CHAPTER

II

SYNTHETIC AND EXPERIMENTAL PROCEDURE

2.1 Sample Preparation and Standardization of procedure for synthesis:

As a prima-facie estimate the solid-state reaction may appear to be a straight forward endeavor to achieve a solid-solution of a known phase inequilibrium. But in actual practice the process of Ceramic Synthesis involves various intricacies and a detailed knowledge of the phase diagram becomes important to establish a sintering schedule, which would led to a required and energetically favoured homomorphic composition.

In general phase diagrams for the parent compositions are available. But, on the other hand no such detailed phase diagrams are available for the solid solutions with partial substitution in the parent composition.

It is envisaged in Section 1, the present dissertation deals with the characterization of the partial substitution of Ti, in $BaTiO_3$, in the form of compensating off-valency and no such phase diagram for the substitutional compositions is available.

In this situation we have adopted certain imperical guide lines and developed a procedure of synthesis, such that a optimum homomorphic phase results. The basic data sets those have has been employed for this purpose is the binary phase diagram of $BaO-TiO_2$ composition (68),the melting points (M.P.) and the boiling points (B.P) of the constituent oxides. The following sections elaborate this procedure.

2.1.1 The Solid Solutions and The Solid-State Reaction

The solid solutions being investigated are MnSb and CoSb substituted $BaTiO_3$ bearing the formulae

1) $Ba\ Ti_{(1-x)}\ Sb_{x/2}\ Mn_{x/2}\ O_3$ -(2.1)

2) $Ba\ Ti_{(1-x)}\ Sb_{x/2}\ Co_{x/2}\ O_3$ -(2.2)

Where x = 0.025, 0.05, 0.1, 0.2, 0.4

The Sb ions are required to be in the valency state +5 while the Mn and Co ions are required to be in state +3. To achieve this compositions the proposed solid state reactions are as given below,

1) $BaCO_3 + x/2\ MnO_2 + x/4\ Sb_2O_3 + (1-x)TiO_2 + x/8\ O_2 =$

$BaTi_{(1-x)}Sb_{x/2}Mn_{x/2}O_3 + CO_2$--- (2.3)

2) $BaCO_3 + x/2\ CoO + x/4\ Sb_2O_3 + (1-x)TiO_2 + 3\ x/8\ O_2 =$

$BaTi_{(1-x)}Sb_{x/2}Mn_{x/2}O_3 + CO_2$ (2.4)

The following points are note-worthy for the reactions in equation (2.3)and (2.4).

1) The ionic radii of Sb^{+5}, Mn^{+3} and Co^{+3} are very close to that of the Ti^{+4} ions and the requirement of matching ionic size of the substitutent ions is well satisfied. The tolerance factor for the perovskite structure for these solid solutions are further discussed in section 2.1.4.

2) Both the reactions are oxidizing reactions and no controlled atmosphere is required during the sintering process

3) The Sb_2O_3 is used as a starting material for Sb substitution. In this case the Sb ions are in state +3. Therefore a care must be taken to stabilize the valency of Sb at +5 during the sintering process.

4) The valency of Mn in MnO_2 is +4 and it is a requirement that

the Mn be stabilized in state +3 . Similarly Co^{+2} in CoO should be stabilized in state +3.

Under certain assumptions the requirements mentioned above are satisfied during the process of sintering designed.

2.1.2 Significance of melting points of the constituent Oxides and The Proposed Sintering Schedules

While designing the sintering schedule phase equilibria of $BaO-TiO_2$ system has been given a primary consideration. The Fig2.1 shows the phase diagram. The most common method of making $BaTiO_3$ is to react $BaCO_3$ and TiO_2. The reaction starts in air by the initial formation of $BaTiO_3$ at $BaCO_3$- TiO_2 grain boundaries. After this nucleation occurs, the reaction becomes diffusion controlled. As the reaction progreses $BaTiO_3$ and $BaCO_3$ react to form Ba_2TiO_4 untill the complete $BaCo_3$ is consumed. The remaining TiO_2 reacts with Ba_2TiO_4 to form $BaTiO_3$. The formation of Ba_2TiO_4 is inhibited below 1100°C because of the presence of CO_2 atmosphere. It is emphasized that this is just an approximate picture as the reaction is a heterogeneous one. The complete reaction is possible by sintering $BaCo_3$ + TiO_2 for temperature nearly at 1200°C for sevaral hours. The duration for which the material is to be sintered should be determined by simultaneous investigations of XRD.

