

# Electrical and Magnetic Transport Properties of $\text{Pr}_{0.1}\text{Ca}_{0.9}\text{MnO}_3$

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**Abstract.** Ceramic  $\text{Pr}_{1-x}\text{Ca}_x\text{MnO}_3$  ( $x = 0.1$ ) samples were prepared by solid-state reaction and the electrical and magnetic transport properties were studied by direct current (DC) and alternating current (AC) methods in different fields. A Curie temperature of 125 K determined by I-V measurements of ceramic  $\text{Pr}_{1-x}\text{Ca}_x\text{MnO}_3$  ( $x = 0.1$ ) samples is consistent with that from vibrating - sample magnetometer (VSM) measurements. Fitting by Arrhenius law, the barrier height of grain boundary is 145 meV which is well coincident with that from fitting the R-T data. The Cole-Cole semicircles and temperature spectrum of impedance in different electrical and magnetic fields show that there is neither notable ER and MR effects above the Curie temperature of  $\text{Pr}_{0.9}\text{Ca}_{0.1}\text{MnO}_3$ .

## Introduction

Rare-earth doped manganites have attracted extensive efforts for exotic physical features and potential application in spin electronics since colossal magneto resistance (CMR) effect was found in manganese oxides [1-5].  $\text{PrMnO}_3$  is an anti-ferromagnetic insulator with a type-A magnetic structure and has a distorted orthorhombic perovskite structure at room temperature.  $\text{Pr}_{1-x}\text{Ca}_x\text{MnO}_3$  shows relatively complicated magnetic and electrical properties for producing hole-type carriers when trivalent  $\text{Pr}^{3+}$  is substituted by divalent  $\text{Ca}^{2+}$  ion. For example, with increasing  $x$  up to  $x = 0.3$ , a phase transition from insulator to metal with a colossal electroresistance (CER) effect [6] can be induced by a strong electric field ( $> 1000$  V) in  $\text{Pr}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$  single crystal. On the base of electroresistance effect (ER), electrical pulse induced resistance (EPIR) effect was first reported by S.Q. Liu et. al. in the sandwich structure of  $\text{Pt}/\text{Pr}_{0.7}\text{Ca}_{0.3}\text{MnO}_3/\text{Pt}$  at room temperature [7]. After the detailed research on EPIR effect by Sawa et al.,  $\text{Pr}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$  was considered as a potential material for non-volatile resistive random access memory (ReRAM) [8]. In our previous work, we systematically studied the magnetic and electrical properties of  $\text{Pr}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$  ( $x = 0.3$ ) samples, and pointed out that both CER and CMR effect exist in  $\text{Pr}_{0.3}\text{Ca}_{0.3}\text{MnO}_3$  for the magnetically related Schottky barrier at grain boundary [9].

In addition, manganites are also good additives for ZnO varistor ceramic. Kutty found that varistors prepared from ZnO with  $\text{La}_{0.6}\text{Sr}_{0.4}\text{MnO}_3$  as the forming additive exhibited higher nonlinearity coefficient [10]. Yang found that ZnO ceramic varistors with doping of  $\text{La}_{0.3}\text{Sr}_{0.7}\text{MnO}_3$  improved their stability against DC accelerated aging stress [11]. Recently, Kutty found ZnO ceramic varistors doped by  $\text{CaMnO}_3$  exhibited voltage-limiting current-voltage characteristics with nonlinearity coefficient  $\alpha$  up to 380 at low voltages of 1.8-12V/mm[12]. Because  $\text{Pr}_{1-x}\text{Ca}_x\text{MnO}_3$  ( $x=1$ ) is a ferromagnetic insulator like  $\text{CaMnO}_3$ , there may be some interesting results on electrical properties of ZnO ceramic on the effect of  $\text{Pr}_{0.9}\text{Ca}_{0.1}\text{MnO}_3$  addition.

