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Effect of exceeding the concentration limit of solubility of silver in perovskites on the dielectric and electric properties of half doped lanthanum–calcium manganite

H. Rahmouni [a,*], B. Cherif [a], M. Smari [b], E. Dhahri [b], N. Moutia [a], K. Khirouni [a]

[a] Laboratoire de Physique des Matériaux et des Nanomatériaux appliquée à l'Environnement, Faculté des Sciences de Gabès, Université de Gabes, cité Erriadh, 6079 Gabès, Tunisia
[b] Laboratoire Physique Appliquée, Faculté des Sciences, Université de Sfax, B.P. 1171, Sfax 3000, Tunisia

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ABSTRACT

Dielectric and electric properties of $La_{0.5}Ca_{0.2}Ag_{0.3}MnO_3$ (LCMO–Ag) manganite have been investigated using admittance spectroscopy technique. AC conductivity analysis shows that the conductivity verifies the Jonscher universal power law. The deduced exponent 's' values prove that hopping model is the dominating mechanism in the material. From dc-electrical resistivity study, conduction process is found to be dominated by thermally activated small polaron hopping (SPH) mechanism. Complex impedance analysis (CIA) indicates the presence of relaxation phenomenon and allows to modelize the sample in terms of an electrical equivalent circuit. Also, impedance study confirms the contribution of grain boundary in the electrical properties. Dielectric studies indicate that the $La_{0.5}Ca_{0.2}Ag_{0.3}MnO_3$ compound has a Debye-like relaxation. The temperature dependence of permittivity is well fitted by the modified Curie–Weiss law. It is found that dielectric permittivity behavior and the estimated relaxation parameter value ($\gamma \approx 2$), support the evidence of the relaxor nature of $La_{0.5}Ca_{0.2}Ag_{0.3}MnO_3$ material. The high dielectric constant and the low loss tangent indicate the material is promising for tunable capacitor applications.

1. Introduction

Perovskite–manganite materials are present in several technological applications. Some industrial applications need a dielectric material which has a low dielectric loss and a high dielectric constant. Tunable capacitance is not only the motivation but also the obtained results in some compounds permit to estimate if these materials are promising for tunable capacitor applications [1]. $La_{1-x}Ca_xMnO_3$ (LCMO) perovskite manganites have been the subjects of intense research efforts [2–10]. LCMO and doped LCMO systems exhibit several transport and magnetic properties. These properties depend sensitively on the stoichiometry and the structure of the materials. The parent compound $LaMnO_3$ is doped by divalent alkaline earths (Ca, Sr, Ba, …). Several studies have been conducted in doping the Mn sites [11–19] which are the heart of the double exchange mechanism. To date, much of the physical characterization of these materials has been done through doping the La sites by only one kind of the dopant element. The physical properties of $La_{1-x}Ca_xMnO_3$ with different Ca concentrations are well studied [2,20]. Recently, $La_{0.5}Ca_{0.5}MnO_3$ manganite has been the focus of scientific interest [21–26]. There are only few reports on the study of transport properties of Ag doped LCMO [27–30]. Once structural, magnetic and optical properties of calcium–lanthanum manganite are investigated and explained, researchers are interested to the study of the effect of doping at Ca site by Sr and Ag elements on the physical properties of these manganites [21,22,31]. At our knowledge, the dielectric properties are not well investigated. In a recent works, more interest has been focused on investigating physical properties of $La_{0.5}Ca_{0.5}MnO_3$ [25,31,32] and magnetic/structural properties of silver-substituted $La_{0.5}Ca_{0.5}MnO_3$ compound [21,22]. The stability of such compounds is found to be improved by the addition of Ag element in LaCaMnO manganite [28]. Previous works have studied the effect of introducing several elements in LaCaMnO system such as Zn [33], Cu [34], Ni [35] and Zr [36]. It is found that all these elements deteriorated the quality of calcium doped lanthanum manganite. In contrary, when silver was added a better connectivity of grains was obtained [37]. But Tao, Pi and Manjusha et al. [38–40] studies show that the solubility of silver in perovskite does not exceed 20%. Consequently, we have prepared $La_{0.5}Ca_{0.5-x}Ag_xMnO_3$

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

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sample with $x=0.3$ in order to investigate the effect of exceeding the concentration limit of silver solubility in perovskites on the dielectric and electrical properties of LCMO system. In the present work, we investigate the dielectric and electrical properties of $La_{0.5}Ca_{0.2}Ag_{0.3}MnO_3$ manganite using impedance spectroscopy technique. Such technique can resolve the conduction components from polycrystalline electrical ceramics, particularly in differentiating the transport characteristics in grains and grain boundaries.

2. Experimental details

The powder of calcium dopant lanthanum manganite is prepared using the conventional solid state reaction method. The details of the preparation and thermal treatment are described in previous work [22]. The powder is sintered in the pellet of 10 mm of diameter and approximately 2 mm of thickness. On the both side of the pellet we deposit a thin aluminum film (200 nm thick) through a circular mask of 6 mm of diameter. The obtained aluminum disks are used to measure the electronic transport across the compound and the capacitance in a plate capacitor configuration. The sample is mounted in a cryostat which allows the variation of temperature from 77 to 700 K. An Agilent 4294A analyzer is used to measure the conductance and the capacitance. We took the measurements with parallel mode for the equivalent circuit and amplitude of 20 mV for signal. All measurements are conducted under vacuum and in dark.

