



High-temperature metal–insulator transition in $Y_xCa_{1-x}MnO_3$ ($0.05 \leq x \leq 0.12$): An electron-spin resonance study



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ABSTRACT

Electron-spin resonance (ESR) studies have been performed on $Y_xCa_{1-x}MnO_3$ ($0.05 \leq x \leq 0.12$) compounds in the temperature range from 140 K to 470 K. It is found that with the temperature increasing, the ESR linewidth increases to the maximum at T_{max} ($=200$ K, 220 K, and 270 K for $x = 0.08, 0.10$, and 0.12 , respectively), and then decreases for all the compounds except that with $x = 0.05$ which shows a continuous decrease in the whole temperature range. For $x \geq 0.08$, the change of the ESR linewidth can be described very well by the adiabatic small polaron hopping model in the temperature range from 140 K to T_{max} . The ESR intensity decreases with temperature increasing for all the compounds between 140 K and 470 K except $300 \text{ K} \leq T \leq 330 \text{ K}$ in which it increases with temperature increasing. Meanwhile, the g -factor reaches the minimum at about $T = 300$ K. The characteristics of the ESR linewidth and intensity indicate the appearance of the short-range magnetic correlations and that the spin–lattice relaxation plays an important role for $x \geq 0.08$. In addition, the electronic transport properties of $Y_xCa_{1-x}MnO_3$ compounds reveal a metal–insulator transition at T_{MI} which varies from 254 K to 293 K with Y content increasing. The resistivity versus temperature between 140 K and T_{MI} can be fitted well by the adiabatic small polaron hopping model. It is suggested that the metal–insulator transition in $Y_xCa_{1-x}MnO_3$ compounds is correlated with the variation of the magnetism under high temperature.

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1. Introduction

Recently, the electron-doped perovskite manganite oxide, $RE_xCa_{1-x}MnO_3$ ($RE = \text{rare earth}$), as an n -type thermoelectric (TE) material with excellent performance, has attracted considerable interest due to its possible applications [1–5]. It has been confirmed that $RE_xCa_{1-x}MnO_3$ ($x \leq 0.12$) compounds are semiconductor at low temperature and exhibit a metal–insulator transition (MIT) at high temperature [6–8]. To increase the thermoelectric performance, materials should have high Seebeck coefficient S , low resistivity ρ and thermal conductivity κ [5]. Both the TE property and resistivity are related to the electron carrier behavior. Making clear the mechanism of the MIT in $RE_xCa_{1-x}MnO_3$ will be helpful for pursuing n -type TE performance materials with more advantage.

Up to date, some investigations have been done on the MIT mechanism. However, the results on the nature of the MIT are still in debate. Taguchi et al. [9] suggested that there may be four t_{2g} electrons in Mn^{3+} at a lower temperature and some t_{2g} electrons transfer to the e_g band at a higher temperature, which induces the MIT. However, Jorge et al. [8] argued that the MIT behavior

at T_{MI} (which defined as the temperature at which the slope is zero in the resistivity – temperature curve) is associated with the appearance of charge-order transition at low temperature, which contradicts to the results of Granado et al. [10]. Wang et al. [7] pointed out that the MIT of $RE_xCa_{1-x}MnO_3$ is induced by the spin-state changing of Mn^{3+} . In generally, with the variation of temperature, MIT can be induced by the transition of crystal structure or the magnetic interactions around T_{MI} . For the $RE_xCa_{1-x}MnO_3$ ($x < 0.5$) compounds, however, many authors have pointed out that there is not any detectable structure phase transition at around T_{MI} [6,9]. The mechanism of MIT is probably related to the change of magnetic interaction. Magnetic and electronic correlations are revealed theoretically in computation models [11]. It is worth noting that by resistivity studies, Lakshmi et al. reported that all the polycrystalline $Nd_{1-x}Na_xMnO_3$ ($0.05 \leq x \leq 0.25$) compounds exhibit insulating behavior down to 5 K and an appearance of MIT under 4T applied magnetic field for $x \geq 0.15$ [12]. Ahmed et al. found that the temperature dependent resistivity data of Zn doped $La_{0.67}Sr_{0.33}MnO_3$ compounds are fitted by the small polaron hopping model [13]. Besides, it is found that Sm doped $CaMnO_3$ compounds sintered at $T_s = 1473$ K show a marked MIT in the temperature range of 300–900 K [14], which is attributed to the charge-ordering, i.e., the ordering of the Mn^{3+} and Mn^{4+} species over the manganese lattice. Recently, Ramirez et al. [15] have

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studied the nature of short-range order in the paramagnetic phase of the Ca-doped LaMnO₃ compounds and revealed that the ferromagnetic-like interaction between Mn ions cannot be explained by the conventional double exchange mechanism. The e_g electrons are localized in Mn³⁺ ions regardless the introduction of holes leading to ferromagnetic/antiferromagnetic superexchange-like interactions.

