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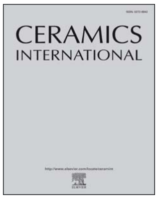

Large temperature coefficient of resistance at near room temperature in Sr-doped $La_{0.72}Ca_{0.28}MnO_3$:$Ag_{0.2}$ polycrystalline composites

Yule Li, Qingming Chen, Zhiyu Li, Xiang Liu, Hui Zhang*

Faculty of Materials Science and Engineering, Kunming University of Science and Technology, Kunming 650093, China

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ABSTRACT

A series of $La_{0.72}Ca_{0.28-x}Sr_xMnO_3$:$Ag_{0.2}$ ($x = 0.00$, 0.01, 0.03, 0.05, 0.07, and 0.10) composites was prepared by sol–gel method using methanol as solvent. Sample composition was analyzed by X-Ray diffraction, which revealed that all samples are pseudo-perovskite. Grain size and morphology were characterized by scanning electron microscopy. The results showed that all samples are of high density and large grain size in the range of 50–100 µm. All samples exhibited sharp metal–insulator (M-I) transitions, along with a drastic transition from paramagnetism to ferromagnetism. With increased Sr doping, radius of A-site ion increased, both Curie temperature T_C and M-I transition temperature shift to higher temperature increases, and transition width turns widener which makes a decreased temperature coefficient of resistance (TCR). Larger ionic radius of Sr^{2+}, which resulted in enhancement of double exchange, enlarges Mn–O–Mn bond angle, hence improves electrical and magnetic properties. It was found that TCR could reach 24.3% K^{-1} by Ag addition at near room temperature, which makes this composite promising potential applications in infrared detection and night vision.

1. Introduction

The research on the preparation, structure, and physical properties of strongly related materials is still one of the frontier areas of condensed matter physics and material physics. Among them, perovskite-type manganese oxide system has attracted significant attention and research interests because of its steep metal–insulator transition characteristics and fascinating magnetoresistance (MR) effect, which make it a strong correlating system in the related research. General formula of perovskite-type manganese oxide is $RE_{1-x}AE_xMnO_3$ (RE is trivalent rare earth ion, La^{3+}, Nd^{3+}, Sm^{3+}, Y^{3+}, etc; and AE is positive dibasic alkaline earth ion, Ba^{2+}, Ca^{2+}, Sr^{2+}, Pb^{2+}, etc.) [1–5]. When the doping amount x of the AE ions changes, the Mn^{3+} ions are converted into Mn^{4+} ions in order to balance the charge of the system, thus resulting in the mixed Mn^{3+}/Mn^{4+} system. Furthermore, the electrons are exchanged between Mn^{3+} and Mn^{4+}, and the phenomenon is called double exchange mechanism. It is generally believed that the double exchange mechanism is the cause of ferromagnetic (FM) coupling and metal conduction behavior. When the dopant elements and concentrations of dopant AE ions are altered, the resulting $RE_{1-x}AE_xMnO_3$ show different physical properties. On the other hand, the properties of the perovskite-type manganese oxide are not only related to the valence of Mn, that is the Mn^{3+}/Mn^{4+} ratio, but also to some chemical factors such as the average radius of the A-site cation, tolerance factor, ion mismatch, oxygen defects, and so on. The formulas for the average radius of the A-site cation $< r_A >$ and the tolerance factor f can be obtained from the literature reports as follows: $r_A = \Sigma x_i r_i$, where x_i is the mole percent of the cation at position A and r_i is the corresponding ionic radius; and $f = (r_A + r_O)/\sqrt{2}(r_{Mn} + r_O)$, where r_A represents the average ionic radius of the A-site cation, r_{Mn} represents the average ionic radius of the Mn ion, and r_O represents the average ionic radius of the oxygen ion [6–8]. Perovskite-type manganese oxides have unique magnetic and electrical properties, such as charge order, monomagnetic resistance effect, phase separation, and orbital order. Moreover, they act as potential candidates for the important basic theoretical research and technology, and have several potential applications, such as magnetic detection, infrared detection, and magnetic sensors [9].

