Chapter 3

EXPERIMENTAL

This chapter deals with various experimental aspect, which describes the detailed method synthesis and characterization of pure and copper doped layered alkali trititanate of composition, \( \text{Na}_{2-x}\text{K}_x\text{Ti}_3\text{O}_7 \) (with \( x = 0.2, 0.3, 0.4 \)).

3.1 SYNTHESIS OF COMPOUNDS

3.1.1 SYNTHESIS OF \( \text{Na}_{2-x}\text{K}_x\text{Ti}_3\text{O}_7 \) COMPOUNDS

Ceramic samples of \( \text{Na}_{2-x}\text{K}_x\text{Ti}_3\text{O}_7 \) (\( x = 0.2, 0.3, 0.4 \)) were synthesized by taking \( \text{Na}_2\text{CO}_3 \) (Merck Germany, 99.9% pure), \( \text{K}_2\text{CO}_3 \) (Merck Germany, 99.9% pure), and \( \text{Ti}_2\text{O}_3 \) (Merck Germany, 99.9% pure) powders in stoichiometric molar ratio. After mixing under acetone, the powders were pre-heated at 1173 K for 16 h to drive off \( \text{CO}_2 \). The heated products were cooled to RT at the rate of 3.0 K per minute and reground to achieve fine powder. The pelletized samples, having 10 mm diameter and 1.5 mm thickness were obtained by applying isostatical pressure of 15 MPa on powder. The heated products were cooled to RT at the rate of 3.0 K per minute and reground to achieve fine powder. The pelletized samples, having 10 mm diameter and 1.5 mm thickness were obtained by applying isostatical pressure of 15 MPa on powder. These pellets were covered with the powder of the same composition to prevent reaction with the wall of the crucible and to diminish soda loss, and then, sintered at 1273 K for 16 h. For the electrical measurements flat faces of the samples are silver painted with high purity silver paint and then air dried.

The undoped potassium mixed samples included in this work are listed below:

1. \( \text{Na}_{2-x}\text{K}_x\text{Ti}_3\text{O}_7 \); \( x = 0.2 \)
2. \( \text{Na}_{2-x}\text{K}_x\text{Ti}_3\text{O}_7 \); \( x = 0.3 \)
3. \( \text{Na}_{2-x}\text{K}_x\text{Ti}_3\text{O}_7 \); \( x = 0.4 \)

3.1.2 SYNTHESIS OF COPPER DOPED DERIVATIVES

All the above samples have been doped by the desired molar percentage (i.e. 0.01, 0.1, 1.0) of copper. In order to prepare copper doped derivatives of pure \( \text{Na}_{2-x}\text{K}_x\text{Ti}_3\text{O}_7 \) (\( x = 0.2, 0.3, 0.4 \)), the desired molar percentage of \( \text{CuO} \) powder (Merck Germany, 99.9% pure) has been added to the starting mixture of alkali carbonates and \( \text{Ti}_2\text{O}_3 \). The mass so obtained has
been subjected to the process described as above. The list of the copper doped derivatives is as follows:

1. $\text{Na}_{1.8}\text{K}_{0.2}\text{Ti}_3\text{O}_7$ doped with 0.01 molar percentage of copper
2. $\text{Na}_{1.8}\text{K}_{0.2}\text{Ti}_3\text{O}_7$ doped with 0.1 molar percentage of copper
3. $\text{Na}_{1.8}\text{K}_{0.2}\text{Ti}_3\text{O}_7$ doped with 1.0 molar percentage of copper
4. $\text{Na}_{1.7}\text{K}_{0.3}\text{Ti}_3\text{O}_7$ doped with 0.01 molar percentage of copper
5. $\text{Na}_{1.7}\text{K}_{0.3}\text{Ti}_3\text{O}_7$ doped with 0.1 molar percentage of copper
6. $\text{Na}_{1.7}\text{K}_{0.3}\text{Ti}_3\text{O}_7$ doped with 1.0 molar percentage of copper
7. $\text{Na}_{1.6}\text{K}_{0.4}\text{Ti}_3\text{O}_7$ doped with 0.01 molar percentage of copper
8. $\text{Na}_{1.6}\text{K}_{0.4}\text{Ti}_3\text{O}_7$ doped with 0.1 molar percentage of copper
9. $\text{Na}_{1.6}\text{K}_{0.4}\text{Ti}_3\text{O}_7$ doped with 1.0 molar percentage of copper

3.2 X-RAY DIFFRACTION (XRD)

XRD-measurements have been used for the phase evaluation of all the samples. As it is the characteristic of crystal structure of a particular compound and thus, ascertains whether a particular compound has actually been made.

