

CHAPTER - V

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SUMMARY AND CONCLUSIONS

Pyrochlores are important materials, which possess many useful properties such as electrical, optical, magnetic and dielectric (1). In addition to this, pyrochlores can be used as electronic materials, electrodes in MHD (Magneto-hydro dynamics) power generation, heating element, oxygen electrode, semiconductive electrode or electrodes for solar energy conversion and as solid electrolytes. Some of the pyrochlore oxides have nuclear potential applications as neutron absorber and radioactive waste forms for final disposal (2). Some non-ferroelectric pyrochlores may serve as technologically useful dielectric in application such as temperature stable and temperature compensating dielectric (3).

The pyrochlore is one that has received a considerable amount of attention because of its ferro electric nature (4). Hence these materials find extensive applications in the field of electronics, electrical, magnetic and computer technology and microwaves.

The general formula of the oxide pyrochlores can be written as $A_2B_2O_7$ or $A_2B_2O_6O'$ with four crystallographic nonequivalent kind of atoms. Interchanging A, B and oxygen atoms and substituting A and B elements can obtain a number of interesting properties. The electric conductivity of various pyrochlore phases and their solid solution has been measured. The conductivity behavior is also explained generally on the disordered structure of pyrochlore, oxygen vacaies and interstitial positions. The electric nature of pyrochlores varies highly insulating through semiconducting to metallic transition. Little

work is done on electrical behavior of these pyrochlores and the conduction phenomenon.

In order to understand the conduction mechanism in pyrochlore, we have undertaken the following work.

1) Preparation of pyrochlores by ceramic method using chemical formula $A_2B_2O_7$ where $A = \text{Ce, Nd}$ and $B = \text{Ti}$

2) X-ray diffraction study for confirmation of single-phase formation and determination of pyrochlore structure.

3) Electrical properties, d.c. Conductivity, TEP measurements, dielectric measurements variation of dielectric constant and loss tangent with frequency and with temperature.

The general formula for pyrochlore can be the electric nature in order to understand

1) Polycrystalline pyrochlore of general formula $\text{Ce}_{2-x}\text{Nd}_x\text{Ti}_2\text{O}_7$ were prepared with $x = 0.0, 0.2, 0.4, 0.6, 0.8$ and 1 by ceramic method at appropriate sintering temperature (presintering temperature 900°C , final sintering temperature 1100°C), Presintering was carried out twice about 14-16 hours and final sintering for 24 hours.

2) Confirmation of the formation of single-phase compound by characterization of FCC structure after determining lattice parameter by Bragg's x-ray diffraction method.

3) The electrical properties were experimentally studied by a) measuring d.c. resistivity in temperature range 300 K to 800 K. b) finding dielectric constant and losses in a.c. frequency range from 100Hz to 1MHz at room

temperature. c) finding dielectric constant (real and imaginary) and losses in temperature range from 300 to 1100 K. d) measuring thermoelectric power and finding Seebeck coefficients at various temperatures.

A brief review of electrical and structural properties, classification of pyrochlores materials and applications of pyrochlores along with orientation of problem are dealt in the chapter I, as a introduction to our work.

In chapter II deals with the standard ceramic method for preparation of pyrochlore and x-ray diffraction method for characterization. Actual method of preparation is described in all also its details with a flow chart. x-ray diffractometer used for x-ray analysis is discussed in briefly.

Pyrochlore series of general formula $Ce_{2-x}Nd_xTi_2O_7$ with $x = 0.0, 0.2, 0.4, 0.6, 0.8$ and 1 were prepared. Very pure oxides of AR (analytical reagent) grade were weighed stoichiometrically and thoroughly mixed in an agate mortar repeatedly. Air-dried mixture was placed in alumina crucible and presintered twice at 900°C for 16 hours and furnace cooled at the rate 80°C per hour. Pellets of approximate diameter 1.5 cm and thickness 0.4 to 0.5 cm were molded in a die by applying the pressure of 7-8 tones/inch² using hydraulic press. The final sintering was carried out at 1100°C for 24 hours and furnace is cooled at the same rate.

Powder method was used to determine the lattice parameters and interplaner 'd' spacing. The observed values of inter planer distance and planes parameter 'a' confirms the formation of pyrochlore material. It is also observed that with increase in Nd content in sample, lattice parameter 'a' decreases, This shows that lattice parameter 'a' decrease with decrease in ionic radius of

substituting atom. The porosity of sample is less than 15%. The particle size is determined with the help of x-ray diffraction peaks which is of the order of μm . The calculated 'd' values are in good agreement with the observed 'd' values (5).