In this work,  $\text{Pr}_{1-x}\text{Ca}_x\text{MnO}_3$  ( $x = 0.1$ ) ceramic samples were fabricated and studied. The result shows that both MR and ER effects are strongly dependent on the Curie temperature, so the two

effects only can be induced below Currier temperature. On the contrary, there is no MR and ER effect above Currier temperature for  $\text{Pr}_{0.9}\text{Ca}_{0.1}\text{MnO}_3$ . Therefore, very different from  $\text{Pr}_{0.9}\text{Ca}_{0.1}\text{MnO}_3$  and  $\text{Pr}_{0.8}\text{Ca}_{0.2}\text{MnO}_3$ [13],  $\text{Pr}_{0.9}\text{Ca}_{0.1}\text{MnO}_3$  is an ferromagnetic insulator at room temperature.

## Materials and Methods

Polycrystalline ceramic sample of  $\text{Pr}_{1-x}\text{Ca}_x\text{MnO}_3$  was fabricated by the conventional solid-state reaction method.  $\text{Pr}_6\text{O}_{11}$ ,  $\text{CaCO}_3$  and  $\text{MnO}_2$  were weighted according to the stoichiometric ratio after the raw material  $\text{Pr}_6\text{O}_{11}$  and  $\text{CaCO}_3$  were baked at  $900^\circ\text{C}$  and  $380^\circ\text{C}$  for 4 hours, respectively. Then, the powder was mixed sufficiently, grinded, and sintered at  $1000^\circ\text{C}$  for decarburization. After that, the powder was grinded again and sintered at high temperature  $1350^\circ\text{C}$  in furnace for 12 hours before cooled down. Afterwards, the burned powder was grinded thirdly, pressed into slice shape, sintered at  $1350^\circ\text{C}$  again for 12 hours, and then cooled down to room temperature to obtain  $\text{Pr}_{1-x}\text{Ca}_x\text{MnO}_3$  samples finally. The burning silver method was used to manufacture the electrodes in order to eliminate the contact resistance between the electrodes and the sample's surface. The magnetic and electronic measurement systems include Keithley 2400 and Wayne Kerr 6420 impedance analyzer for measuring R-T and I-V curves.

## Results and Discussion

There are two ways of two-wire and four-wire method to measure I-V characteristic curves. Resistance measured by the two-wire method usually consists of the resistances from electrode contacts and bulk of sample. However, the resistance measured by the four-wire method can exclude the contact's resistance and only includes that from the bulk of sample [9]. R-T curves are shown in Fig.1 by both measuring methods to see if there is contacting resistance between silver electrode and the surface of  $\text{Pr}_{0.9}\text{Ca}_{0.1}\text{MnO}_3$ . From Fig.1 we can see that the resistances and R-T curves are almost identical in the whole range of temperature, which indicates that the contacting resistance is very small and there is ohmic contact between Ag electrode and  $\text{Pr}_{0.9}\text{Ca}_{0.1}\text{MnO}_3$  sample.

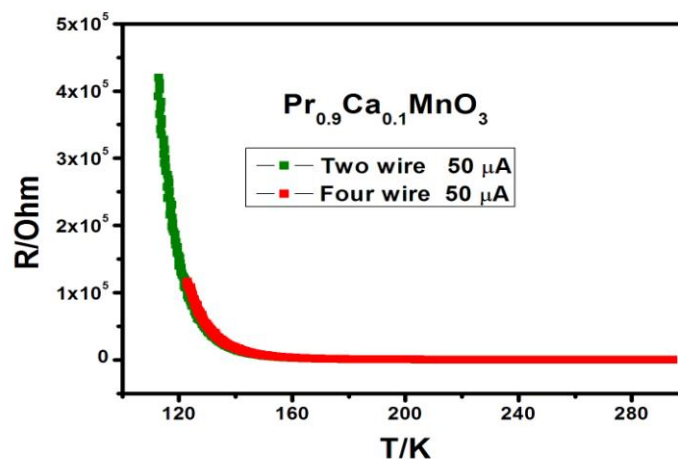


Fig.1 R – T curves for serial  $\text{Pr}_{0.9}\text{Ca}_{0.1}\text{MnO}_3$  samples within a temperature range

