Polaron relaxation related to localized charge carriers in Pr$_{1-x}$Ca$_x$MnO$_3$

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Abstract. Low-temperature (23 \(T\) \(\leq 150\) K) dielectric properties of Pr$_{1-x}$Ca$_x$MnO$_3$ (PCMO) (0.1 \(\leq x \leq 0.9\)) were investigated systematically. A thermally activated relaxation was found in both charge-ordered and no-charge-ordered samples with localized charge carriers, but it was not detected in samples with free carriers. The dielectric behaviour can be well described based on the Jonscher’s power law or ‘universal dielectric response’. Our results strongly support the point that the dielectric properties of PCMO are associated with the hopping motions of polaronic carriers among the localized centres.

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1. Introduction

In recent years, the perovskite system $\text{Pr}_{1-x}\text{Ca}_x\text{MnO}_3$ (PCMO) has been extensively investigated because of its rich electric and magnetic phase diagram [1]. Of particular interest is the study of the behaviour of the ordered states in this system. Charge ordering (CO) as one of the states, is usually accompanied by orbital ordering which exhibits significant change in lattice parameters and consequently the reduction of magnetic properties [2]–[4]. These features include the knowledge of interaction among the spin, charge and lattice degrees of freedom. Numerous efforts have been made to characterize and understand the CO effect and other related phenomena in this system [5]–[12].

An interesting property associated with the CO effect is the anomalous dielectric response at the temperature where CO transition occurs. Both theoretical [13] and experimental [14]–[17] works reveal an enhanced dielectric response in the CO temperature. This indicates that the CO state plays an important role in the dielectric properties. On the other hand, PCMO as a perovskite manganite also holds interest in the studies of dielectric permittivity pioneered by the work of Yamada et al [18] and Sichelschmidt et al [19]. Yamada et al reported giant dielectric constants ($\varepsilon' \sim 10^3$) at different doping levels of PCMO samples in the low-temperature range ($24 \leq T \leq 135$ K) and they proposed a small-polaron-hopping model to describe their results. More recently, Freitas et al [20] found that the dielectric behaviour of $\text{Pr}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ ($T < 100$ K) was associated with the hopping of polaronic charge carriers. A Spanish group [21] argued that the colossal dielectric constant ($\varepsilon' \sim 10^3$–$10^5$) found in $\text{Pr}_{0.6}\text{Ca}_{0.4}\text{MnO}_3$ in the temperature range $30 \leq T \leq 100$ K was ascribed to the Schottky barriers at electrical contacts.

These works reveal some interesting dielectric properties of PCMO at low temperatures. However, many features about the properties still remain open questions. A good comprehension of these properties would help us to understand the vast striking phenomena in PCMO and other related systems. In this paper, we present a detailed investigation of PCMO in a low-temperature range ($23 \leq T \leq 150$ K) with the doping level of $x$ varying from 0.1 to 0.9. Our results indicate the dielectric behaviour of PCMO in the temperature range can be ascribed to dipolar effects induced by the hopping motions of the localized carriers.

2. Experimental details

The polycrystalline PCMO with nominal composition $x = 0.1$–0.9 in steps $dx = 0.1$ were synthesized by a standard solid-state ceramic technique. Stoichiometric amounts of $\text{Pr}_6\text{O}_{11}$, $\text{CaCO}_3$ and $\text{MnO}_2$ powder were thoroughly mixed and fired at $1100$ and $1250$ °C for 20 h with intermediate grinding. Then the reactants were reground, pressed into pellets, and sintered at $1300$ ($x = 0.1$–0.3), $1360$ ($x = 0.4$–0.6) and $1450$ °C ($x = 0.7$–0.9) for 20 h, respectively. The resulting samples were found to be pure phase as examined by x-ray diffraction. The temperature dependent dielectric properties were measured using a QuadTech 1730 LCR Digibridge at the frequencies $f = 100$ Hz, $120$ Hz, $10$ kHz, $20$ kHz, $50$ kHz and $100$ kHz with a cooling/heating rate of $2$ K min$^{-1}$. Electrodes were made by printing silver paste on both sides of the disk-type samples, which were then fired at $650$ °C for 15 min in order to remove the polymeric component. The dc resistance was measured by the four-probe technique.

