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Chromium effects on the transport properties in $La_{0.7}Sr_{0.3}Mn_{1-x}Cr_xO_3$

H. Rahmouni [a,*], A. Selmi [b], K. Khirouni [a], N. Kallel [c]

[a] Laboratoire de Physique des Matériaux et des Nanomatériaux appliquée à l'Environnement, Faculté des Sciences de Gabès cité Erriadh, 6079 Gabès, Tunisia
[b] Laboratoire de Physique des Semiconducteurs et des Composants Electroniques, Faculté des Sciences de Monastir, Avenue de l'Environnement, 5018 Monastir, Tunisia
[c] Laboratoire de Physico-Chimie des Matériaux, Département de Physique, Faculté des Sciences de Monastir B. P. 22, 5019 Monastir, Tunisia

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ABSTRACT

Transport measurements have been performed on $La_{0.7}Sr_{0.3}Mn_{1-x}Cr_xO_3$ using impedance spectroscopy technique, in order to study its electrical properties. The results indicate that the electrical properties of the material are strongly dependent on temperature and frequency. Evidences of temperature dependent electrical relaxation phenomena in the material have also been observed. Impedance spectrum analysis shows that the material can be described as a grain and grain boundary medium and permits to estimate the grain boundary contribution. Hopping mechanism dominates at small concentration. Electronic conduction is found to be dominated by thermally activated hopping of small polarons at high temperature and variable range hopping at low temperature. When the concentration of chromium increases, electrical behaviour of the material changes from semi-insulating to metallic behaviour. A regime of percolation appears and a metallic conduction becomes dominant.

1. Introduction

Perovskite material has received considerable attention due to the fact that they often exhibit properties considered useful for the development of thermoelectric devices. It shows high melting points, a wide range of thermal and electrical conductivities, ferroelectricity and ferromagnetism properties [1]. The search for materials that possess the structural stability and electrical conductivity required in fuel-cell applications has led to the investigation of a number of substitutionally mixed perovskites [2]. A series which has prompted considerable investigation [3–6] due to its potential usefulness in fuel cells is $LaCrMnO_3$. $LaCrO_3$ exhibits a thermally activated high-temperature electrical conductivity due to p-type small polaron hopping among the Cr-site cation and is extremely stable to high temperatures over a wide range of oxygen partial pressures. The less-stable $LaMnO_3$ has been thought to conduct via the same mechanism as $LaCrO_3$, but has a significantly greater conductivity.

Currently $La_{1-x}A_xMnO_3$ and $La_{1-x}A_xCrO_3$ are used in SOFCs as cathode and interconnect materials respectively [7]. $La_{1-x}Sr_xCrO_3$ is stable in the low oxygen pressure of the anode environment but as an anode it exhibits an unacceptably high polarization resistance. $La_{1-x}Sr_xMnO_3$ might be expected to be a good catalyst for fuel oxidation but it is thermodynamically instable under anode condition.

It is quite possible that $LaSrMnCrO_3$ profits of the advantage of each $LaSrCrO_3$ and $LaSrMnO_3$. In the aim to explore and to understand electrical properties of this class of materials, we have studied the electrical properties of $La_{0.7}Sr_{0.3}Mn_{1-x}Cr_xO_3$ by impedance spectroscopy technique.

2. Experimental procedure

$La_{0.7}Sr_{0.3}Mn_{1-x}Cr_xO_3$ samples are prepared by the standard ceramic method. The starting reagents, La_2O_3, $SrC0_3$, Cr_2O_3 (dried before use at 373 K) and MnO_2 were weighted in stoichiometric proportions. The mixed powders were first heated in air at 1173 K during 72 h to achieve decarbonization. The obtained powders were ground, heated again at 1473 K for 24 h to ensure homogenization. Intermediate cooling and mechanical grinding steps were repeated in order to get an accurate homogenization and complete reaction. Then the product was pelletized under 4 tonnes/cm^2 and sintered at 1673 K. Finally these pellets were cooled down to the room temperature. The structural properties were studied by Kallel et al. [8]. They conclude that the obtained samples have good structural properties.

