

The infrared absorption spectra in perovskite manganite $\text{La}_{0.27}\text{Pr}_{0.4}\text{Ca}_{0.33}\text{MnO}_3$

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Abstract

The polycrystalline compound of perovskite manganite $\text{La}_{0.27}\text{Pr}_{0.4}\text{Ca}_{0.33}\text{MnO}_3$ was prepared by the standard solid-state reaction method. The magnetic moment vs temperature was measured in the field $H = 0.2\text{T}$ to obtain T_C . The result indicates that the ferromagnetic–paramagnetic (FM–PM) transitions occur near 115 K and a peak due to the charge ordering (CO) near 210 K appears in the sample. Infrared absorption spectra of the sample were measured by a Fourier transform infrared spectrophotometer with the wave numbers between 400 and 4400 cm^{-1} in the temperature interval from 20 to 300 K. The infrared absorption intensity, which related with the effective carrier numbers obtained from the optical conductivity, decreased with increasing temperature. From the integration of the absorption intensity, it can be seen that the effective carrier numbers also decrease with increasing temperature, which can be attributed to the localization of the polarons. The absorption peak of stretching mode, rising from the vibration of Mn–O bond, was also observed clearly in the sample.

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1. Introduction

The intense interest in the properties of doped LaMnO_3 (ABO_3 -type) perovskites, was prompted by the observation of colossal magnetoresistance (CMR) and other intricate physical properties [1,2]. The competition, between different crystal phases structure in manganites with CMR effect, can be strong enough to cause phase separation (metallic ferromagnetic and insulating charge-modulated states). Charge carrier doping in antiferromagnetic (AFM) insulators has revealed extraordinary phenomena such as high-temperature superconductivity, electronic phase separation, and charge ordering [3].

In $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$, the CMR effect has occurred for $0.2 < x < 0.5$ [4,5]. Especially with the $x = 0.33$, the CMR effect is optimized. The prototypical (La, Pr, Ca) MnO_3 system, according to the report by Uehara [6], is electronically phase separated into a sub-micrometer-scale mix-

ture of charge-ordering insulating domains and metallic ferromagnetic domains. It is obvious that the coexistence of largely scaled domains will influence the macroscopic properties of the compound [7]. Considering the fact that MnO_6 octahedra distortion, which exciting the infrared absorption due to the vibration of Mn–O bond, will occur in different phases and that the infrared spectrum is rather sensitive to local lattice distortions, we expect to probe this information of the manganite by infrared analysis.

2. Experimental

Polycrystalline sample of $\text{La}_{0.27}\text{Pr}_{0.4}\text{Ca}_{0.33}\text{MnO}_3$ was synthesized by a standard solid-state reaction. A well-mixed stoichiometric mixture of La_2O_3 , Pr_6O_{11} , CaCO_3 and MnCO_3 was calcined at 900 °C in air for 12 h. The product thus obtained was reground and calcined at 1200 °C for 24 h, then pelletized and sintered at 1300 °C for 48 h, then furnace cooled to room temperature. X-ray diffraction reveals that the sample is of single phase with an

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orthorhombic distorted perovskite structure (space group Pbnm).

The magnetization was measured with the field of 0.2 T (Fig. 1). The result indicates that the ferromagnetic–paramagnetic (FM–PM) transition occurs near 115 K and a peak near 210 K due to the charge ordering (CO), which has been observed in many perovskite manganites, also appears in the compound (inset in Fig. 1). The peak at ~ 40 K, according to the Ref. [7], originates from long-range antiferromagnetic order of the CE type.

The infrared absorption spectra were collected by a Fourier transform spectrophotometer with the wave numbers between 400 and 4400 cm^{-1} in the temperature interval from 20 to 300 K (Fig. 2). The compound was fine milled and diluted by KBr and then pressed into thin pellet. It is defined as $O_d(\omega) = -\log(I_S/I_{\text{KBr}})$ [1], which is proportion to the optical conductivity, where I_S and I_{KBr} are the transmitted infrared intensities of the KBr pellet with and without the compound, respectively.

3. Results and discussion

Fig. 2 shows the infrared absorption spectra of compound. When the temperature is below T_c , three absorption peaks clearly appear near ~ 530 , ~ 590 and $\sim 620\text{ cm}^{-1}$. The intensity of the peak at 530 and 620 cm^{-1} is weakened gradually across T_c and the peak at 590 cm^{-1} develops with increasing temperature. According to Kim et al. [3], the two peaks with the higher frequency correspond to Mn–O bond stretching mode, and each peak corresponds to two different bond lengths due to the Jahn–Teller distortion. The absorption peak at 530 cm^{-1} , considering to the investigation we have done on the other perovskite manganites elsewhere, may be the reflection of the electrical property. But the nature of this absorption peak should be investigated in depth.