Electron-spin resonance (ESR) is a useful technique to study static and dynamic magnetic correlations on a microscopic level and can provide helpful information about the complex magnetic state in doped manganese perovskite [16–18]. In this paper, the ESR was employed to investigate the magnetic properties of the electron-doped Y_xCa_{1-x}MnO₃ in which Y³⁺ is an ideal non-magnetic ion of rare earth. It is found that the magnetization at high temperature is larger than that at low temperature, which is different from the result reported by Wang et al. [7]. The characteristics of ESR and electronic transport indicate that the MIT of Y_xCa_{1-x}MnO₃ is correlated with the variation of the magnetism under high temperature.

2. Experimental procedures

Y_xCa_{1-x}MnO₃ ($x = 0.05, 0.08, 0.10$ and 0.12) polycrystalline compounds were prepared by a standard solid-state reaction method [19]. A stoichiometric amount of reagent-grade Y₂O₃, CaCO₃, and MnO₂ powders were mixed and well ground. The powder was heated at 900 °C and 1100 °C for 24 h in air with intermediate grinding. Then, the resulting powder was calcined at 1300 °C for 24 h in air with intermediate grinding, and then pressed into disk-shaped pellets and sintered at 1300 °C for 24 h in air. The resulting compounds were cooled down to 600 °C at 1 °C min⁻¹, and then cooled down to room temperature in the furnace.

X-ray diffraction (XRD) measurements were carried out by a Rigaku TTR III X-ray diffractometer with Cu K α ($\lambda = 1.54187\text{\AA}$) radiation at room temperature. The scanning range and step are $20^\circ \leq 2\theta \leq 80^\circ$ and 0.02° in 2θ , respectively. The resistance was measured by a standard dc four-probe method between 140 K and 310 K. The Scanning Electron Microscopy (SEM) measurements were carried out by FEI Sirion200 Scanning Electron Microscopy at room temperature. The ESR measurements were performed with a Bruker JES-FA200 spectrometer at the X band (9.06 GHz) between 140 K and 470 K. The ESR line intensity, $I(T)$, was obtained by the double integration of the experimental derivative absorption curve.

3. Results and discussion

XRD patterns of the polycrystalline Y_xCa_{1-x}MnO₃ ($x = 0.05, 0.08, 0.10$ and 0.12) compounds at room temperature are shown in Fig. 1. Based on the previously reported results [20,21], all the XRD peaks can be indexed with the orthorhombic *Pnma* symmetry, which reveal that all the compounds are single phase without a

detectable secondary phase within the limit of X-ray detection, which is typically 1%. It can be found that the XRD peaks obviously shift to lower angle (2θ) with increasing Y³⁺ content, as shown in the inset of Fig. 1, indicating the enlargement of the unit cell. It is notable that the substitution of Y³⁺ ions for Ca²⁺ ions can result in an equal content of Mn³⁺ ions to that of Y³⁺ content at the Mn⁴⁺ matrix for the equilibrium of the valence. The ionic radii of Mn⁴⁺, Mn³⁺, Ca²⁺, and Y³⁺ are 0.53, 0.645, 1.18, and 1.075 Å, respectively [22]. As a result, the increase of the mean ionic radius of the Mn-site will be bigger than the decrease of that at Ca-site. The lattice parameters of the unit cell increase when partial Ca²⁺ ions are replaced by Y³⁺ ions. Fig. 2 shows the SEM images of the Y_xCa_{1-x}MnO₃ compounds with different content x , which reveal that the morphologies of all the compounds are similar and the average grain size is about 5 μm . Both the XRD patterns and the SEM images confirm that the crystalline of the compounds is in high quality. Further studies by Raman and Infra-red spectra (not shown here) reveal that there is no evident crystallographic variation around the MIT, which is consistent with Refs. [6–8].

