STUDIES ON ELECTRICAL PROPERTIES OF 
Cr$_{2-x}$Ti$_x$O$_{3+\delta}$ BY IMPEDANCE SPECTROSCOPY

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A b s t r a c t

The compounds with compositions Cr$_{2-x}$Ti$_x$O$_{3+\delta}$ (where $x = 0, 0.1, 0.2$ and $0.3$) were prepared by gel-entrapment method and characterized by XRD and thermal techniques. The electrical properties, such as dielectric constant and ionic conductivity of these compounds were studied in the frequency range 10 MHz to 1 Hz, in the temperature interval 400 to 800 K, using impedance spectroscopy. The study showed that the dielectric constant of the sample increases up to 10 mole% of TiO$_2$ doping and decreases on further increase in dopant concentration. In the dielectric constant versus temperature plot a phase transition is noted in the temperature range 650-700 K in all the samples. From Arrhenius plot, the activation energy for different compositions was derived, below and above the transition temperature. The results of the electrical measurement are explained on the basis of defect formation and ordering.

Introduction

In recent years, there has been increased demand to develop newer sensor materials for applications in electronic and other industries. Ternary transition metal oxides have been investigated extensively for this purpose for reactive gases, since they exhibit both high selectivity and sensitivity for several gases [1]. One of the ways to increase the selectivity of these sensors, towards a desired gas, is by doping a suitable ion in the host matrix. At elevated temperatures, it is seen that the resistivity of doped oxides changes even for trace levels of reactant gases. Therefore, the studies pertaining to the electrical properties of the semi-conducting oxide sensor materials are important to explain their sensing behavior. Mosely and Williams [2] used chromium titanium oxide of composition Cr$_{1.8}$Ti$_{0.2}$O$_{3+\delta}$ for monitoring ammonia in percentage level in air, at 773 K. Jayaraman et al [3] have studied the sensor properties of TiO$_2$-doped Cr$_{2}$O$_3$ (Cr$_{2x}$Ti$_x$O$_{3+\delta}$). In this paper, we describe the synthesis
of Cr$_{2-x}$Ti$_x$O$_{3+\delta}$ by a novel solution-based preparation method, their characterization and the electrical conductivity and dielectric properties of the compounds at different temperatures.

**Experimental**

The compounds, Cr$_{2-x}$Ti$_x$O$_{3+\delta}$ were prepared by gel-entrapment method [4]. For the preparation of the compounds, the metal nitrate solutions of appropriate concentrations were mixed together and gradually gelled at room temperature by slow addition of 3 molar hexamine solution with continuous stirring. The gel obtained in the process was then dried in an oven at 150°C and heated to 200°C to obtain the precursor material. The precursors were further heat-treated, at 750°C in air for 4 h, to get phase-pure compounds. The compounds were characterized by TG-DTA (Setaram, Model 92-16.18) and DSC (Setaram, Model 131) techniques. The samples were pelletized into 10 mm diameter disks of thickness 1.5 mm at a pressure of 250 MPa and sintered in air at 1000°C for 12 h. The pellets were then polished and coated with thin layer of silver on flat ends to have better contact with the electrode for electrical property measurement.

The electrical properties of the samples were measured using a Solartron AC Frequency Analyzer (Model 1260) in the frequency range 10 MHz to 1 Hz. The impedance spectra were recorded in the temperature interval of 400 to 800 K with the step of 25 K for all the samples. The temperature was controlled by a microprocessor and measured by a K-type thermocouple placed very close to the sample. At each temperature, the samples were equilibrated for 20 min. before recording the spectra.

**Results**

The room temperature XRD analysis of the samples indicates, that the materials are single phase with hexagonal lattice structure. The cell parameters of the compounds obtained from least square fitting of the XRD data were found to be in good agreement with the reported values. The DSC studies of these samples showed a diffused phase transition in the temperature range 650-700 K. However, the high-temperature XRD data for the sample did not show any crystallographic modification of the samples above the transition temperature. The observed phase transition in the DSC studies could, therefore be attributed to the electronic transition in the compounds.