Fig.2 illustrates I-V characteristics of the  $\text{Pr}_{0.9}\text{Ca}_{0.1}\text{MnO}_3$  sample measured by four-wire method in different magnetic fields and temperatures. Since ohmic contact exists between Ag electrode and the sample's surface, the I-V characteristic only reflects electrical properties from the ceramic sample. As shown in Fig.2, we can see that the I-V curves separate for with and without magnetic field when temperature is below 125 K. Furthermore, the discrepancy becomes more remarkable with decreasing temperatures, indicating that there is correlation between resistance and magnetic field at

low temperatures. However, we can see from figure 2 that the difference becomes less and even to disappear with increasing temperatures at 125 K for I-V curves of with and without magnetic field. It indicates that 125 K may be the Currie temperature for  $\text{Pr}_{0.9}\text{Ca}_{0.1}\text{MnO}_3$ , which actually coincides with the result measured directly by vibrating sample magnetometer (VSM). In Fig.3, the M - T curve clearly shows that the magnetic phase transition point is about 121 K for  $\text{Pr}_{0.9}\text{Ca}_{0.1}\text{MnO}_3$ , nearly matching with the result in Fig.2 by electrical measuring.

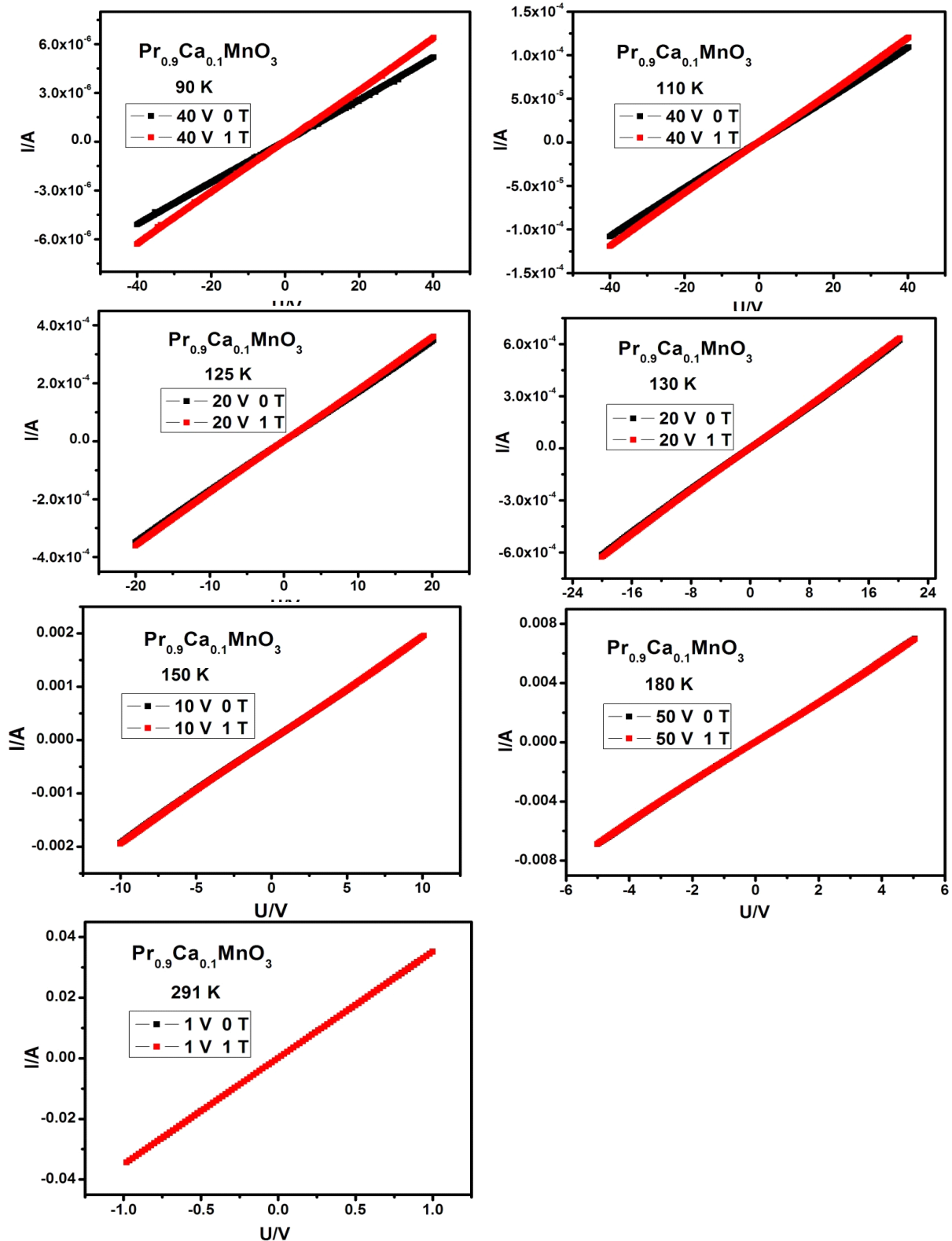


Fig.2 I-V characteristic curves of  $\text{Pr}_{0.9}\text{Ca}_{0.1}\text{MnO}_3$  in 0 or 1 T magnetic field at different temperatures

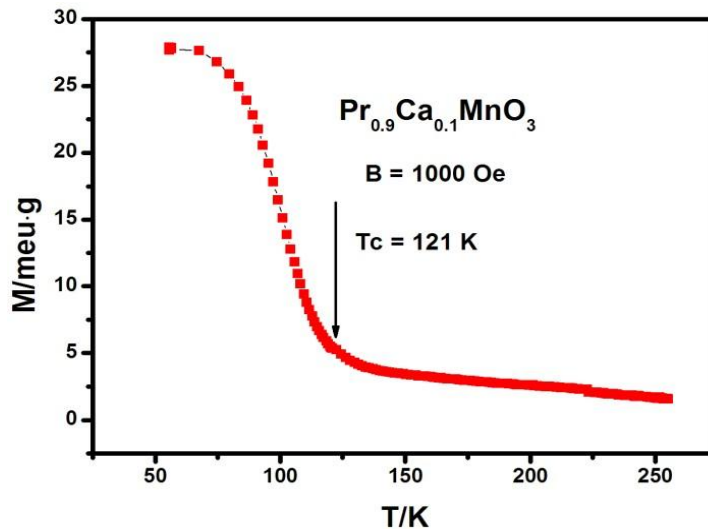


Fig.3 M-T curve of Pr<sub>0.9</sub>Ca<sub>0.1</sub>MnO<sub>3</sub> from 50K to 250K