$La_{1-x}Ca_xMnO_3$ (LCMO) and $La_{1-x}Sr_xMnO_3$ (LSMO) are giant materials with the giant magnetoresistive phase of the two materials. Their inherent physical mechanisms including Jahn–Teller effect, double exchange mechanism, hyper-exchange mechanism, and phase separation are relatively clear and well-understood. Jahn–Teller distortion supports insulator behavior, while the double exchange mechanism leads to metal behavior, thereby leading to metal–insulator phase change in LCMO. The resistance-temperature curve clearly reflects the existence of the maximum resistance, and the corresponding metal–insulator transition temperature (T_p). The value of the temperature coefficient of resistance (TCR) is an important indicator for the

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* Corresponding author.
E-mail address: harry_zhang71@163.com (H. Zhang).

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preparation of thermal radiation meters, and it is calculated by using 1/R (dR/dT) × 100%. Notably, the maximum MR and TCR of the doped perovskite-type manganese oxides occur near the temperature of the metal–insulator transition T_p and are accompanied by ferromagnetic (FM)–paramagnetic (PM) transitions [10–12]. It is well known that the transition temperature from the FM to PM state is the Curie temperature (T_c). The magnetic properties of perovskite-type manganese oxides, including T_c and saturation magnetization, strongly depend on doping; therefore, these typical materials are considered to be a good choice for magnetic refrigeration at various temperatures. The steepness of the metal–insulator transition determines the sensitivity and activity of these sensors. In fact, we hope that the perovskite-type manganese oxide has a higher TCR, MR, and magnetic entropy change near room temperature (about 300 K). LCMO system often has a high TCR; however, its T_p is relatively low. In contrast, the LSMO system exhibits a wide range of T_p from near-room temperature to 400 K; nonetheless, it has relatively small TCR attributed to wide metal–insulator phase transition range [13–15]. Therefore, preparation of materials both with T_p near room temperature and high TCR is the relentless pursuit of the scientific researchers.

Recently, a large number of experimental studies have shown that perovskite-type manganese oxide with added silver (Ag) can produce enhanced values of T_c, T_p, and MR [16–20]. Furthermore, it also results in the reduction in resistivity and improvement in the TCR value. Our previous research on $La_{1-x}Ca_xMnO3:Ag_{0.2}$ (x in the range of 0.25–0.33) indicated that $La_{0.72}Ca_{0.28}MnO_3:Ag_{0.2}$ exhibited a higher value of TCR, which even reached 78.8% K^{-1}. However, its T_p was only 256 K, which significantly limits its practical application. Therefore, with the objective of increasing the value of T_p and improving the magnetic properties, $La_{1-x}Ca_xMnO3:Ag_{0.2}$ was doped with strontium (Sr). In this study, a series of $La_{0.72}Ca_{0.28-x}Sr_xMnO_3:Ag_{0.2}$ ($0.00 \leq x \leq 0.10$) polycrystalline ceramics was prepared by the sol–gel method. Compared to the solid-phase method and coprecipitation method, the stoichiometry of the composite prepared by sol–gel method was more accurate, the chemical uniformity was better, the reproducibility of the experiment was found to be higher, and the experimental results were more accurate.

2. Experiments

A series of polycrystalline ceramic samples $La_{0.72}Ca_{0.28-x}Sr_xMnO_3:Ag_{0.2}$ (x = 0.00, 0.01, 0.03, 0.05, 0.07, and 0.10) was prepared by sol–gel technique, and 0.2 was the nominal theoretical molar ratio of Ag. First, stoichiometric amounts of $C_6H_8O_7{\cdot}H_2O$, $La(NO_3)_3{\cdot}nH_2O$, $Ca(NO_3)_2{\cdot}4H_2O$, $SrCl_2{\cdot}6H_2O$, and $Mn(NO_3)_2{\cdot}4H_2O$ were accurately weighed, placed in the beaker, and then a certain amount of methanol was added with continuous stirring. The molar ratio of metal atoms to citric acid was 1:2. When the contents were completely dissolved, ethylene glycol (~ 20 mL) was added and stirring was continued. Herein, citric acid was used as a chelating agent and ethylene glycol as a gelling agent. After stirring for about 10 min, the solution was placed in a magnetic water bath with the temperature maintained at 88 °C until an orange transparent gel was formed. The gel was then placed in the oven at 140 °C and a xerogel was obtained after 24 h. The xerogel was ground in an agate mortar for 30 min to obtain powdered sample. The powder was calcined at 500 °C for 8 h to obtain an LCMO phase. Next, a certain amount of LCMO and Ag powder were mixed, the mixture was milled for 30 min, and pressed into a cylindrical slice with diameter of 20 mm and height of 2.5 mm. Finally, the cylindrical sheet sample was sintered at 1475 °C for 12 h to obtain a bulk polycrystalline ceramic target.