It has been observed that the sintering process may leave traces of Ba_2TiO_4 and $Ba\ Ti_3O_7$. The $Ba\ Ti_2O_5$ is unstable below 1210°C and no partial phase of $BaTi_2O_5$ occurs in the ceramic product. The occurrence of Ba_2TiO_4 and $BaTi_3O_7$ is detected by the presence of the characteristic reflections of these elements in the XRDs of the product. To determine the time for which $BaCO_3$

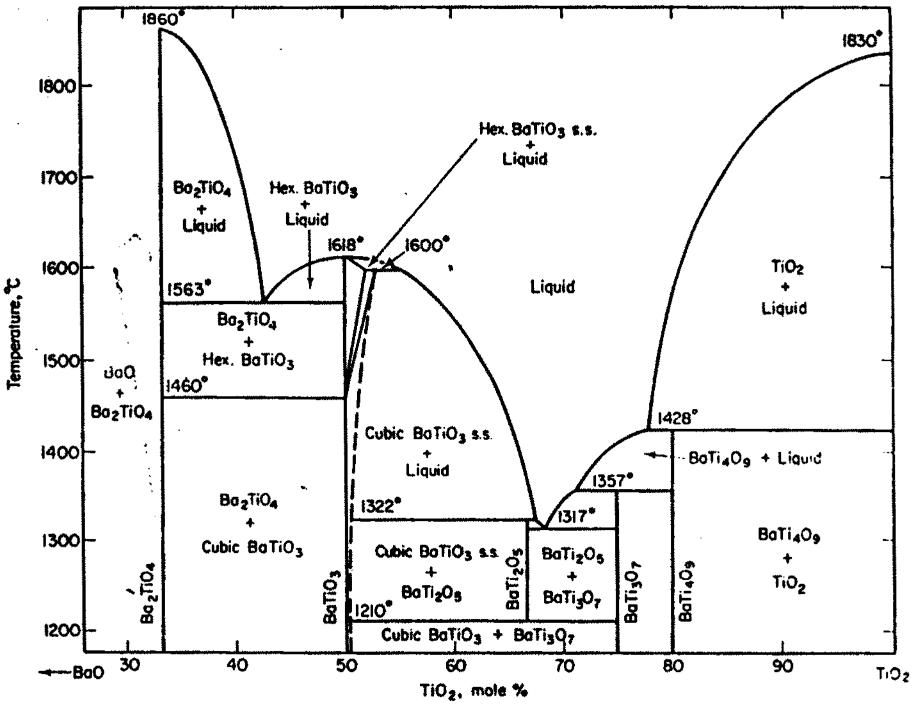

Fig. 2.1 Phase equilibria in the system BaO–TiO$_2$.

and TiO_2 are to be reacted at 1200°C, we have followed the following procedure.

Initially we have reacted the $BaCo_3$ and TiO_2 mixture as per the sintering schedule given in table 2.1 . The XRD of the product was determined. It has been observed that a fraction of $BaCO_3$ is present in the product. Along with $BaCo_3$ traces of $BaTi_3O_7$ and TiO_2 are recorded in this graph. The characteristic 'd' values of $BaCo_3$, $BaTi_3O_7$,Ba_2TiO_4 and TiO_2 are given in table 2.2. It was concluded that the reaction is incomplete. To achieve the complete reaction the product was resintered at 1180°C for 12 hours and XRD of the product was analyzed. It has been observed that no trace of $BaCo_3$ is present in the material, but a fraction of Ba_2TiO_4 and $BaTi_3O_7$ is present in the product. It has been reported(69) that sintering the compound even at 1520°C does leave traces of Ba_2TiO_4 and $BaTi_3O_7$.