Chemical properties of the sample are presented in a previous work [21,22]. The sample is stoichiometric in oxygen. Powder X-ray diffraction pattern of $La_{0.5}Ca_{0.2}Ag_{0.3}MnO_3$ sample has three phases: magnetic perovskite phase is the major phase, metal Ag and Mn_3O_4 are the minor phases. Such diffraction indicate that the sample is crystallized in a orthorhombic structure with Pnma space group, in which the La/Ca atoms are at 4c (x, 1/4, z) position, Mn at 4b (0, 0, 1/2), and O at 8d (x, y, z) position. The cell parameters are found to be $a\sim c=5.46$ Å and $b=7.71$ Å.

3. Results and discussion

3.1. AC-conductivity

The frequency dependence of ac-conductivity at various temperature for the LCMO–Ag sample is shown in Fig. 1a. At low frequency, the spectrum is characterized by the appearance of a plateau for each temperature. In this frequency region, the conductivity increases with increasing temperature. Such behavior indicates that electrical conductivity in the material is thermally activated process. At high frequency, the conductivity is governed by $\sigma\alpha\omega^s$ where 's' is a constant and ω is the angular frequency. From Fig. 1a, it is clear that ac-conductivity can be described by the Jonscher power law [41], $\sigma(\omega)=\sigma_{DC}+A\omega^s$ where σ_{DC} is the dc-conductivity and A is a pre-exponential factor. The frequency dependence of the conductivity is typical of hopping conductivity. Such conclusion is confirmed by the variation of the exponent 's' with temperature which is presented in Fig. 1b. It is found that $0\le s\le 1$ and 's' decreases with increasing temperature. These results prove the existence of hopping mechanism.

3.2. DC-electrical resistivity

The variation of the dc-electrical resistivity with temperature is shown in Fig. 2. It is found that resistivity decreases when increasing temperature. Hence, the investigated sample behaves as semiconducting material. The transition from metallic to semiconducting behavior is absent. As shown in the inset of Fig. 2 the plot of $\log(\rho/T)$ vs $1/T$ indicates that conduction process is dominated by the thermal activated SPH mechanism. The experimental results are well fitted by the Mott law [42]: $\rho=\rho_0 T\exp(-E_a/k_BT)$ where E_a is the activation energy and k_B is Boltzmann's constant.

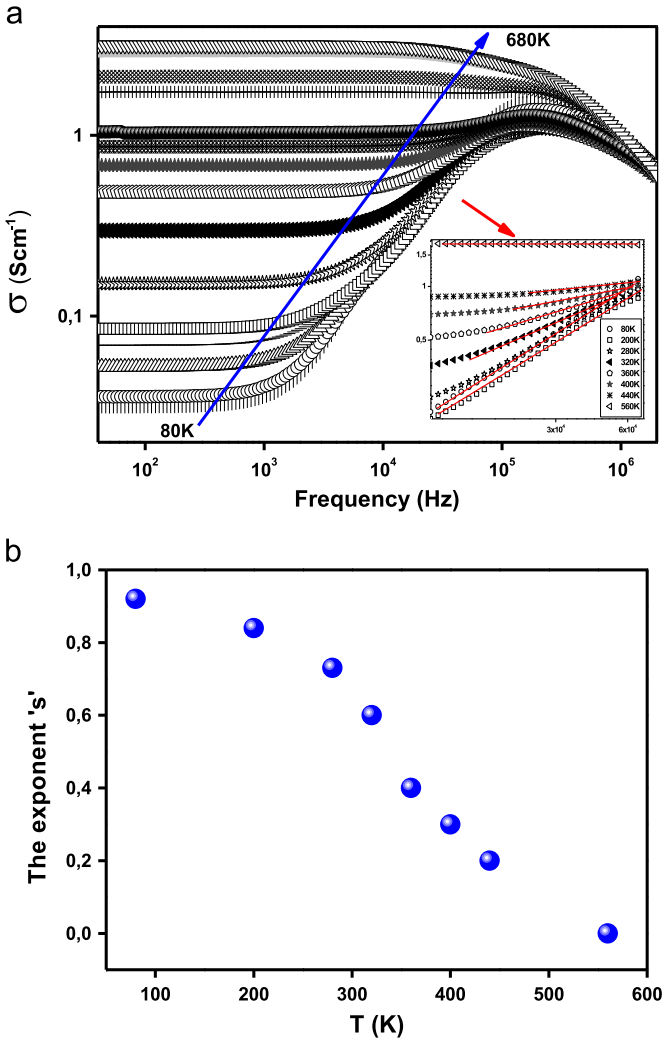

Fig. 1. (a) Plots of $\log(\sigma)$ vs $\log(\omega)$ for the LCMO–Ag manganite at different temperatures. (b) Temperature dependence of the frequency exponent 's'.

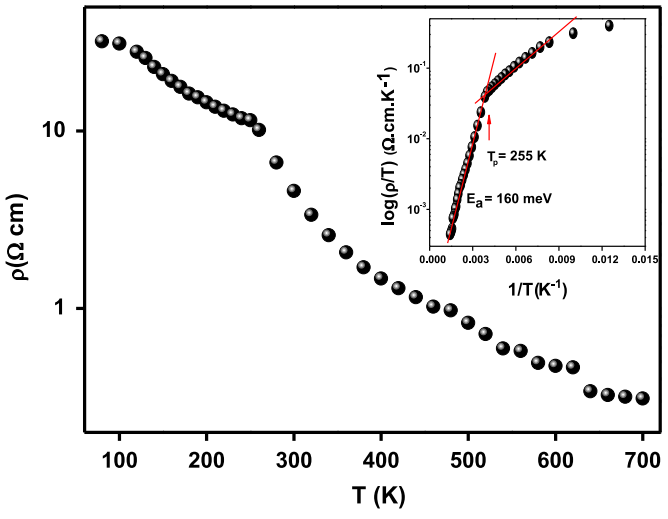

Fig. 2. Resistivity vs temperature for LCMO–Ag manganite. Inset shows the resistivity plotted against inverse temperature using SPH model.