For electrical measurements, two indium pads separated by a distance of 5 mm are deposited on the pellet to ensure ohmic contact. An Agilent 4294A impedance analyzer was used to collect impedance measurements over a wide frequency range. We employ a parallel mode to measure both conductance G and susceptance B using

* Corresponding author. Fax: +216 73500278.
E-mail address: rahmounihedi@yahoo.fr (H. Rahmouni).

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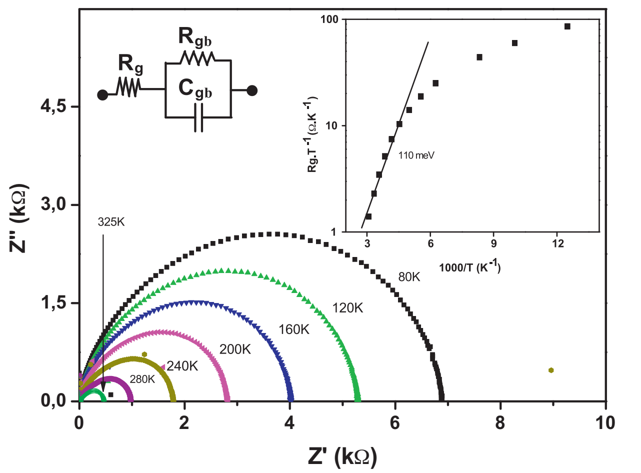

Fig. 1. AC impedance diagram of $La_{0.7}Sr_{0.3}Mn_{0.7}Cr_{0.3}O_3$ sample at different temperatures. The equivalent circuit and the Arrhenius plot of $R_{gb}T^{-1}$ are shown in the inset.

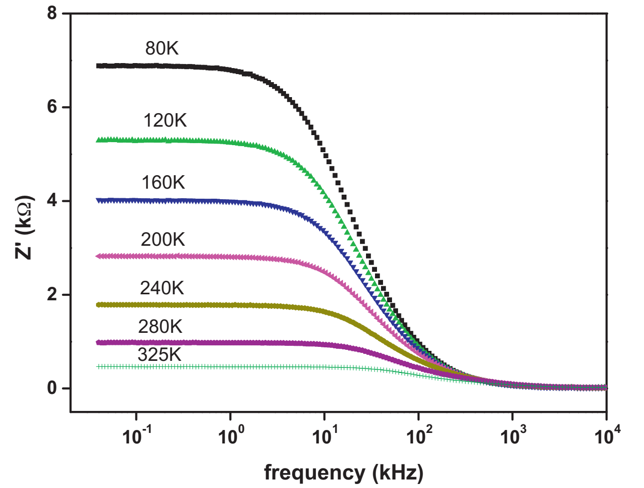

Fig. 2. Variation of real part of the impedance (Z') as a function of frequency for some representative temperatures.

an alternating signal with a voltage amplitude of 50 mV. To vary the temperature between 80 K and 325 K, the sample was mounted on the cold plate of a liquid nitrogen cooled cryostat. In such temperature domain, only electronic conduction is explored.

3. Results and discussion

3.1. Impedance spectrum analysis

The impedance spectroscopy technique is used to study the electrical behaviour of the system. It enables us to separate the real and imaginary components of the electrical parameters and hence provides a true picture of the materials properties.