Table no. 2.1: Sintering Schedule for $BaCO_3$

Time	Activity
Initial Sintering	
0 to 12 h	Heating 0 to 1180°C
12 to 18 h	Sintering at 1180°C
18 to 19 h	Furnace Cooling to 920°C
19 to 23 h	Constant T = 920°C
24 to 30 h	Furnce Cooling to room temperature
Pre-Sintering	
0 to 12 h	Heating from 0 to 1180°C
12 to 24 h	Sintering at 1180°C
24 to 32 h	Furnace Cooling to room temperature

Final Sintering

0 to 12 h	Heating from 0 to 1180°C
12 to 30 h	Sintering at 1180°C
30 to 38 h	Furnace Cooling to room temperature

Table 2.2: Characteristic 'd' values

Compound	d (A^{o})	Structure
$BaCO_3$	3.72	Orthorombic
TiO_2	3.51	Orthorombic
$BaTi_3O_7$	3.14	Perovskite
Ba_2TiO_4	3.05	Perovskite

Table no. 2.3: Boiling Points and Melting points of the Constituent oxides

Compounds	M.P.°C	B.P.°C
Sb_2O_3	573	656
Sb_2O_4	d930	---
Sb_2O_5	d380	---
MnO	1785	---
Mn_2O_3	d940	---
MnO_2	d530	---
CoO	1805	---
Co_2O_3	d895	---

d--- dissociation

As a final step the same product was subjected to the final sintering at 1180°C for 18 hours. It was observed that no further improvement in the product is achieved because of such a long span of final sintering. In the final sintered product also the mild occurrence of reflections corresponding to $BaTi_3O_7$ is recorded. Therefore it is concluded that the sintering time of about 18 hours at 1180°C is sufficient for maximum possible phase formation. It is assumed that the reaction time required for the MnSb and CoSb substitutated compositions is same as that of pure $BaTiO_3$. In addition to the XRD investigations, investigations of ɛr are carried on the pre-sintered and final sintered products to determine the phase purity. These observations are reported in Section 4.2

Additional care is required while designing the sintering schedules for the substituted Ba TiO_3. As discussed in section 2.1.1 we need to stabilize the valency of Sb at +5, Mn at +3 and Co at +3. The melting points and the boiling points of the oxides of Sb Mn and Co are given in table no 2.3 (70). The Sb may stabilize in valency state +3, +4, +5. The Manganese may exhibit valancies of +2, +3, or +4. Similar is case for Cobalt. From the melting point data for these oxides it is observed that a particular valency state is favoured in a temperature range. Therefore we have given a consideration to these valency prefrences while designing the sintering schedules. The sintering schedules for SbMn and SbCo are given in table 2.4 and 2.5 respectively. During presintering for SbMn system the temperature was stabilized at 570°C for 4 hours . This temperature the Sb_2O_3 may react with $BaCo_3$ and MnO_2 to form the Columbite or pyrochlore phases of $MnSb_2O_6$ or $Ba_2Sb_2O_7$ respectively. The columbites may have quite high a melting point. The material has been sintered at 1180°C for 6 hours, so as to achieve the complete reaction. During the cooling sequence the furnace was held at 920°C for 2 hours. At this temperature Mn preferes to be in valency state +3.

Thus the Sb and Mn are stabilized in the required valency states. The material was quenched in a air below 600°C, so that the Mn ions do not oxidies to state +4. During final sintering the product is held at 1180°C for 18 hours to led to a homomorphic composition. During final sintering also the temperature was stabilized at 920°C to stabilize Mn in state +3.

Using similar logic, sintering schedule for $BaTi_{(1-x)}Sb_{x/2}Co_{x/2}O_3$ is designed, table 2.5. For the SbCo substituted system quenching is not required as in case of Mn Sb substituted system.