In this case of ohmic Ag contacting, the resistance of Pr<sub>1-x</sub>Ca<sub>x</sub>MnO<sub>3</sub> ceramics actually consists of resistances from grain and the grain boundary, which the capacitance, resistance of grain boundary are normally several orders greater than that of grain [10]. Generally, it is AC but not DC method can distinguish the contributions from grain and grain boundary. Fig.4 shows Cole-Cole semicircles for Pr<sub>0.9</sub>Ca<sub>0.1</sub>MnO<sub>3</sub> with and without magnetic field at different temperatures. The semicircles in figures have two intersection points with the horizontal axis, actually reflecting the real part of the impedance, which the small resistance in higher frequency region at left intersection, around ten ohms here, is the contribution from the grain while the huge one at right intersection with lower frequency is the component from grain boundary since it is much larger in resistance and capacitance [10]. From the Cole-Cole features of figure 4 (a) and (b), we can see that the resistance component at right decreases rapidly with increasing temperatures while the left intersecting point keeps almost the same with changing temperatures, indicating that the right part at lower frequency corresponds to the contribution from grain boundary and the grain boundary's resistance reduces quickly with raising temperatures. Besides, the influence of electrical and magnetic field on the resistance, especially on the grain boundary's component is also shown in figure 4 (c), (d) and (e) for Pr<sub>0.9</sub>Ca<sub>0.1</sub>MnO<sub>3</sub> at different temperatures. We can see that there is neither clear ER nor MR effect in Pr<sub>0.9</sub>Ca<sub>0.1</sub>MnO<sub>3</sub> when temperature is more than 120 K. However, certain ER and MR become to appear when the temperature goes down less than the Curie temperature of around 125 K even though the effects are not notable as that in Pr<sub>0.7</sub>Ca<sub>0.3</sub>MnO<sub>3</sub>. It is perhaps because that Pr<sub>0.9</sub>Ca<sub>0.1</sub>MnO<sub>3</sub> is a ferromagnetic insulator with few carriers and is incapable of producing a semiconducting grain boundary or space charge layer due to the too lower concentration of carrier. Therefore, the ER and MR are not so remarkable for Pr<sub>0.9</sub>Ca<sub>0.1</sub>MnO<sub>3</sub>. On the contrast, Pr<sub>0.7</sub>Ca<sub>0.3</sub>MnO<sub>3</sub> possesses more carriers to result in complicated magneto-electric behaviors and obvious CER and CMR effects due to increasing Ca<sup>2+</sup> constitutions [8]. In addition to the Cole-Cole figures, the ER and MR of Pr<sub>0.9</sub>Ca<sub>0.1</sub>MnO<sub>3</sub> also can be illustrated in figure 5, the temperature spectrum of impedance at different electrical and magnetic fields. Form figure 5 (a) and (b), we can see that the impedance curves are almost overlapped for different measuring electrical fields of 0.5 and 2 V, and different magnetic fields of 0 and 1 T. It implies that there is no notable ER and MR effects in Pr<sub>0.9</sub>Ca<sub>0.1</sub>MnO<sub>3</sub>, which is consistent with the result of Cole-Cole data in figure 4 (c) – (e).

For the transport features of Pr<sub>0.9</sub>Ca<sub>0.1</sub>MnO<sub>3</sub>, the grain boundary components play a crucial role owing to the Schottky barrier for the space charge layer at the interface between grains. The higher is the height of Schottky barrier, the larger resistance of grain boundary is. The barrier's height can be obtained from the temperature spectrum of real part of impedance for Pr<sub>0.9</sub>Ca<sub>0.1</sub>MnO<sub>3</sub>. Fig.6 shows the

temperature spectrum of impedance at different frequencies from 1 kHz to 3 MHz for  $\text{Pr}_{0.9}\text{Ca}_{0.1}\text{MnO}_3$ . We can see from figure 6 (a) to (c) that an impedance peak exists at the temperature spectrum for certain measuring frequency, in which the peak moves towards the higher temperature with increasing the measuring frequency, indicating the nature of activation energy.

Where  $R$  and  $R_0$  are respectively the resistance at temperature  $T$  K and 0 K;  $\phi$  the Schottky barrier,  $T$  temperature,  $K_B$  the Boltzmann constant,  $\omega$  and  $\omega_0$  are respectively the frequency of the largest dielectric loss and the intrinsic frequency of sample. Figure 7 (a) and (b) give the experimental data and fitting curves using *Arrhenius* law (1) and (2), respectively. A barrier height of 145 meV is obtained by fitting the experimental resistance data in figure 6 (a). It is very consistent with the value of 152 meV by fitting the frequency data and the value of 156 meV by fitting the DC  $R$ - $T$  data in figure 8, which means that the barrier height is around 150 meV for the grain boundary of  $\text{Pr}_{0.9}\text{Ca}_{0.1}\text{MnO}_3$ .