The crystal structure of the polycrystalline ceramic samples was characterized by X-ray diffraction (XRD, CuKα radiation, $\lambda = 0.154056$ nm) at room temperature. The surface morphology and microstructure of the samples were characterized by scanning electron microscopy (SEM). The resistance-temperature relationship of the samples was measured by the standard four-probe method in the temperature range of 200–340 K. The magnetization-temperature profile of the sample was obtained using a superconducting quantum interference device as a magnetometer at a temperature range of 75–330 K under 100 Oe magnetic field conditions.

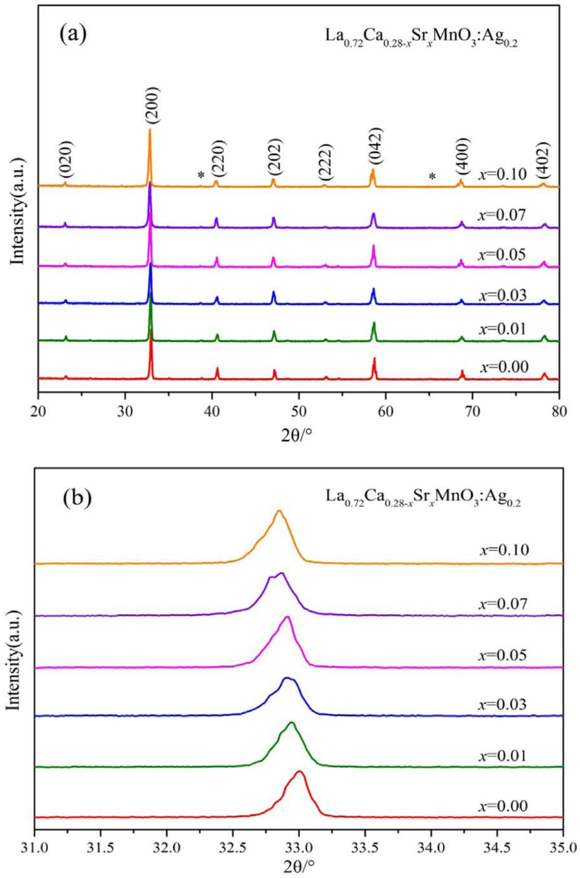

Fig. 1. (a) XRD patterns of $La_{0.72}Ca_{0.28-x}Sr_xMnO_3:Ag_{0.2}$ (x = 0.00, 0.01, 0.03, 0.05, 0.07, and 0.10) and (b) enlarged view of the strongest diffraction peak.

3. Results and discussions

3.1. Analysis of the X-ray diffraction patterns

Fig. 1(a) shows the XRD patterns of $La_{0.72}Ca_{0.28-x}Sr_xMnO_3:Ag_{0.2}$ (x = 0.00, 0.01, 0.03, 0.05, 0.07, and 0.10) polycrystalline ceramics. Clearly, all the samples exhibit pseudo-perovskite structure. Moreover, the diffraction peaks of the samples are sharp, indicating their good crystallinity. The samples exhibit the diffraction peaks of cubic structure of Ag (marked with an asterisk). The diffraction peak of Ag is very weak, indicating the participation of some of the Ag ions in the reaction occurring during the sintering process, which resulted in entering of the Ag ions in the A position; however, this reaction occurred to a limited extent. The melting point of Ag is 961.8 °C; however, the sintering temperature of this experiment was 1475 °C. Therefore, Ag was volatile in the sintering process, to the extent significantly below the theoretical stoichiometry, thus its peak intensity was very weak. Furthermore, the crystal structure did not change significantly due to the low doping amount of Sr. Fig. 1(b) shows an enlarged view of the strongest diffraction peak. Noteworthy, the strongest diffraction peak shifts to smaller angle with the increase in the amount of Sr doping. This is attributed to the replacement of Ca^{2+} having smaller ionic radius by Sr^{2+} with larger ionic radius, resulting in increase in the A-site cationic average radius, and larger interplanar spacing. The Prague equation $2d\sin\theta = n\lambda$ indicates that the interplanar spacing becomes larger and