Chapter III deals with thermoelectric power and electrical resistivity. The basic electrical properties are briefly reviewed. The details of the experiments, with required formula are given. The graphs of $\log \rho$ Vs temperature were plotted. From this plots it is seen that for the present samples resistivity is constant or stable up to 450K. Above 450K they shows semiconductor behavior. The present results clearly have shown that the conduction from ionic drift current is predominant in this anomalous region 400K. After 400 K, resistivity decreases with increase in temperature. This indicates that behavior of titanate pyrochlore is semiconducting in nature above 400K up to 600K. The present results show that electrical resistivity is decided by the effect of concentration and mobility of charge carriers. The overall transport property of compound may depend on the type and concentration of defects contributing to electrical conduction of which how ever can vary with temperature. In general the transport properties of oxide are determined by the defects formed in response to both impurities and influenced by both the temperature and oxygen pressure. Activation energy for all composition are calculated and shown in table 5.1. From this graphs it is also observed that resistivity decreases with increase in Nd content i.e. the conductivity increases with increase in Nd content.

Table 5.1: - Activation energy of all the compositions

Composition (x)	Activation Energy (eV)
0.0	0.2079
0.2	0.3436
0.4	0.3919
0.6	0.5376
0.8	0.6279
1	0.6452

Form the variation of TEP with temperature shows, that all samples show n-type behavior. The CUSP in α Vs T curve shows near to 450-500K. Above 500K the absolute α value decreases and n-p transition takes place around 650-700K. The conductivity plots also show change in slope near to 650-750K. Anomalous behavior of ρ near to temperature of CUSP in α . Hence it is clear that in oxide materials the charge transport is characterized by both ionic and electronic conduction. Form plots it is observed that all samples show almost similar thermal variation with negative Seebeck coefficient. Often one type charge carriers dominates the charge transport but transition to other type of conduction may occur at certain temperature as a result of a change in composition or stoichiometry of the solids(6). In pyrochlores depending upon the type of the substituent ion as well as temperature and oxygen pressure interaction with atmosphere can take place according to either of the following reactions.



where all notations are written according to Kroger-Vink notation of defects.

Under certain condition p or n type defect exists, hence the observed variation for the present systems may be due to oxygen concentration in the material. T. Van Dijk et.al.(7) reported that if the oxygen vacancies are completely ordered in stiochiometric materials, vacancies are change d in to non occupied structural sites.

Chapter IV the basic theory of a.c. conductivity (or dielectric properties) is discussed. In this topic, theories of dielectric polarization, dielectric constants and loss tangent (or power loss) are discussed briefly. All the dielectric measurements are carried out in the frequency range 100 Hz to 1MHz with the help of Hewlett Packard Precision LCR meter.

All the samples reveal the dielectric dispersion. The dielectric constant (ϵ') decreases rapidly with increase in frequency and reaches a constant value. Plots of dielectric dispersion with frequency shows that the rate of decrease in the value of ϵ' at low frequencies is higher than that at the high frequencies. The dielectric constant ϵ' is almost constant (or independent) after a certain higher frequency. For the present selected titanate pyrochlore samples dielectric constant at high frequencies lie between 20 to 40. At low frequencies, dielectric constant is high, due to the effect of heterogeneity of the samples like pores, surfaces and layers of grains(8,9). Some times some electronic polarization effect is supposed to be connected with the conduction hopping mechanism itself and could be contributing low frequency dielectric dispersion ϵ' (10).

From plots of dielectric constant Vs temperature at fixed frequency 10KHz it is observed that the dielectric constant increases slowly with increase in temperature up to 600K. But above it increase in temperature. The temperature minimum in dielectric constant shows n to p transition. The temperature maximum in resistivity shows n to p transition. Both temperature minimums in dielectric constant and temperature maximums in resistivity are nearly same. The rapid rise in dielectric constant with increase in temperature is due to the exponential decrease in electrical resistivity.

The power loss (loss tangent) due to electric conduction is negligible in such high resistivity insulating material, which is similarly observed for the present samples.

From the variation of ϵ' with temperature of different frequencies for the composition $x = 0.0, 0.4,$ and 0.8 ; it is observed that the dielectric constant increases with increases in frequency at different temperature for particular composition. It is noted that the increases in frequency. This can be related with the relaxation process of the type of charge carriers.

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