Table no. 2.4: Sintering Schedule for SbMn

Time	Activity
	Pre-Sintering
0 to 4 h	Heating from 0 to 570°C
4 to 8 h	Sintering at T = 570°C
8 to 13 h	Heating from 570 to 1180°C
13 to 19 h	Sintering at 1180°C
19 to 20 h	Furnace Cooling 920°C
20 to 22 h	Constant T = 920°C
22 to 25 h	Furnace Cooling to 600°C
25 to onwards	Cooling in free air
Final Sintering	
0 to 10 h	Heating from 0 to 1180°C
10 to 28 h	Sintering at 1180°C
28 to 29 h	Furnace Cooling to 920°C
29 to 31 h	Constant T = 920°C
31 to 34 h	Furnace Cooling 600°C
34 to onwards	Cooling in free air

Table no. 2.5: Sintering Schedule for SbCO system

Time	Activity
Pre-Sintering	
0 to 4 h	Heating from 0 to 570°C
04 to 08 h	Sintering at 570°C
08 to 13 h	Heating from 570 to 1180 °C
13 to 19 h	Sintering at 1180°C
19 to 21 h	Furnace Cooling to 885°C
21 to 23 h	Constant T= 885°C
23 to onwards	Cooling to room temperature
Final Sintering	
0 to 10 h	Heating from 0 to 1180°C
10 to 28 h	Sintering at 1180°C
28 to 30 h	Furnace Cooling to 885°C
30 to 32 h	Constant T = 885°C
32 to onwards	Furnace Cooling to Room Temperature

2.2 Sample Mount and Procedure for Measurement:

In the following section the actual experimental setups are discussed with technical specifications of the meters used for the measurement.

2.2.1 The Sample Mount

Fig 2.2 shows schematic of the sample mount . While designing the sample mount a few points are important.

i) The total heat load introduced by the sample mount should be minimum.

ii) The sample should be located in the constant temperature zone of the furnace.

iii) The sample mount should have a provision to record temperatures on both the ends of the sample. As well as it should be possible to measure electrical voltage across the sample.

iv) The sample should be possible to be pressed against the electrical contacts to have minimum error because of the surface space charge layer.

v) Both the ends of sample should be electrically insulated. The insulation used should be mechanically sturdy and a commercially available product.

The sample mount used for the present investigations satisfies all the requirements mentioned above. In fact we have developed sample mounts with a few variations. Each version is suitable for a type of measurement. The sample mount described in this section is the most general one.

The Fig.2.2 of the sample mount is self explanatory . The thermocouples and connection wires are mounted between the spacer and base rod. While mounting the thermocouples, the thermocouples are insulated from the base rod, using the mica sheets. The base rod at the bottom has a provision to install 3/16 inches screw head and an auxiliary heater could be screwed to other end of this screw head. The sample is pressed against the base rods with a uniform load being applied by the tension springs on the studs. The over all diameter of the sample mount is 45 mm. Further the

1. STUD
2. NUT-3/16 B.S.W
3. SPRING
4. M.S. PLATE
5. PIPE
6. NUT - 1/2'' B.S.W.
7. GUIDE PLATE
8. BOBBIN
9. SPACER
10. BASE ROD
11. BASE ROD
12. Auxiliary Heater

