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Impedance spectroscopic investigation on electrical conduction and relaxation in manganese substituted pyrochlore type semiconducting oxides

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Abstract

The effect of simultaneous substitutions of Mn in both A and B sites of the pyrochlore type semiconducting oxides: $(CaCe_{1-2x}Mn_{2x})(Sn_{1-x}Mn_xINb)O_{7-\delta}$ ($x=0$, 0.1, 0.2, 0.3 and 0.4) on the electrical conduction and relaxation was studied in detail using impedance analysis as a function of frequency over a wide range of temperature. Impedance and modulus analysis clearly explain the relaxation in these materials and its dependence on Mn concentration. Grain boundary dominant electrical characteristics have been observed with progressive Mn substitution. Correlated barrier hopping model was successfully applied for explaining the conduction mechanism in these compounds. Variation of hopping parameters with Mn substitution in these materials indicates strong dependence on the grain and grain boundary contributions. This insight to the conduction mechanism of the system offers in tuning the electrical properties for desired applications such as NTC thermistors.

Keywords: Impedance; Electrical conductivity; Electrical properties

1. Introduction

Many of the technologically important pyrochlore type materials with fascinating electrical and magnetic properties have been developed by the effective utilization of mixed valence nature of rare earth and transition metal oxides [1–3]. Among them cerium and manganese containing pyrochlores deserve special attention as they can take different crystallographic sites. Performance of these materials found in the heart of many applications depends mainly on their electrical transport properties. For improving the performance of materials in devices, a better knowledge of the conduction mechanism in materials will be very useful. Impedance spectroscopy (IS) is often used as a powerful tool to understand the conduction mechanism in materials. Normally, polycrystalline ceramics contain intra-grain, inter-grain and electrode effects and possess different physical properties also. In order to understand the electrical properties of a given sample, the contributions from each of these effects must be separated and this can be done and analyzed in detail using IS.

Impedance spectroscopy can be effectively used to study any of the intrinsic properties that influence the conductivity of an electrode–materials system such as conductivity, dielectric constant, mobility of charge carriers, etc. These properties ultimately depend on the distribution of resistive and capacitive components in the material [4]. An equivalent circuit consisting of these elements can be modeled which enables one to extract physically meaningful properties of the system [5]. Altogether, impedance and modulus formalisms along with the measurement of ac conductivity provide an idea about the relaxation and its associated conduction mechanism in disordered solids. The variation of conductivity with temperature and frequency generally follows the same power law behavior in disordered solids [6]. Various models, such as quantum-mechanical tunneling model (QMT), small polaron

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tunneling model (SPT), large polaron tunneling model (LPT), atomic hopping model (AH) and correlated barrier hopping (CBH) model have been proposed to explain the ac conduction mechanism [6]. From the variation of ac conductivity with frequency over a range of temperature the suitable model for a given material can be identified.

From our earlier investigations on Mn substituted pyrochlore type semiconducting oxides in $CaCeSnNbO_7$ system, it was observed that Ce and Mn predominantly existed as Ce^{3+} and Mn^{2+} and were responsible for the semiconductivity of the materials [7]. It was also found that the extent of Mn^{2+} concentration and hence the localization of electrons associated with Mn^{2+} at the A site played an important role in tuning the electrical transport properties and in turn the NTC thermistor behavior of the materials. To increase the Mn^{2+} concentration, in the present investigation we tested the possibility of simultaneous substitution of Mn in both A (Ce) and B (Sn) site of the pyrochlore. We succeeded in it and were able to increase the extent of phase purity by doing double substitution [8]. Further, these semiconducting oxides show better NTC thermistor properties and with the aid of IS we were able to confirm the dominance of grain boundary dependent NTCR behavior in compositions with higher Mn concentration. The presence of mixed valence ions along with the localization of conduction electrons of Mn^{2+} ions opens up the possibility of exploring the charge transport in these materials. In this article we report the impedance spectroscopy studies of these Mn double substituted pyrochlore type semiconducting oxides to understand the conductivity relaxation and the charge transport mechanism. These understandings are helpful in tuning the electrical characteristics for particular applications such as catalysis, temperature sensing, etc.