Temperature dependent resistivities of Y_xCa_{1-x}MnO₃ are shown in Fig. 3, which show that all the compounds are semiconductor at low temperature and exhibit a metal–insulator transition at high temperature T_{MI} . The T_{MI} of Y_xCa_{1-x}MnO₃ is 254 K, 263 K, 291 K, and 293 K for $x = 0.05, 0.08, 0.10$, and 0.12 , respectively. The adiabatic small polaron hopping model has been confirmed to be a suitable one to understand the electronic transport characteristics of doped perovskite manganites [1,23,24]. In the model the relationship between the resistivity and temperature T can be expressed as:

$$\rho = \rho_0 T \exp(E_a/k_B T) \quad (1)$$

which can be rewritten as:

$$\ln(\rho/T) = A_0 + \frac{E_a}{1000 \cdot k_B} \cdot \frac{1000}{T} \quad (2)$$

where ρ is the resistivity, ρ_0 and A_0 are constants, k_B is the Boltzmann constant, E_a is the activation energy. The $\ln(\rho/T) - 1000/T$ curves between 140 K and T_{MI} are shown in Fig. 3i–b ($i = A, B, C, D$), from which it can be found that the electronic transport properties of Y_xCa_{1-x}MnO₃ compounds can be well described by the adiabatic small polaron hopping model and the E_a obtained is 23.7 meV, 24.5 meV, 26.4 meV, and 28.4 meV for $x = 0.05, 0.08, 0.10$, and 0.12 , respectively. However, it can be found that the temperature dependent resistivities at high temperature ($T > T_{\text{MI}}$) show a different trend, or a metal-like property.

The temperature dependence of the ESR linewidth of Y_xCa_{1-x}MnO₃ is shown in Fig. 4, from which it can be found that the linewidth increases to a maximum at T_{max} and then decreases lightly with temperature increasing for all the compounds except $x = 0.05$ for the measured temperature range. The T_{max} is 200 K, 220 K, 270 K for $x = 0.08, 0.10$, and 0.12 , respectively. The linewidth trend above T_{max} of $x \geq 0.08$ is similar to that of $x = 0.05$, which decreases with temperature increasing between 140 K and 470 K, and coincides with the linewidth trend for La_{0.05}Ca_{0.95}MnO₃ [10].

Granado et al. pointed out that there are short range magnetic correlations in RE_xCa_{1-x}MnO₃ which play an important role in the magnetic behavior of RE_xCa_{1-x}MnO₃ [10]. From this point of view, the short range magnetic correlations may present in the Y_xCa_{1-x}MnO₃ compounds and play an important role in the magnetic properties for $x = 0.05$ from 140 K to 470 K and for $x \geq 0.08$ from T_{max} to 470 K. On the other hand, the ESR linewidth broadening in the range $140 \text{ K} \leq T \leq T_{\text{max}}$ for $x \geq 0.08$, which is similar with the results reported previously [16,25], may reveal the existence of the bottleneck effect [26,27] which can be described as following: in the mixed valence compounds, such as Y_xCa_{1-x}MnO₃ with Mn⁴⁺ and Mn³⁺ ions, there is a strong ferromagnetic (FM)

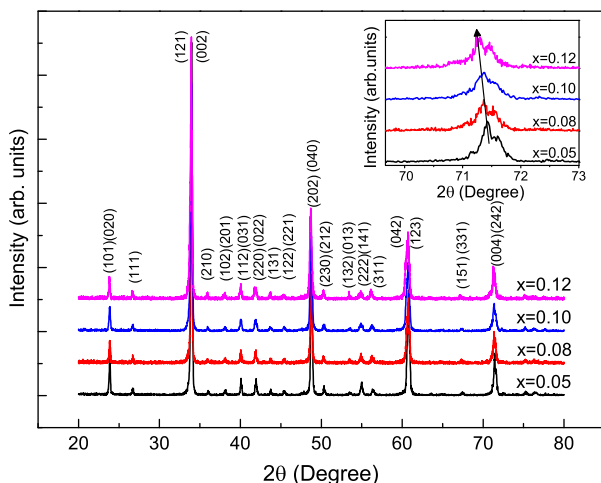


Fig. 1. XRD patterns of Y_xCa_{1-x}MnO₃ ($x = 0.05, 0.08, 0.10, 0.12$) at room temperature. Inset: the enlarged view of (242) and (004) peaks.

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