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Figure 1. Temperature dependence of the dielectric constant (a) and loss tangent (b) for Pr$_{0.8}$Ca$_{0.2}$MnO$_3$ measured at frequencies of 100 Hz, 120 Hz, 1 kHz, 10 kHz, 20 kHz, 50 kHz and 100 kHz (from left to right).

3. Results and discussion

As a typical representative, the variation in dielectric constant ($\varepsilon'$) and loss tangent ($\tan \delta = \varepsilon''/\varepsilon'$, where $\varepsilon''$ is the imaginary part of the complex permittivity) with temperature for Pr$_{0.8}$Ca$_{0.2}$MnO$_3$ are shown in figure 1. We can see from the figure that the $\varepsilon'(T)$ exhibits similar features to those found in CaCu$_3$Ti$_4$O$_{12}$ [22]. That is, at high temperatures $\varepsilon'(T)$, reaching a value as high as $\sim 10^4$, shows small variations with temperature and frequency; with decreasing temperature, $\varepsilon'(T)$ displays a steplike decrease to a low value of about 40. The steplike decrease in $\varepsilon'(T)$ was accompanied by a peak in the corresponding loss tangent. The peak shifts to higher temperatures with increasing frequencies, indicating a thermally activated relaxation. This relaxation appears in the samples with Pr content, $1 - x \geq 0.4$, and generally, occurs at lower temperatures when $1 - x$ decreases. While for samples with $1 - x \leq 0.3$, the relaxation is absent.

Figure 2 displays the Arrhenius plots of the measured frequency, $f$, versus the reciprocal of the peak position, $T_p$, which is defined as the temperature where $d(\tan \delta)/dT = 0$. The obtained data fall perfectly on straight lines in the measured temperature range, implying that the relaxation follows the Arrhenius law

$$\tau = \tau_0 \exp(E/k_B T),$$

where $\tau$ is the relaxation time, $\tau_0$, the pre-exponential factor, $E$, the activation energy, and $k_B$, the Boltzmann constant. The deduced values of $E$ and $\tau_0$ according to equation (1) are listed in table 1, from which we can see that the activation energy decreases on the whole when the Pr
Figure 2. Arrhenius plots for PCMO series samples. The solid lines are fittings based on Arrhenius law. Dotted curves are guards to the eye which illustrates that the low frequency data deviate from the Arrhenius relation.

Table 1. Relaxation parameters deduced from equation (1) for samples with different Pr concentrations \((1 - x)\). The parameters for \(\text{Pr}_{0.7}\text{Ca}_{0.3}\text{MnO}_3\) and \(\text{Pr}_{0.8}\text{Ca}_{0.2}\text{MnO}_3\) are obtained in the frequency range \(f \geq 10\ \text{kHz}\).

| Sample \((1 - x)\) | 0.4 | 0.5 | 0.6 | 0.7 | 0.8 | 0.9 |
|-------------------|-----|-----|-----|-----|-----|-----|
| \(E\) (meV)       | 39  | 46  | 18  | 64  | 56  | 136 |
| \(\tau_0 (\times 10^{-9}\text{s})\)| 2.45| 3.19| 1.70| 0.581| 0.970| 0.0339|

content decreases, though \(\text{Pr}_{0.6}\text{Ca}_{0.4}\text{MnO}_3\) shows obvious abnormality which might be caused by the sintering temperature. However, peculiarity is also seen in figure 2 that for the samples with \(1 - x = 0.7\) and 0.8, the Arrhenius relation only holds in the frequency range \(f > 1000\ \text{Hz}\), whereas in the low frequency range \(f \leq 1000\ \text{Hz}\), distinct deviation from the Arrhenius relation as indicated by the dotted curves can be clearly seen. This deviation is not detected in samples with lower Pr contents because the low-frequency peak moves out of the measuring temperature window. This fact as well as the absence of the deviation in \(\text{Pr}_{0.9}\text{Ca}_{0.1}\text{MnO}_3\) will be discussed in the following.