XRD-patterns for all compositions have been collected by Iso-Debyeflex 2002, Richseifert and Co. differactometer using CuKα radiation generated at 30 kV and 20 mA with settings; sweep = 3.0°/min, range (CPM) = 5 K and time Constant = 10.0.

3.3 DIELECTRIC AND AC CONDUCTIVITY MEASUREMENTS

The pelletized samples prepared are mounted in the sample holder to keep in the furnace. The vacuum in the sample holder chamber was created up to $10^{-3}$ m bar with the help of Vacuum Unit. The upper part of the sample holder kept cold by continuous flow of chilled water.

The loss tangent ($\tan \delta$) and parallel capacitance ($C_p$) of the pelletized samples have been directly measured as a function of frequency in the range of 100 kHz-1 MHz and as a function of temperature in the temperature range of 373-748 K by HP 4194A impedance analyzer. All the measurements are performed at the interval of 25 K by stabilizing the
temperature at the desired value. The relative permittivity ($\varepsilon_r$) and the bulk a.c. conductivity ($\sigma$) of the samples have been calculated by using expressions:

$$\varepsilon_r = \frac{C_p}{C_0}$$  \hspace{1cm} (3.1)

$$\text{Conductance } G = \omega C_p \tan \delta; \ \omega = 2\pi f$$  \hspace{1cm} (3.2)

and $$\sigma = G(t/A)$$  \hspace{1cm} (3.3)

where $f$ is the frequency of a.c. signal, $t$ is the thickness and $A$ is the area of the cross-section of the pellet.

### 3.3.1 EXPERIMENTAL SETUP

The block-diagram of experimental setup for dielectric-spectroscopic and ac conductivity measurements have been shown in Fig. 3.1. For the dielectric and conductivity measurements, the pelletized silver coated ceramic sample is sandwiched between silver electrodes of diameter 11 mm inside the metallic jacket of sample holder (Fig. 3.2). The silver electrodes are welded with silver wires which taken out from the metallic jacket to get connection with the impedance analyzer provided proper insulation between wires and jacket. A chromel-alumel thermocouple is also attached with sample holder to measure the temperature of the sample, which is connected to a digital multi meter (Rish Multi 18S) that measures the temperature as a function of voltage. From the calibrated tables one can calculate the temperature of the sample. A temperature controller (Indotherm 400) is used to control the furnace temperature. The various components of this setup have been discussed above in details.

**Figure 3.1** Block diagram of the experimental set up used in dielectric spectroscopic and ac conductivity measurements.
3.4 THE EPR MEASUREMENTS

The EPR spectra of the copper doped samples have been recorded on a Varian E-line century series spectrometer model E-109, which operates at X-band frequencies (~9.2GHz). All the spectra have been recorded with 100 kHz modulation. The maximum calibrated power available is 200 mW. Conventional first derivative of absorption signals are recorded. Depending on the experimental condition, various scan ranges between 0.08T to 1.0T with appropriate scanning rates have been used. The high frequency modulation field amplitude is ranged typically from $5 \times 10^{-3}$ mT to 0.50 mT with E-231 rectangular (TE$_{102}$) cavity (unloaded Q ~ 7000) at 100 kHz field modulation. The samples for the recording of the EPR spectra are kept in quartz tube (O.D. ~.5mm). An incident microwave power level of 2 mW is adequate for most of the cases to given levels of $1 \times 10^3$. The field stability of the spectrometer after stabilization is of the order of 10 ppm with temperature coefficients of 2 ppm/° C between 0.3T and 1.5T. The magnetic field is calibrated using a DPPH standard marker (g =2.0036).