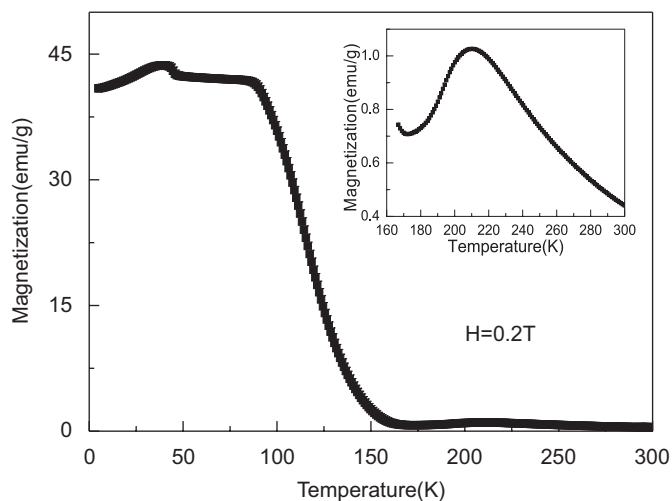


Fig. 1. Magnetization of $\text{La}_{0.27}\text{Pr}_{0.4}\text{Ca}_{0.33}\text{MnO}_3$ measured in the field of 0.2 T after zero field cooling (ZFC). The inset is the enlargement of the part of M – T curve at high temperature.

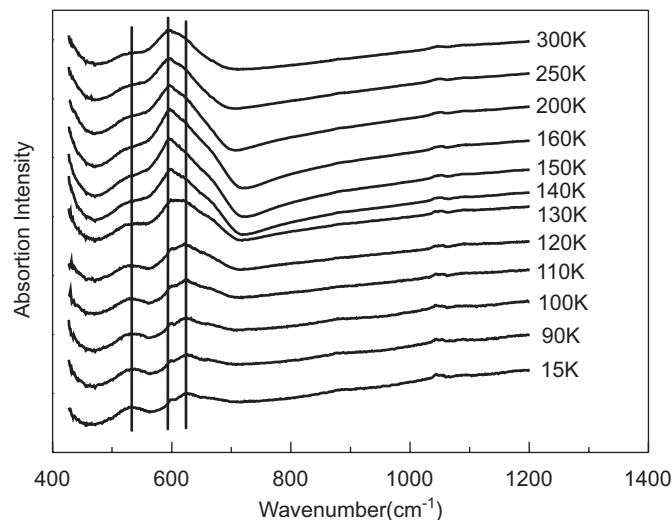


Fig. 2. Infrared absorption of the sample collected in different temperature.

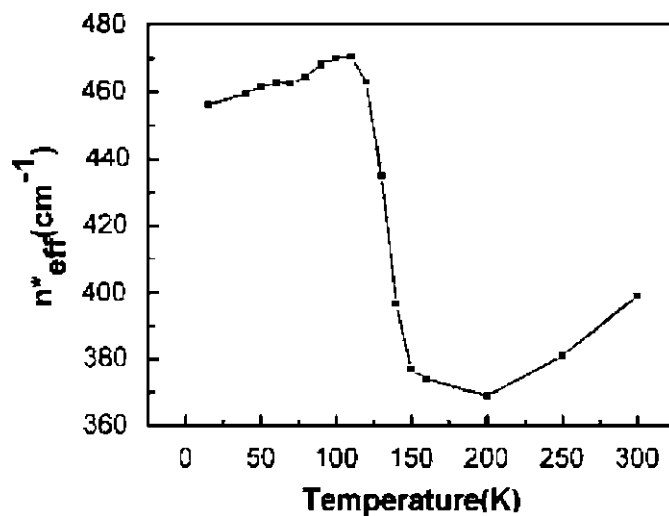


Fig. 3. The variety of effective carrier numbers as a function of temperature.

To discuss the effective carrier numbers, we introduce n^* in proportion to n (the effective carrier numbers obtained from the optical conductivity), so it is valid to qualitatively represent that $n^* = \int O_d(\omega) d\omega$ [8]. The integration range is from 420 to 1200 cm^{-1} and the result is shown in Fig. 3. The effective carrier numbers decreases dramatically as the temperature approaches T_c . This result is consistent with the rapid increase of resistivity of LCMO near the Curie temperature as observed by Hwang et al. [2] in Pr-doped $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$.

In summary, the compound of $\text{La}_{0.27}\text{Pr}_{0.4}\text{Ca}_{0.33}\text{MnO}_3$ undergoes a ferromagnetic transition at T_c and the charge ordering (CO) near 210 K. The effective carrier numbers decreased with increasing temperature, which can be attributed to the localization of the polarons. The absorption peak of stretching mode, rising from the vibration of Mn–O bond near 590 and 620 cm^{-1} , arising from the Jahn–Teller distortion, has also been observed

clearly in the sample. And the origin of the peak near 530 cm^{-1} should be investigated in the future.

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