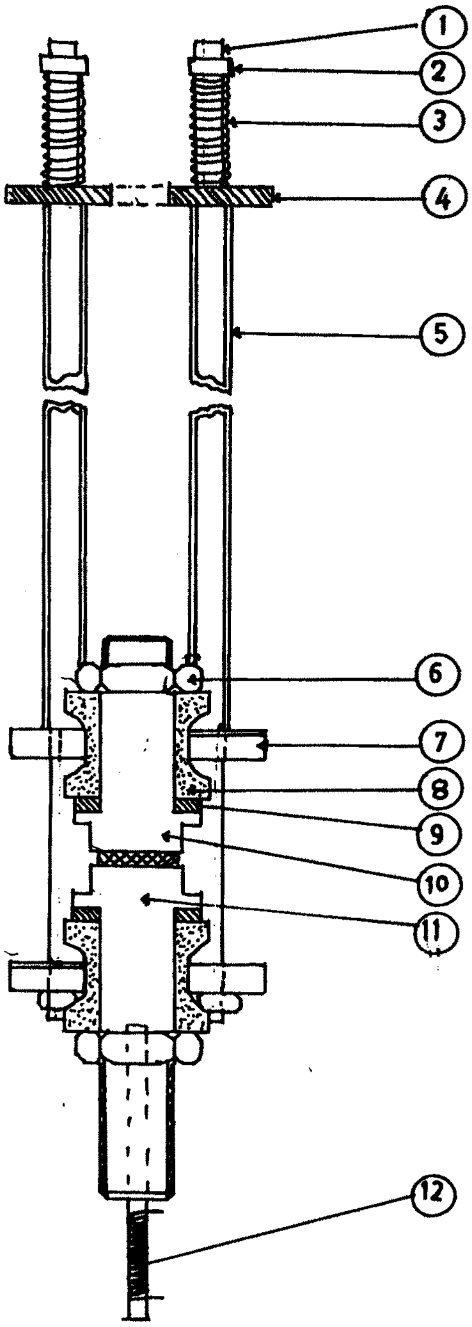

Fig2.2 The Schematic of sample mount

sample mount is so designed that it could be suspended in a tubular furnace of internal diameter equal to 50 mm and length nearly 60 cms. A custom built tubular furnace is used for the present investigations. The furnace is wound using super canthol wire of 18 SWG. The room temperature resistance of the heater is nearly 10 ohms. The power in to the heater is controlled using a dimmerstat. This is referred here further as the main heater. The furance has been calibrated to determine the required power in to the main heater to heat the furnace at a rate 2°C per minute.

2.2.2 Measurement of Dielectric Constant:

The dielectric constant is determined by the measurement of the capacitance formed across a disc shaped sample of diameter 1.5 cms and thickness between 2 to 3 mm . Two faces of the sample are silvered using the silver paint.(Conductive silver paste type- 1013). The capacitance across the sample is measured using the LCR-Q meter(Aplab LCR-Q meter Model No 4910). The measurements are carried out at a frequency of 1KHz in the parallel equivalent circuit form. Knowing the value of C,ϵ_r is determined using the formula.

$$\epsilon_r = \frac{1.3 * d * C}{\epsilon_o A}$$

Where d- thickness of the sample

C- Capacitance of the Sample

A- Area of Cross Section of the Sample

ϵ_o- dielectric constant of free space

ϵ_r- 8,85 * 10^{-12} in S.I. Units

The factor 1.3 is used as a electrical field correction for the measurements on the disc shaped samples. The value of capacitance is recorded at an interval of $2^{o}C$.

The important technical specifications of the Meter used are as below.

Technical Specifications

Meter	: Aplab LCR-Q Meter Model No. 4910
Variable Measured	: L,C,R
Mode	: Series or parallel equivalent
Measurement frequency	: User selectable 100 Hz or 1 KHz
Measurement update rate	: 2 per second
Display	: 4 digit, 11 mm LED with automatic decimal point.
Max. Voltage across component	: 283 mv RMS(0.8 V peak to peak)
Max. time for valid reading after user connecting component	: 1 second
Connection to component under test	: 4 terminal test jig.
Measurement Ranges	: C=9999 microfarad : L=9999 Henry : R=100 Mga Ohms.
Measurement Accuracy	: 0.25 % of reading in parallel equivalent at 1 KHz

2.2.3 Measurement of Conductivity

The current through the sample is determined for the measurement of electrical conductivity. A standard D.C. source of ripple less than 0.1% or better is used to excite a D.C. voltage of 20 volts across the sample and the current through the sample is measured using the meter (Digital Multimeter, HIL 2665). With the excitation of 20 volts across the sample the actual electrical field across the sample(~ 100 volts/cm) is sufficiently small. At these field levels no non linearities in the 'I' versus 'V' behavior are expected. The electrical conductivity 6 is calculated using the formula

$$6 = \frac{I}{V} * \frac{l}{A} (\text{ ohm m})^{-1}$$

Where I- Current through the Sample

V- Voltage across the Sample

l- Thickness of the Sample

A- Area of cross section of the Sample

All quantities are taken in SI units

The important technical specifications of the meter used are as below

Technical Specification

Meter : Digital Multimeter, HIL 2665

Variable measured : V, I, R

Display : 3 and 1/2 digit LCD with automatic/manual decimal point.

