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Metal–insulator transition and hopping conduction mechanisms in the $La_{0.7}Ba_{0.3}MnO_3$ compound

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ABSTRACT

The $La_{0.7}Ba_{0.3}MnO_3$ compound, obtained in volume by sol–gel with a cubic crystal lattice, exhibits metal–insulator phase transitions near 336 K and a ferromagnetic–paramagnetic transition near 375 K. The correlation between the magnetic and transport properties is evidenced by AC susceptibility measurements, impedance spectroscopy and DC conductivity. The activation energy values obtained by impedance spectroscopy and by the four-point method differed slightly. The real part of the conductivity $\sigma'(\omega)$ for different temperatures showed a plateau (DC regime) for various frequency decades followed by a dispersive region following a Jonscher's power law tendency. The value of the exponent n, which was less than one, showed a distribution of relaxation times. The cross-frequency ω_p, which was associated with the carrier hopping frequency, showed a thermally activated tendency with an almost constant carrier density for the entire range of temperatures. The relaxation time distribution was also verified by the dielectric modulus $M(\omega)$.

1. Introduction

The manganites belong to the family of $AMnO_3$ (A=rare earth) perovskites and are materials commonly used in technological applications, which is why they are continually investigated to improve their performance as active elements in devices [1–7]. $LaMnO_3$ is considered the prototype of the manganites, where Mn ions have a partially filled *3d* band with high spin (2/3). If the La cation is replaced by a divalent cation, a percentage of the Mn^{3+} manganese ions are changed to Mn^{4+}. The ratio of these ions (Mn^{3+}/Mn^{4+}) is critical for the transport and magnetic properties. These properties are explained in terms of the double exchange (DE) effect [8], a mechanism by which electron mobility is favored between the nearest Mn ions and preferentially those with aligned spins. Another relevant factor in the physical properties of manganites with partial substitution of cations is the ionic radius of the incorporated element. If the ionic radius is smaller as compared with the space available to fill the octahedrons of MnO_6, the latter would have a tendency to rotate and tilt toward the interior to minimize the energy. An implicit consequence of this spatial relaxation is the decrease in the bond angle for Mn–O–Mn, which, in turn, results in a decrease in the electron orbital overlap of the Mn and O atoms, an effect that is reflected in the properties of the material. A direct consequence of crystal lattice is the incorporation of defects into the material, leading to charge and spatial disorders. This incorporation is observed for the substitution of lanthanum by barium, where the difference between the corresponding radii ($r_{La^{3+}} = 1.36$ Å and $r_{Ba^{2+}} = 1.61$ Å) [9] is significant. However, it has been reported that the $La_{1-x}Ba_xMO_3$ compound, synthesized by solid-state reaction, exhibits different phases depending on the concentration x [10]. For the specific case of $x=0.33$, this compound exhibits a ferromagnetic metallic (FMM) phase transition to a paramagnetic insulating (PMI) phase near 340 K. Conversely, for $x=0.44$ and 0.38, the compounds show a metal–insulator transition at a temperature (T_{MI}) near the Curie temperature (T_c) with resistivity of the order of 10^{-3} (Ω cm). In many cases, the conduction mechanism is associated with the possible formation of polarons in the material. For compounds in the form of films, it has been reported that thetemperatures T_c and T_{MI} are notably near each other at approximately 314 K [11]. This transition temperature is always limited by the substrate-film coupling, a parameter that regulates the tension effects, which are less significant for $x=0.33$. Conversely, it has been found that the crystal structure adopted by $La_{1-x}Ba_xMO_3$ is highly correlated with the doping concentration (x), as well as with the methodology followed when determining such values. For example, Beznosov et al. [10] reported that for a value of $x=0.33$ obtained by solid-state reaction, orthorhombic and rhombohedral phases can coexist at room temperature with a rhombohedral phase majority. Zhong et al. [12] reported that the sol–gel-synthesized compound crystal structure has a cubic perovskite structure, which is strongly

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dependent on oxygen vacancies. The dielectric properties of polycrystalline ceramics are determined to a great extent by the effects of grain, grain boundary and interface. When differentiating the contributions to conduction, the complex impedance formalism is frequently used. With this formalism, it is possible to determine resistances (both in bulk and on the grain boundary), relaxation frequencies and electronic conductivity. Within the framework of this formalism, we have opted to study the dielectric conductivity (σ^*), the dielectric modulus (M^*), and their correlations as a function of the frequency and temperature of the $La_{0.7}Ba_{0.3}MnO_3$ compound synthesized by a sol–gel method.

2. Experimental data

Starting from the precursors, La_2O_3 (99.99% purity), MnO_2 (85.0% purity) and $Ba(NO_3)_3$ (99.0% purity), the compound $La_{0.7}Ba_{0.3}MnO_3$ (LBMO) was obtained by a sol–gel method. In stoichiometric proportions, the following compounds were dissolved separately: La_2O_3 in nitric acid (HNO_3), MnO_2 in hydrochloric acid plus deionized water as a diluting agent, maintained at a constant temperature of 623 K, and $Ba(NO_3)_2$ in distilled water at a temperature of 363 K. The compounds were mixed for approximately 15 min at a temperature of 363 K until reaching a homogeneous mixture. Nitric acid is added to the resulting mixture and serves as a complexing agent under constant stirring; in addition, the mixture pH was controlled with ammonium hydroxide ($\simeq 1.0$). The stoichiometric reaction for this reaction is given by

$$La(NO_3)_2 + Ba(NO_3)_2 + MnCl_2 + C_6H_8O_7 + NH_3 \rightarrow La_{1-x}Ba_xMnO_3 + CO_2 + N_2Cl_2 + H_2O \quad (1)$$