A possible origin of the deviation would be that the samples might exhibit two sets of relaxations as suggested by the two steplike increases in the curve of \(\varepsilon'(T)\) for \(\text{Pr}_{0.7}\text{Ca}_{0.3}\text{MnO}_3\) (the upper inset of figure 3). Indeed, a new relaxation is well developed at higher temperature after \(\text{Pr}_{0.7}\text{Ca}_{0.3}\text{MnO}_3\) was annealed in high purity nitrogen at 800°C for 2 h (figure 3). This result seems to support the inference that the deviation is caused by the multirelaxation. We now check the Arrhenius behaviour of the separated relaxations. To this end, in order to extract the peak position accurately, two Gaussian peaks superimposed on an exponential increasing background in a form of \(a + be^{(-c/T)}\), with \(a\), \(b\) and \(c\) as adjustable parameters, were used to fit the
Figure 3. Temperature dependence of the loss tangent for Pr$_{0.7}$Ca$_{0.3}$MnO$_3$ after annealing in nitrogen at 800°C for 2 h. The measuring frequencies are 100 Hz, 120 Hz, 1 kHz, 10 k Hz, 20 kHz, 50 kHz and 100 kHz. The upper inset: temperature dependence of the dielectric constant for as-sintered Pr$_{0.7}$Ca$_{0.3}$MnO$_3$ measured at 1 kHz. The lower inset: Arrhenius plots of the separated relaxations.

experimental data of tan $\delta$. The least-squares fitting results were presented as solid curves in figure 3. Perfect agreement between the experimental data and the fittings can be achieved. The lower inset of figure 3 plots the Arrhenius relations of the separated relaxations; the deviation still exists for each relaxation. This suggests a mechanism other than multirelaxation underlies the deviation, which would be helpful for understanding the physics of the observed relaxations. Since the newly appeared relaxation still awaits detailed studies to clarify its characteristics, this issue is out of the scope of this paper. So, in the following, we limit our discussion to low-temperature relaxation.

We now turn our attention to the origin of the low-temperature relaxation. We can first rule out the possibility that the relaxation is associated with the CO state, because it also occurs in the no-charge-ordered samples (Pr$_{0.8}$Ca$_{0.2}$MnO$_3$ and Pr$_{0.9}$Ca$_{0.1}$MnO$_3$). It seems that the extrinsic origin resulting from, for example, electrical contacts, grain boundaries, and intrinsic disorder caused by doping or inherent inhomogeneous distribution of charge carriers, might be responsible for the relaxation. For these cases, dielectric relaxation is associated with inhomogeneity, which is the well known Maxwell–Wagner interfacial polarization. Since the interfacial polarization dominates in the low frequency region and follows the Arrhenius law perfectly, it could be expected that the relaxation would become much weaker with increasing temperatures as the relaxation would occur at higher frequencies. Our recent work [23] showed that the relaxation strength (dielectric loss peak height), $\Delta$, exponentially decreases with increasing temperature in the form

$$\Delta = A/[B + C \exp(-U/k_B T)],$$

(2)

where $A$, $B$, $C$ and $U$ are constants. To justify whether or not the low-temperature relaxation has a Maxwell–Wagner-type origin, the relaxation peaks of Pr$_{0.7}$Ca$_{0.3}$MnO$_3$ extracted from the fittings

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Comparison of the low-temperature relaxation peaks of Pr$_{0.7}$Ca$_{0.3}$MnO$_3$ with the measuring frequencies of 100 Hz, 120 Hz, 1 kHz, 10 kHz, 20 kHz, 50 kHz and 100 kHz. These peaks were extracted from the least-squares fittings as described in the text. Inset: plot of the peak height as a function of the reciprocal peak temperature, the straight line is the result of linear fit.