2. Experimental

The polycrystalline samples were prepared through the conventional solid-state reaction method using $CaCO_3$ (99.9%, Acros Organics), CeO_2 (99.9%, Aldrich), MnO_2 (99.5%, Merck), SnO_2 (99.9%, Aldrich), and Nb_2O_5 (99.5%, Aldrich) as the starting materials. The standard procedure for weighing, mixing and drying was strictly followed [8]. The resulting homogeneous mixture was calcined at 1200 °C for 6 h. Disc shaped pellets of 10 mm diameter and 2 mm thickness were prepared by isostatic pressing at a pressure of 250 MPa. 4 wt.% polyvinyl alcohol (PVA) was used as a binder for good compaction of the pellets. The pellets were heated at 600 °C for 1 h to burn off the PVA and then sintered at 1250 °C for 9 h.

For the ac conductivity measurements the sintered pellets were coated with a high temperature silver paste and cured at 600 °C for 30 min and silver wires were attached to the silver coated surfaces. The ac impedance analysis of the samples was carried out by a computer-controlled impedance analyzer (Solartron, SI 1260) in the frequency range 10 Hz to 1 MHz over a temperature range from 30 °C to 600 °C. The complex impedance plots were made with SMART software supplied by M/s Solartron, UK.

3. Results and discussion

3.1. Impedance analysis

X-ray diffraction studies confirmed the formation of complete solid solution in the range $0.1 \le x \le 0.3$. These Mn substituted compounds have cubic pyrochlore type structure with high sintering density ($\ge 94\%$) [8]. Complex impedance spectroscopy is a widely used powerful tool to analyze the electrical behavior of polycrystalline ceramics. A wide range of temperature (30–600 °C) and frequency (10 Hz–1 MHz) has been chosen for the impedance spectral studies. Here, the dependence of electrical relaxation on frequency and temperature has been effectively analyzed by using the impedance and modulus formalisms. Fig. 1 shows the variation of imaginary part of impedance (Z") with frequency in $(CaCe_{1-2x}Mn_{2x})(Sn_{1-x}Mn_xNb)O_{7-\delta}$ ($x=0$, 0.1, 0.2, 0.3 and 0.4) at different temperatures. A peaking behavior can be observed for all the compositions and the peak maximum shifts towards higher frequencies with the increase of temperature. This indicates the temperature triggered relaxation process dominating in the polycrystalline samples. Intensity of the peaks decreases gradually due to the decreased resistance of the material with temperature. The full width at half maxima calculated from the spectra is greater than 1.141 decade (1.141 decade for ideal Debye relaxation). This deviation clearly indicates the presence of non – Debye type relaxation in the materials [9]. Additionally, the curves are found to be merging at high frequencies irrespective of the temperature indicating the release of space charges. Asymmetric peak broadening suggests broad distribution of relaxation time [10].

A close examination of the spectra gives the interesting information that the peaks occur at rather high frequencies for compositions $0 \le x \le 0.2$ and at low frequencies for $x=0.3$ and 0.4. In impedance spectra the bulk properties or grain effects occur at high frequencies and the grain boundary effects at low frequencies. Hence it can be assumed that the compositions in the range $0 \le x \le 0.2$ exhibit the grain effects and the $x=0.3$ and 0.4 display the grain boundary effects in the given range of temperature and frequency. The peak maximum of grain shifts rapidly to high frequencies with increase in temperature while the grain boundary remains in the low frequency region.

Fig. 2 shows the typical Cole – Cole plots of $(CaCe_{1-2x}Mn_{2x})(Sn_{1-x}Mn_xNb)O_{7-\delta}$ ($x=0$, 0.1, 0.2, 0.3 and 0.4) at 200 °C. Analysis of Cole-Cole plots enable to separate various contributions from grain, grain boundary and electrode effect on the relaxation processes involved in the polycrystalline materials [11]. Only one depressed semicircle can be observed for the given system of compounds. Intercept of the semicircle on the real axis Z′ provides the resistance of the sample. Fig. 2 also depicts the compositional dependence on resistance of the samples. It can be observed that the resistance decreases with Mn substitution for the compositions up to $x=0.2$ and then an abrupt increase can be observed for $x=0.3$. The increased carrier concentration with Mn substitution (discussed in the electrical conductivity studies) is one of the main reasons behind the decreased resistance. The increased grain boundary area for compositions with higher Mn