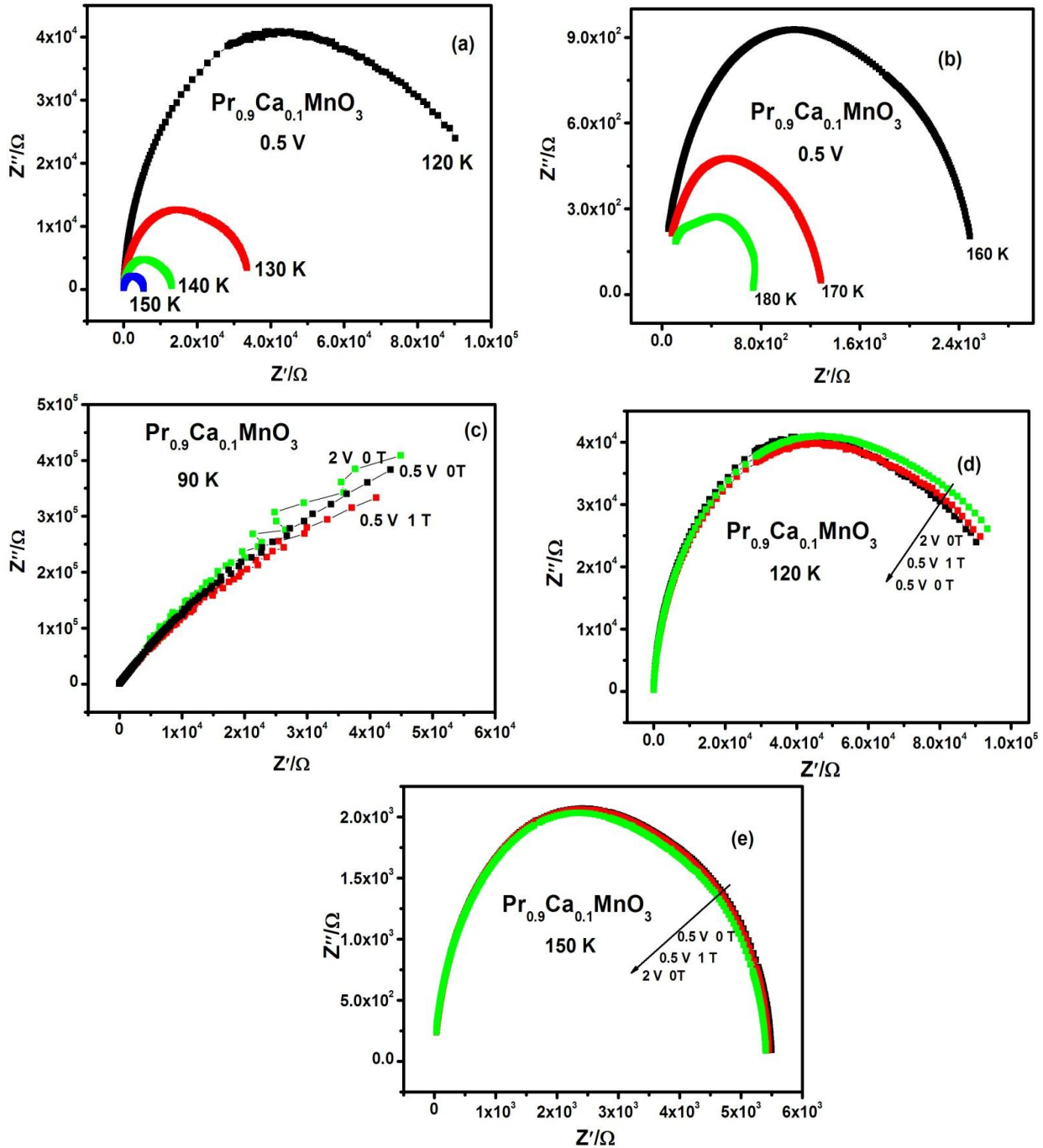


Fig.4 Cole-Cole semicircles for  $\text{Pr}_{0.9}\text{Ca}_{0.1}\text{MnO}_3$  (a) and (b): temperature's dependence; (c) – (e) electrical and magnetic field's dependence at 90 K, 120 K and 150 K