were illustrated in figure 4 for comparison. It is seen that the peak height does not follow the exponentially decreasing relation, and it is therefore unlikely that the Maxwell–Wagner effects are the origin of the relaxation. On the contrary, an Arrhenius plot of $\Delta$ versus $1/T_p$ produces good straight line (inset of the figure) indicating that the relaxation strength exhibits a thermally activated behaviour. This is a strong indication of a dipolar relaxation produced by the localized charge carriers, since the hopping motions of localized charge carriers under an applied electric field not only contribute to conductivity but also give rise to dipolar effects. For this kind of relaxation, the static dielectric constant is proportional to the thermally activated carriers [24], one has the relation

$$\Delta \propto \varepsilon_s - \varepsilon_\infty \propto \exp(-H/k_B T),$$

(3)

where $\varepsilon_s$ and $\varepsilon_\infty$ are the static and high-frequency dielectric constants, and $H$ is the activation energy. Hence, a thermally activated behaviour of the $T$-dependent relaxation strength can be observed as seen in the inset of figure 4.

On the other hand, the frequency dependence of the dielectric behaviour for this kind of relaxation can be described by Jonscher’s power law, i.e. the so-called universal dielectric response (UDR) [25]

$$\varepsilon'' = (P/\varepsilon_0)\omega^{s-1},$$

(4)

$$\varepsilon' = (P/\varepsilon_0)\tan(s\pi/2)\omega^{s-1},$$

(5)
where $P$ and $s$ (with values between 0 and 1) are the temperature-dependent constants, $\varepsilon_0$ is the vacuum permittivity, and $\omega = 2\pi f$ is the angular frequency. Equation (5) can be rewritten as:

$$f\varepsilon = Q(T) f^s,$$

with the temperature-dependent constant $Q(T) = (P/\varepsilon_0) \tan (s\pi/2)$. Therefore, at a given temperature, a straight line with a slope of $s$ should be obtained in the plot of $\log_{10}(f\varepsilon)$ versus $\log_{10} f$. This speculation is well demonstrated in figure 5 wherein quite good straight lines are obtained at high temperatures. With decreasing temperature, the data points gradually deviate from the straight line at the highest frequencies. This is because more and more carriers are becoming frozen with decreasing temperature, which reduces the dipolar effect and causes the steplike decrease in $\varepsilon'(T)$. Obviously, the freezing process depends strongly on the measuring frequency. So, the temperature at which the steplike decrease in $\varepsilon'(T)$ occurs exhibits a thermally activated feature. In addition, the freezing of carriers leads to a great reduction in number of the hopping carriers that greatly increases the resistance, as confirmed by the temperature dependence of dc resistance (see figure 6). The frozen carriers no longer contribute to polarization; the observed dielectric behaviour is therefore dominated by the remaining charge carriers. These carriers still obey the UDR law, so, as the freezing process moves to lower frequencies at low temperatures, the linear behaviour appears again in the higher frequency range as observed.

These features provide good evidence that the relaxation process is linked with the freezing process of the charge carriers, and strongly support the idea that the low-temperature dielectric relation in PCMO is related to polaron relaxation. In the freezing process, the involved charge carriers are sufficiently localized. In other words, their inertial mass (the eigenfrequency) becomes sufficiently large (low). Then, they can not follow the field variations and the resulting effect is a dielectric relaxation with the relaxation peak appearing at the temperature where the eigenfrequency of the carriers equals the frequency of the applied field.

