auxilary heater on sample mount it self.

As the disc type samples are used for the characterisation the tubular furnace in the vertical geometry is a suitable choice. An Allumina  $(Al_2 \ O_3)$  tube with inner diameter of 49 mm is employed to wind the furnace. Allumina is an refractory material usable upto 1800°c.

The heating elements could be formed using various alloys of transition metals. For ready reference the alloy types and their recommended maximum temperaturers are reproduced in table 2.3(60). The maximum voltage that could be applied across the heater wire is decided by the factors like

1) The maximum temperature of operation 2) The type of insulation used. Neverthless, 260v is a safer maximum limit.

The shape of heating element we have selected is the helix form. The constraint to be followed is the pitch of the helix should be grater than three times the diameter. We have made use of canthal wire of 20SWG. stretched in the helical form of constant pitch as a heating element. The helix is stretched over a length of 36 cm to achieve constant temperature zone of about 6 cm at the highest temperature of operation.

The furnace thus formed is insulated using high-quality refractory material and was subjected to the calibration procedure.

#### b)Calibration of the furance:

The main intention of the development of the experimental setup is to automate the complete data acquisition procedure. As far as the automation in the furnace setup is concerned one needs to know the power to be inputed to the furnace to achieve desired temperature cycle.

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## TABLE 2.3

## <u>Electric Furnace Resistor Materials & Temperature Ranges</u>

| Material            | Maximum Res | <pre>istor Temp; *f(*C)</pre>        |
|---------------------|-------------|--------------------------------------|
| 1ajor Elements      | In Air      | In Reducing Or<br>Neutral atmosphere |
| * 35% Nickel; 20%   |             |                                      |
| Chromium            | 1900(1040)  | 2100(1150)                           |
| * 60% Nickel; 16%   |             |                                      |
| Chromium            | 1800(980)   | 2000(1090)                           |
| * 68% Nickel; 20%   |             |                                      |
| Chromium; 1% Cobolt | 2250(1230)  | 2250(1230)                           |
| * 78% Nickel; 20%   |             |                                      |
| Chromium            | 2250(1230)  | 2250(1230)                           |
| * 15% Chromium;     |             |                                      |
| 4.6% Alumium        | 2050(1020)  | Not Used                             |
| * 22.5% Chromium;   |             |                                      |
| 4.6% Alumium        | 2150(1180)  | Not Used                             |
| * 22.5% Chromium;   |             |                                      |
| 5.5% Alumium        | 2450(1340)  | Not Used                             |
| Silicon Carbide     | 2800(1540)  | 2500(1370)                           |
| Platinum            | 2900(1590)  | 2900(1590)                           |
| + Molybdenum        | Not Used    | 3400(1870)                           |
| + Tungsten          | Not Used    | 3700(2040)                           |
| + Graphite          | Not Used    | 5000(2760)                           |

\* Balance is largly iron, with Ø.5-1.5% Silicon

+ Usable only in pure Hydrogen, Nitrogen, Helium or oxygen or in vaccum because of in ability to form protective oxide. For this purpose the furnace is operated with the constant voltage and the variation of tempearture "T" with time "t" is recorded, fig.2.3. These are the basic data elements of the calibration.

Though not attempted at present, the next part of the procedure is to plot ( determine ) rate of change of temperatures as a function " V " for various temperature Now, having the temperature cycle known, i.e. required T as a function of t, a microcomputer can make use of this set to vary the input voltage in the desired form to achieve the controlled heating.

#### c) The sample Mount and Experimental set up:

The schematic of the sample mount is shown fig 2.3. It is taken care to introduce minimum heating load in the furance. The sample is held between two brass disks of 2.5cm in diameter and the sample is electrically insulated from the mount using this mica flakes. Temperature on two sides of the sample are recorded using two seperate Cr-Al thermocouples as required for a measurement.

The auxiliary heater shown could be screwed to one end of mount if the thermal gradients are to introduced across the sample. The heater is useful for the measurement of the



Fig. 2.3 : THE VARIATION OF TEMPERATURE WITH TIME.



Big. 2.3 : The schematic sample mount.

pyroelectric coefficient and the seebeck coefficient.

It is proposed to measure all the physical parameters like capacitance formed by the sample cell, resistance of the sample, thermo emf, pyroelectric current within the same temperature cyclation, after the setup is automated using an microcomputer. At present we have made use of band switches to select a mode of measurement while using the microcomputer the analog switches will replace the bandswicches used at present.

The bandswitch arrangement for the measurement of sample capacitance, sample resistance, thermo emf, temperature on top side of the sample "Tc<sub>1</sub>, temperature on the bottom side of the sample "Tc<sub>2</sub>, temperature difference " $\Delta$ T" is shown in fig.(2.4) S<sub>1</sub> and S<sub>2</sub> are the connections across the sample, while chromel 1,2 and Alumuel 1,2 are the corresponding thremocouple wires. The throws corresponding capacitance measurement are indicated as C<sub>1</sub>, C<sub>2</sub>, while those for resistance measurement are indicated with R<sub>1</sub>, R<sub>2</sub>. The same voltmeter will be used to measure Tc<sub>1</sub>, Tc<sub>2</sub>,  $\Delta$ T and  $\Delta$ V.

We shall conclude the discussion of experimental setup with a mention that the actual procedure of measurement of a parameter is included in the respective section itself.



Fig. 2.4: The band switch arrangement for switch No. 1  $(SW_1)$ .



Fig. 2.4

: The band switch arrangement for switch No. 2 (SW<sub>2</sub>).

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