CHAPTER III
EXPERIMENTAL

3.1 Sample preparation

3.1.1 Synthesis of pure polycrystalline Na₂Ti₃O₇ fine ceramics

The polycrystalline samples of Na₂Ti₃O₇ were prepared by heating a mixture of Na₂CO₃ powder (99.9 % pure, AR grade) and TiO₂ powder (99 % pure, AR grade) in the molar ratio 1.1:3 at 1100K for 16 hrs. The heated product was cooled to RT and mixed in acetone for grinding to achieve fine powder, then compressed to 15 MPa to get a pellet of Na₂Ti₃O₇, 10.25mm in diameter and 1.2mm in thickness. The pellet so obtained was wrapped in platinum foil and heated again at 1100 K for 14 hrs. The product was cooled to RT at a rate of 3.0 K/min and its flat faces were coated with silver for electrical measurements.

3.1.2 Synthesis of manganese doped derivatives of Na₂Ti₃O₇

The manganese doped derivatives (x =0.01, 0.1, 1.0) of Na₂Ti₃O₇ were prepared by mixing MnO₂ powder (99% pure, AR grade) to the starting mixture of alkali carbonate and TiO₂. The mass so obtained was treated as mentioned above and the pellets were made accordingly.

3.1.3 Synthesis of iron doped derivatives of Na₂Ti₃O₇

The iron doped derivatives of Na₂Ti₃O₇ were prepared by mixing Fe₂O₃ powder in place of MnO₂ powder in the appropriate molar percentage following the above procedure.

3.1.4 Synthesis of pure polycrystalline K₂Ti₄O₉ fine ceramics

The polycrystalline samples of were prepared by heating a mixture of K₂CO₃ powder (99.9 % pure, AR grade) and TiO₂ powder (99 % pure, AR
grade) in the molar ratio 1.3:4 at 1100 K for 16 hrs. The remaining method of preparation has been same to that for pure Na$_2$Ti$_3$O$_7$.

3.1.5 Synthesis of manganese doped derivatives of K$_2$Ti$_4$O$_9$

The manganese doped derivatives of K$_2$Ti$_4$O$_9$ were prepared by mixing MnO$_2$ powder (99.9 % pure, AR grade) with alkali carbonate and TiO$_2$ and follow the same procedure as above.

3.1.6 Synthesis of iron doped derivatives of K$_2$Ti$_4$O$_9$

The iron doped derivatives of K$_2$Ti$_4$O$_9$ were prepared by mixing Fe$_2$O$_3$ powder (99.9 % pure, AR grade) in place of MnO$_2$ powder and following the procedure described as above.

3.2 XRD Measurements

Like any other material the alkali titanates could be characterized through XRD-measurements. The x-ray diffractometer run of the compound would be characteristic of its crystal structure and thus, it can be ascertained whether a particular compound has actually been made in the sintering process.

Accordingly, all the above prepared samples were characterized using X – ray powder diffractometer Model no. ISO – Debyeeflex 2002, Rich–Seifert & co. (West German ) Which uses Cu Kα line with the following settings : sweep = 3.0°/min, range (CPM) = 5K, time constant (s) = 10.0, target = Cu, current = 20mA, voltage across the cathode and target = 30KV.

3.3 Dielectric-spectroscopic and a. c. conductivity measurements

The dielectric loss tangent (tanδ) and parallel capacitance ($C_p$) of pure Na$_2$Ti$_3$O$_7$ and K$_2$Ti$_4$O$_9$ sample were directly measured in 100Hz to 1MHz frequency range of the a.c. signal having oscillating level 0.50v from
373-898K on HP 4194A impedance analyzer. The conductivity could subsequently be evaluated as -

\[
\begin{align*}
\text{Dielectric constant (Real)} & : \quad \varepsilon' = \frac{c_p}{c_0} \\
\text{Dielectric constant (Imaginary)} & : \quad \varepsilon'' = \varepsilon' \tan \delta \\
\text{Conductance} & : \quad G = \omega c_p \tan \delta \\
\text{Conductivity} & : \quad \sigma = G \left( \frac{t}{A} \right)
\end{align*}
\]

Where ‘t’ is the thickness and ‘A’ is the area of the sample.

The dielectric-spectroscopic and a.c. conductivity measurements were made on the samples mentioned below :-

1) Pure Na$_2$Ti$_3$O$_7$ and K$_2$Ti$_4$O$_9$

2) 0.01, 0.1, 1.0 molar percentages of manganese and 0.1, 1.0 molar percentages of iron doped derivatives of Na$_2$Ti$_3$O$_7$.

3) 1.0 molar percentage of manganese and 0.1, 1.0 molar percentages of iron doped derivatives of K$_2$Ti$_4$O$_9$.

### 3.3.1 Experimental arrangement

The block diagram in Fig. 3.1 shows the experimental set up for the conductivity experiments. The sample whose electrical and dielectric properties are to be measured is made in the form of a pellet by applying a force of 15MPa. After applying necessary silver coating, the pellets are placed between the silver electrodes of diameter 11mm in the sample holder. The silver electrodes are brazed (using gas welding) to silver wires to provide connection to the impedance analyzer, and chromel-alumel thermocouple is attached with the sample holder to measure the temperature of the sample, which is connected to a Keithley DMM (Digital Multi Meter) which will measure the temperature as a function of voltage. From the calibrated tables one can calculate the temperature of the sample. A temperature controller (Indotherm 401D) is used to control the furnace
temperature. The various components of this setup were discussed in detail above.

Impedence Analyzer  Furnace and Sample holder  Temperature Controller  DMM

Silver Leads  Chromel-Alumel Thermocouple

Fig. 3.1 Block diagram of the experimental set up used in the conductivity and dielectric-spectroscopic measurements

3.4 Pyroelectric measurements

The experimental set up for measuring the pyroelectric current is shown in Fig. 3.2. These pyroelectric measurements have been made in vacuum without applying potential difference across the samples, the current so generated being measured with an electrometer amplifier (Kiethley 614). The temperature of the specimen was controlled by using Libratherm PRC 309 temperature controller and programmer. A chromel-alumel thermocouple was properly connected to the programmer one end of which was placed close to the crystal. All the measurements were made by stabilizing the temperature of the sample for about 5 minutes at each desired value.
$S_1, S_2$ --- samples to be investigated

Fig. 3.2 Experimental set-up for pyroelectric/electrical conductivity measurements with two samples together