The dielectric constants of the compounds, determined from the capacitance values obtained from the Nquist’s plot, indicate that, there is a sharp increase in the values of dielectric constants around 650-700 K for all the samples. Fig. 1 gives the variation of dielectric constant of Cr$_{1.7}$Ti$_{0.3}$O$_{3+\delta}$ as a function of temperature for different
frequencies. From Fig. 1 it can be noted that there is a sharp increase in the values of dielectric constant in the temperature range 650 to 750 K for all frequencies. The corresponding plots for the other compositions are similar to Fig. 1. Table 1 gives the variation of dielectric constant of all the samples with temperature calculated from the maxima (nmax) of the Nquist’s plot.

Fig. 2 gives the representative Nquist’s plot for the composition Cr$_{1.9}$Ti$_{0.3}$O$_{3+\delta}$ at 660 K. From the real part of this plot, the resistance of sample was determined as a function of temperature. Using the measured cell constants, the conductivity ($\sigma$) of the samples was calculated for all compositions, as a function of temperature. From the plot of $\ln(\sigma T)$ vs $1/T$, the activation energies for the movement of charge carriers were calculated. The extrapolation of linear least-square fitting of the experimental data at temperatures above and below the diffused transition gave the intersection point, which was attributed to the average transition temperature for the particular composition. Table 2 gives the transition temperature and the activation energies of the compositions. Fig. 3 gives the Arrhenius plot $\ln(\sigma T)$ vs $1/T$ for all compositions.
**Conclusion**

The transition in the temperature range 650-700 K obtained from extrapolation of \( \ln (\sigma T) \) vs 1/T curve is attributed to the electronic transition from the valence band to the conduction band of the system. In contrast to the electronic transport at high temperatures, the transport below the transition is mainly governed by the cationic movements. From the analysis of powder XRD data it is clear, that TiO_2 forms a homogeneous solid solution with Cr_2O_3 up to 15 mole % TiO_2 and creates the cationic vacancies in the lattice.

**References**

About the Authors

Mr. Rajesh V. Pai joined Fuel Chemistry Division, BARC after graduating from the 40th batch of Training School in the year 1997 after completing his M.Sc. (Applied Chemistry) from Cochin University of Science & Technology. He is mainly associated with the development of sol-gel process thoria, urania and plutonia-based ceramics. In this, he has developed process sheets for the fabrication of ThO$_2$, (Th,U)O$_2$, UO$_2$, (U,Pu)O$_2$ dense pellets based on internal gelation process. His research interest includes development of sensor materials, high technology materials and nanoceramics.

Dr. S.K. Mukerjee joined Department of Atomic Energy after completing his M.Sc. (Chemistry) from Nagpur University. Currently he is Head, Process Chemistry Section, Fuel Chemistry Division, BARC. He has been mainly associated with the development of ceramic materials for application of nuclear technology. He has extensively studied sol-gel processing of nuclear materials for advanced fuel fabrication. He has obtained doctorate from Mumbai University in the year 1993.

Dr. R. Mishra, Ph.D (Mumbai University) is working in Chemistry Division, BARC. He specialized in high temperature chemistry and chemical thermodynamics. He derived thermodynamic data on several nuclear materials and intermetallic compounds, phase diagram studies of binary and ternary oxide systems. He was been awarded the TA instrument–ITS Young Scientist Award–2004 and Alexander von Humboldt Fellowship for post-doctoral studies in the University of Munich, Germany.

Dr. D. Das, M.Sc. in Chemistry (University of Calcutta), joined BARC through Training School in 1974. He is currently the Head, Chemistry Division. His contributions include thermodynamic characterization of compounds, alloys and intermetallics, the physico chemical compatibility studies of corrosive liquids and vapours in high temperature contaminants, the development of techniques of pyrometric calibrations up to 3000 K, the development of high power electron beam source for large scale evaporation of metals etc.

Dr. V. Venugopal is the Director, Radiochemistry & Isotope Group, BARC. He is a specialist in the field of high temperature thermodynamics and chemical quality control of Pu based fuels. He has worked at Nuclear Research Centre, Julich on the development of nickel-based binary super alloys required for Rocket Jet Nozzle and turbine blades and also on the development of high intensity metal halide vapour lamps at high temperature. He has been honoured with NETZSCH-ITAS and ISCAS for his outstanding contributions in the field of thermal science and solid state chemistry respectively. He is the regional editor for the *Journal of Thermal Analysis and Calorimetry*. 