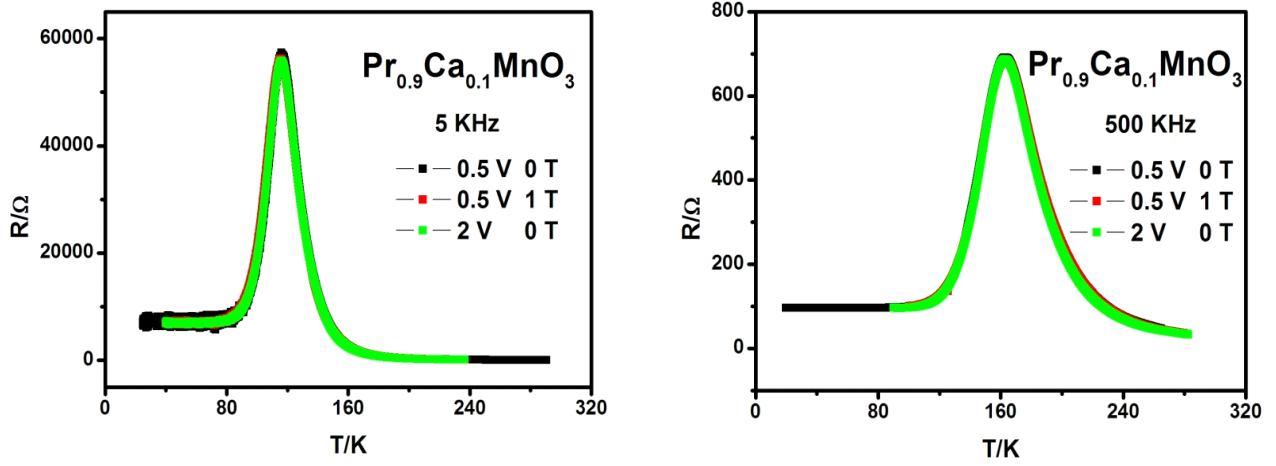


Fig.5 Impedance spectrum of  $\text{Pr}_{0.9}\text{Ca}_{0.1}\text{MnO}_3$  in different magnetic fields and measuring voltages

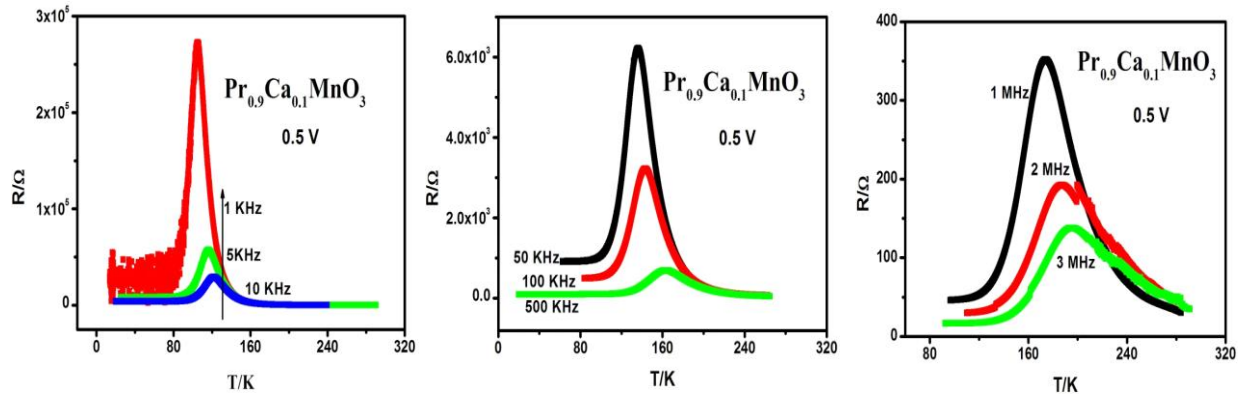


Fig.6 Temperature spectrum of impedance for  $\text{Pr}_{0.9}\text{Ca}_{0.1}\text{MnO}_3$  with the measuring voltage of 0.5 V