Fig. 1 shows the complex impedance spectrum of $La_{0.7}Sr_{0.3}Mn_{0.7}Cr_{0.3}O_3$ for some representative temperatures. The impedance spectrum is characterized by the appearance of semicircle arcs whose pattern changes when the temperature is increased but its shape is conserved. Such pattern indicates the electrical processes occurring within the sample and their correlation with the sample microstructure when modelled in terms of an electrical equivalent circuit model [9,10]. The equivalent circuit of the sample is shown in the inset of Fig. 1. It is composed of a serial association of a resistance R_g with a capacitance C_{gb} associated in parallel with a resistance R_{gb}. The capacitance modelizes the grain boundary capacitance. R_g and R_{gb} modelize the grain and grain boundary resistance respectively. The intersect with real axis of the semicircle at low frequencies is ascribed to the total resistance $R_T = R_g + R_{gb}$. On the other hand, the impedance response of grain dominates at high frequencies and the resistance of grain R_g can be deduced from the left intersect of the semicircle with real axis.

Fig. 2 shows the variation of real part of the impedance Z' with frequency at different temperatures. The impedance value is typically higher at lower temperatures in the low frequency region and decreases gradually with increasing frequency. Also, Z' decreases with increasing temperature indicating an increase of AC conductivity. The value of Z' appears to merge in the high frequency region irrespective of temperature. This result may possibly be related to the release of space charge as a result of reduction in the barrier properties of material with rise in temperature, and may be a responsible factor for the enhancement of conductance of the material with temperature at high frequencies. The merging of the value of Z' for all temperatures at higher frequencies can be interpreted by the presence of space charge polarization. This interpretation was confirmed by the higher impedance values at lower frequencies. The same behaviour of Z' at lower frequencies was observed by Shrabanee Sen et al. [11]. Also, its evolution at higher frequencies for all temperatures was observed by Suchanicz et al. [12]. It is worth mentioning that an increase in the impedance with frequency has been reported for $La_{0.7}Sr_{0.3}MnO_3$ [13]. This behaviour is in agreement with the reported results in the literature [14]. Fig. 3 shows the variation of imaginary part of impedance Z'' with frequency for some representative temperatures. The spectra are characterized by the appearance of peak which shifts to higher frequencies with increasing temperature. Such behaviour indicates the presence of relaxation process in the system. From this peak we deduce the value of relaxation frequency f_r for each temperature and we then calculate C_{gb} using the relation $2\pi f_r R_{gb} C_{gb} = 1$

Deduced values of R_g, R_{gb} and C_{gb} for different temperatures are listed in Table 1. As the grain resistance R_g is too weak, the total resistance R_T which is the sum of grain and grain boundary ones is approximately equal to grain boundary component [15,16]. Table 1 shows that grain boundary resistance decreases with rise in temperature. Such behaviour in similar materials has been reported in literature [17]. It seems to be due to the fact that the grain boundary effect has assisted in lowering the barrier to the motion of charge carriers paving the way for increased electrical transport

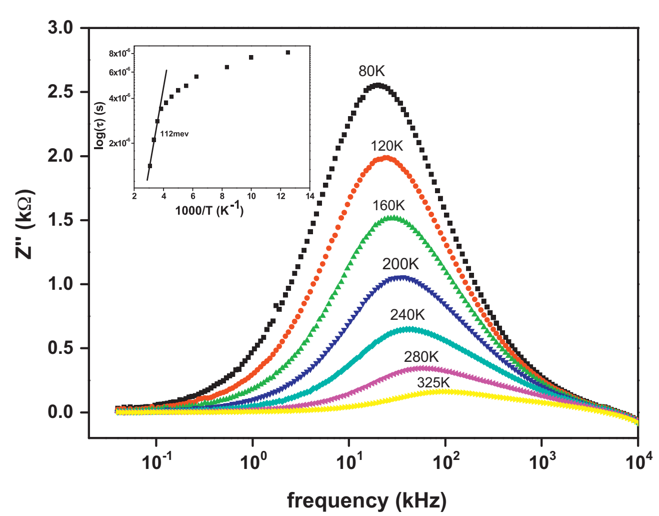

Fig. 3. Variation of imaginary part Z'' of impedance as a function of frequency at different temperatures of the sample $La_{0.7}Sr_{0.3}Mn_{0.7}Cr_{0.3}O_3$. The Arrhenius plot of time relaxation τ is shown in the inset.