Based on this point, the above results, i.e. the low-temperature deviation from the Arrhenius relation and the absence of relaxation in the samples with $1 - x = 0.1, 0.2$ and 0.3 can be well understood.
In the polaronic scenario [26], thermally activated nearest-neighbour hopping predominates in the high-temperature region resulting in an Arrhenius-like law

\[ \rho \exp \left[ \frac{(W_H + W_D)}{k_B T} \right], \]

where \( W_H \) and \( W_D \) are the polaron hopping energy and disorder energy, respectively. While in the low-temperature region, Mott’s variable-range-hopping (VRH) sets in and the activation energy is essentially due to the disorder energy. This implies that the polaronic relaxation would feature the Arrhenius and VRH behaviours in the high- and low-temperature regions, respectively. Thus, at the crossover temperature, \( T^* \), where VRH hopping takes over from thermally activated nearest-neighbour hopping, deviation from the Arrhenius behaviour can be observed. Localization in solids is connected with disorder, hence, \( T^* \) would strongly depend on the doping level and sample preparation process. As already seen from table 1, the gradual reduction in activation energy with decreasing Pr content indicates that the localization of the charge carriers becomes more and more weak. Therefore, \( T^* \) also decreases with the Pr doping level such that in the samples with \( 1 - x = 0.6, 0.5 \) and \( 0.4 \), the temperature might move below the lowest temperature measured, as a result, the deviation can not be detected in these samples. Whereas in \( \text{Pr}_{0.9}\text{Ca}_{0.1}\text{MnO}_3 \), the absence of the deviation might be because, as seen from figure 2, \( T^* \) moves to a high temperature which can only be detected by a frequency higher than the largest frequency of our equipment. On the other hand, disorder induced by the inevitable existence of defects and strain depends strongly on the sample preparation process. In particular, the oxygen vacancies are often unavoidable in perovskite oxides under a high firing temperature. The oxygen vacancies can change the ratio of \( \text{Mn}^{3+}/\text{Mn}^{4+} \) and thus affect the state of disorder, since \( \text{Mn}^{3+} \) is a Jahn–Teller ion. This is the reason why the observed dielectric properties depend on the sintering temperature and annealing treatment.
The above discussion is also confirmed by the dc resistance measurements. Displayed in figure 6 is the comparison of the normalized resistance, $R(T)/R(200\text{ K})$, as a function of temperature for samples with $1 - x = 0.1$, $0.2$, $0.3$ and $0.4$. It is seen that the great upturn in resistance, reflecting the freezing process of the charge carriers, successively shifts to lower temperatures such that in the samples with $1 - x = 0.1$, $0.2$ and $0.3$, the resistance upturn moves out of the measured temperature window. So, no relaxation can be detected in these samples. In the inset of figure 6, we present further evidence from the dielectric behaviour in support of this point. Based on equation (4), straight lines with the slope $s - 1$ can be obtained at fixed temperatures in the log–log plot as illustrated in the inset. The values of $s - 1$ deduced from the linear fittings are also listed beside the lines. The value of $s$ actually scales the extent to which charge carriers have been localized. In the case of $s = 0$, equation (4) shows the usual reciprocal frequency behaviour, and the system displays nondispersive transport of free charge carriers. We note that, at a relatively low temperature, $T = 40\text{ K}$, the straight lines for samples with $1 - x = 0.1$, $0.2$ and $0.3$ have a common slope, $-1$ (i.e. $s = 0$). This means the carriers in these samples are free ones. Meanwhile the slope obtained from Pr$_{0.4}$Ca$_{0.6}$MnO$_3$ shows a value of $-0.8$, reflecting the confined nature of the carriers in the sample. These results demonstrate the affinity between the relaxation and the localized carriers, and strongly support the point that the dielectric properties of PCMO are dominated by the dipolar effects associated with the hopping motions of the localized charge carriers.

4. Conclusions

In summary, the low-frequency ($10^2$–$10^5$ Hz) dielectric properties of PCMO ($0.1 \leq x \leq 0.9$) were investigated as a function of temperature ($23$–$150\text{ K}$). A thermally activated relaxation appearing in the low-temperature region was found to be closely linked with the localized charge carriers, and was ascribed to a dipolar relaxation associated with the hopping motions of the carriers. Our results would be helpful for understanding the physics of the colossal dielectric response found in a number of materials in recent years.

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