Measurement ranges

Voltage :0.01 mv (min), 1000V(max.)

Current :0.01 A (min.), 10 A (max.)

Resistance :0.01 ohm (min.), 25 Mega ohm (max.)

2.2.4 Measurement of Thermopower

Measurement of thermopower is a little bit crucial one. The resistance of the sample below 200°C is too high, therefore measurement meter gets loaded due to high resistance of the sample. To avoid this difficulty LF 357 buffer is connected between meter and the sample. For high input impedance systems the thermal noise and electrical pickups worsen the situation. To overcome the fluctuations a capacitance is connected in the input circuit of the buffer. This circuit is shown in Fig 2.3

The measurement procedure is described below. The technique is commonly known as the differential method of determination of seeback co-efficient. The main heater, Section 2.2, is used to stabilize the temperature of the sample at a fixed value. After the temperature is stabilized initial gradients of about 1°C to 1.5°C are observed across the sample. These gradient creat an initial off-set in the thermopower output. The off-set has other sources also. Mainly loading of the input stage is an unvoidable source of the off-set. For this reason the static values of thermo emf are not useful to calculate the seeback co-efficient. In the differential technique of measurement an auxiliary heater is used to create a time varying temperature gradient across the sample. The auxiliary heater is activated after the temperature is stabilized. Because of the auxiliary heat the sample is heated on one end Fig 2.2 . A time varying thermal gradient is now observed across the sample. Temperature on both the ends of the sample and the thermo emf are recorded simultaneously. It is taken care that the readings are taken where the $\Delta V/\Delta T$ is almost linear. These readings are used to calculate the seeback

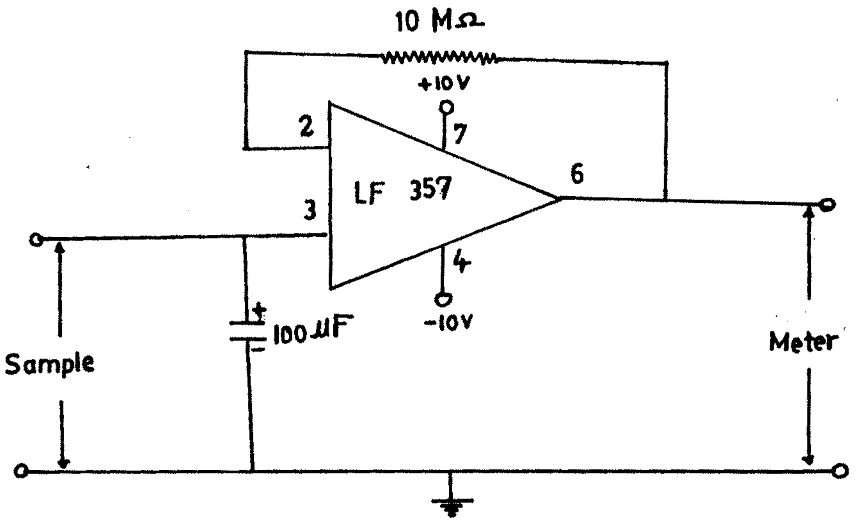

Fig 2.3 LF-357 Buffer Circuit.

coefficient as $\Delta E/\Delta T$. The maximum gradient created across the sample is less than 8°C to 10°C. Owing to this fact the T.E.P. is determined at an interval of nearly 20°C The technical specifications of the meter used are as represented in Section 2.2.3.