By the *Arrhenius* law, the barrier height of grain boundary can be calculated:

$$R = R_0 \exp \frac{\phi}{k_B T} \quad (1)$$

$$\omega = \omega_0 \exp \frac{\phi}{k_B T} \quad (2)$$

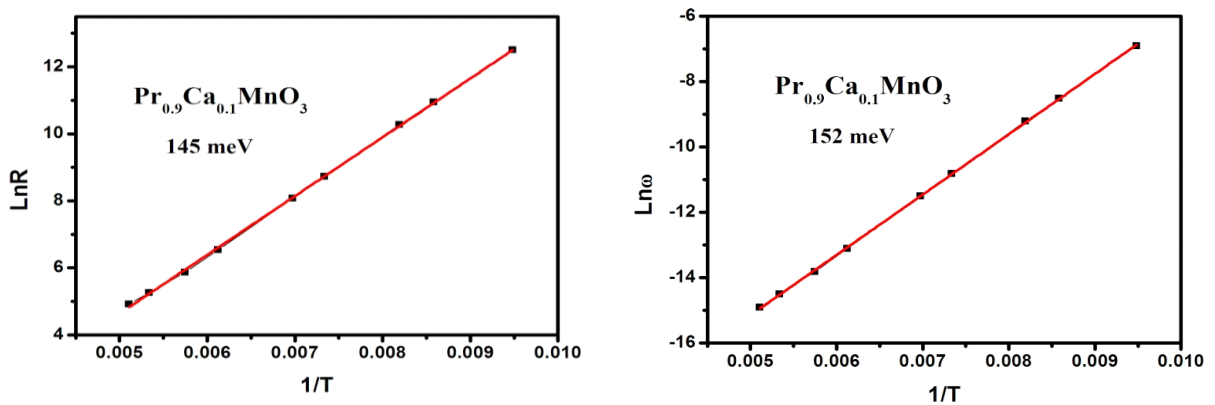


Fig.7 Variation of  $\text{Pr}_{0.9}\text{Ca}_{0.1}\text{MnO}_3$  ceramics in the AC case peak resistance corresponding to the real part of  $R$ , frequency of  $f$  and temperature  $T$ . The black points are experimental data. The red lines are calculated by *Arrhenius* curve equation



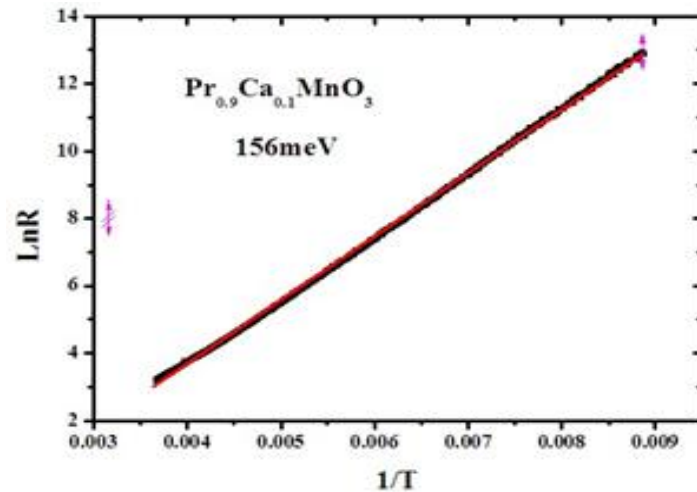


Fig.8 activation energy of  $\text{Pr}_{0.9}\text{Ca}_{0.1}\text{MnO}_3$  obtained by fitting the DC R-T data

## Summary

The magnetic and electrical transport properties of the  $\text{Pr}_{0.9}\text{Ca}_{0.1}\text{MnO}_3$  ceramic sample were studied by DC and AC methods. The results show that the transport properties of  $\text{PrCaMnO}$  are strongly dependent on its Curie point, which implies that there is a coupling between electrical and magnetic components in this material. The Curie temperature of ceramic  $\text{Pr}_{1-x}\text{Ca}_x\text{MnO}_3$  ( $x = 0.1$ ) samples is 120 K, so there is neither notable ER nor MR effect above the Curie temperature. Fitting by Arrhenius law, the barrier height of grain boundary is 145 meV which is well coincident with that from fitting the R-T data.

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