The mixture was heated to 623 K for 24 h to evaporate the solvents. The resulting product, which acquired a dark brown color, was calcined following a series of drops and holding times at each isotherm until reaching a final temperature of 1373 K. The last isotherm was maintained for an additional 24 h and cooled at a rate of 10°/min until reaching room temperature. X-ray diffraction of the powder material at room temperature was conducted with a Miniflex 2 equipment with Cu Kα ($\lambda = 1.5406$ Å) radiation in the range of $20^\circ < 2\theta < 80^\circ$, in steps of 2°/min. The AC susceptibility as a function of temperature was measured using the lock-in technique implemented in our laboratory, at a frequency of 40 kHz with an amplitude of 1.0 V and $H = 8.3$ Oe. The material was compacted (50 psi) into a cylindrical form and coated with silver paint at four symmetrical points to determine its DC conductivity as a function of temperature, using the four-point method. The electrical AC conductivity was determined from impedance measurements, $Z(\omega) = Z'(\omega) + iZ''(\omega)$ ($i = \sqrt{-1}$, $\omega = 2\pi f$ (Hz), using a Solartron1260 in the two-electrode configuration (stainless steel) with a cell designed in our laboratory. The excitation signal was set at 500 mV within a nitrogen environment. A type-K thermocouple was placed in close proximity to the sample and was used as a temperature sensor. The temperature range was between 294 and 517 K. The temperature was changed, and the corresponding isotherm was kept at ± 1 K.

3. Discussion and results

3.1. X-ray diffraction

Fig. 1 shows the X-ray diffraction of LBMO at room temperature. Starting from the parameters reported in Ref. [12] and with the help of the GSAS software, it was determined that the material crystallizes with a cubic structure within the *Pm*3*m* spatial group and a lattice constant $a = 3.89 \pm 0.02$ Å with the adjustment parameter *Chi*^{2}:1.99. The results are conclusive when considering that the sol–gel methodology used to obtain the LBMO compounds promotes a cubic structure, which is a result that is in agreement with reports in the literature [12–14].

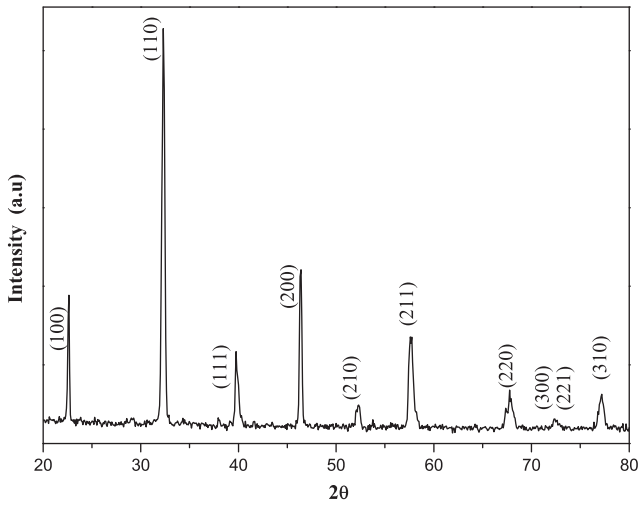

Fig. 1. Powder X-ray diffraction patterns at room temperature of $La_{0.7}Ba_{0.3}MnO_3$ polycrystalline obtained by sol–gel method.

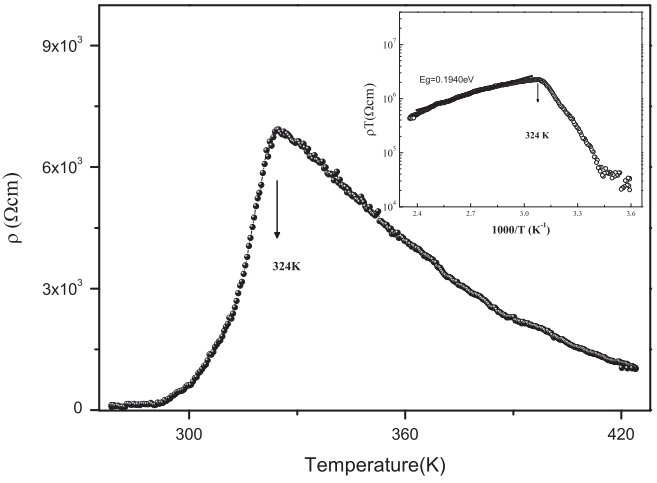

Fig. 2. Temperature dependence of the electrical resistivity of $La_{0.7}Ba_{0.3}MnO_3$ polycrystalline. Inset shows the activation energies for insulating region. Solid line is best-fit to Arrhenius model.

3.2. Resistivity vs. temperature

Fig. 2 shows the resistivity variation as a function of temperature for the $La_{0.7}Ba_{0.3}MnO_3$ compound, as measured by the four-point method. The results imply that the material exhibits a metal–insulator transition near a temperature of $T_{MI} = 330$ K. The relationship of σT with the inverse of temperature (inset in Fig. 2) suggests that for this material doping level, the conductivity is Arrhenius-type thermally activated, with activation energy regions of $E_g = 0.194$ eV for the insulated region. In many cases, this conduction process is related to the electron delocalization phenomenon that is present in this type of material (electron transfer between pairs of Mn^{3+} ($t_{2g}^3 e_g^1 : S = 2$) and Mn^{4+} ($t_{2g}^3 e_g^0 : S = 3/2$) via oxygen), which presumably involves a tendency to form small polarons in the material [14]. The energy values are associated with the presence of insulating phase.