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Manganese effect on the relaxation behaviors of the space charge polarization in $Pb(Fe_{2/3}W_{1/3})_{0.9}Ti_{0.1}O_3$ ceramics

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Abstract

The effects of manganese on the space charge polarization in $0.9Pb(Fe_{2/3}W_{1/3})O_3$–$0.1PbTiO_3$ (0.9PFW–0.1PT) ceramics are discussed using the Debye theory and the Arrhenius law. The static dipole moment of the space charge polarization is decreased by the MnO additives. The values of the Debye relaxation time τ_0 and the activation energy E_τ of the space charge polarization are similar at any temperature range before adding MnO. These values are changed after adding MnO and are obviously changed only at the lower temperature range. According to these results, it is suggested that the space charge polarizations are induced due to the charge imbalance in the micropolarization region and the conductive carriers. The charge imbalance and the conductive carriers are reduced by adding MnO additives since the compositional fluctuation is restrained and the electronic compensation is induced.

Keywords: Relaxor; Space charge polarization; Debye; Arrhenius; Relaxation time

1. Introduction

The complex perovskite type relaxor ferroelectric materials (RFE) show the ABO_3 structure where the A site and B site can be occupied by different metal cations which cause the compositional fluctuation effect [1–5]. In RFE materials, the polarization microregions have slightly different compositions which cause polarization of different natures. Hence, the peculiar dielectric physical properties are induced by such dipoles and their interactions [6]. To describe this phenomenon, researchers have provided several kinds of models, such as the inhomogeneous micro region model [7–14], the superparaelectric model [1,15,16], the glass model [17–19], the order-disorder model [20–23], the random fields model [24,25], the breath model [6], the micro-macro domain transition model [26,27] and the relaxation time distribution model [3,28]. In addition, the Debye theory considers that the dipoles have specific relaxation time and the dielectric response depends on the frequency of the external field [29]. The Arrhenius law considers that the relaxation time of dipoles depends on the environmental temperature [29]. These models can be used to discuss the characteristic of a dipole in a dielectric medium [3,6,28,30].

$Pb(Fe_{2/3}W_{1/3})O_3$ (PFW) is one of the classical relaxors with lower sintering temperature (about 900 °C) and can be applied for multi-layer ceramic capacitors [31,32]. However, the lower Curie temperature T_c at -90 °C and the higher dielectric loss are disadvantages for practical applications [4,30–36]. The lattice structure and the dielectric properties of the pure PFW can be easily changed by adding $PbTiO_3$ (PT) composition, adding the dopants or changing the synthesizing process [4,30,33–36]. Zhou et al. synthesized the $Pb[(Fe_{2/3}W_{1/3})_{1-x}Mn_x]O_3$ solid solution for

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pure PFW ceramics doped with $Mn(NO_3)_2$ [34]. When doping manganese cations, the dielectric loss is decreased, the second dielectric peak induced from the space charge polarization is vanished and the diffused phase transition is sharper. Similarly, Szwagierczak and Kulawik report that the resistivity is increased and the second dielectric peak is diminished after adding MnO_2 in pure PFW ceramics [30]. The MnO-additive effects in $(1-x)$PFW–xPT ceramics are investigated by authors on the diffused phase property, the dielectric loss and the charge compensation [37].

Due to the compositional fluctuation in RFE materials, the charge imbalance in the micropolarization region and the conductive carriers are often induced and cause the space charge polarization [38–44]. In PFW–PT ceramic system, the space charge polarization is usually existent and is effectively decreased by doping manganese cations [30,33–37]. However, few papers carefully report the effect of the manganese cations on the dielectric relaxation behaviors of the space charge polarization for PFW–PT ceramic. In the present work, the relaxation behaviors of the space charge polarization are investigated using the Debye theory and Arrhenius law for pure and MnO added 0.9PFW–0.1PT ceramics. According to the experimental data and fitting results, the static dipole moment, the Debye relaxation time and the activation energy of the space charge polarization are determined and discussed. Furthermore, the effects of MnO additives on the dielectric relaxation behaviors of the space charge polarization are also investigated.

2. Experiment and ceramic preparation

Raw materials were mixed using pure reagent PbO, Fe_2O_3, WO_3, TiO_2 and MnO powders (99.5% purity). The materials $0.9Pb(Fe_{2/3}W_{1/3})O_3$–$0.1PbTiO_3$ with or without adding 0.15 wt.% MnO were synthesized by calcining at 750 °C for 2 h, then followed by pulverization. After that, the samples were pressed into a disk of 12-mm diameter and 2-mm thickness at a pressure of 25 kg/cm^2. Specimens were sintered isothermally at a heating rate of 5 °C/min at about 900 °C for 2 h. In order to measure the electrical properties, silver paste was coated to form electrodes on both sides of the sample, and then subsequently fired at 750 °C for 25 min. The dielectric properties of the samples were measured using an impedance analyzer (HP4294A) in the temperature-controlled container. The phase relations for the sintered samples were identified using an X-ray diffractometer (XRD). Fig. 1 shows the X-ray patterns of 0.9PFW–0.1PT and 0.9PFW–0.1PT–0.15 wt.% MnO compounds. Pure perovskite structures are obtained [37].

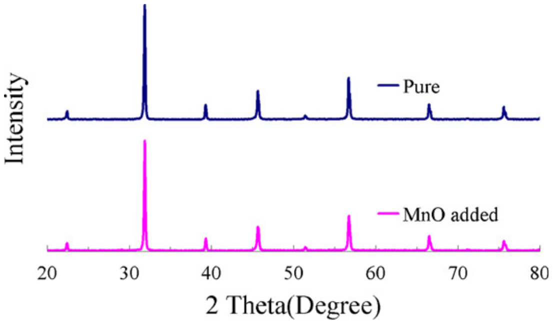

Fig. 1. The Bragg peaks of 2θ in the range between 20° and 80° of pure and MnO added 0.9PFW–0.1PT ceramics.

3. Theory

3.1. Debye theory

The dielectric response is caused by the polarization of dipoles. These dipoles can be switched by the external field. When the frequency of the external field is lower, the relaxation processes of these dipoles are rapid compared with the external field and cause the polarization. When the frequency of the external field is higher, some motions of these dipoles exhibit a time lag with respect to the external field and induce the relaxation phenomenon. This relaxation phenomenon is suggested by the Debye theory. The Debye equations are shown as [29]:

$$\varepsilon^* = \varepsilon_s \frac{1}{1+\omega^2\tau^2} + j\varepsilon_s \frac{\omega\tau}{1+\omega^2\tau^2} \tag{1}$$

$$\varepsilon' = \varepsilon_s \frac{1}{1+\omega^2\tau^2} \tag{2}$$

$$\varepsilon'' = \varepsilon_s \frac{\omega\tau}{1+\omega^2\tau^2} \tag{3}$$

where ε^* is the complex dielectric constant, ε_s is the static dielectric constant as the frequency of external field is zero, ω is the measurement angular frequency and τ is the relaxation time of dipoles. ε' is the real dielectric constant. ε'' is the dielectric loss and is induced by the relaxation effect of dipoles in an applied alternating field. Eq. (3) is usually used to find the relaxation time of dipole and the static dielectric constant ε_s by $\varepsilon_s = 2\varepsilon'$ when $\omega\tau = 1$.

3.2. Arrhenius law

As mentioned before, the frequency response of dipole mainly depends on its relaxation time. The relaxation time of the dipoles not only depends on the mechanisms of polarization, the atomic polarization, the ionic polarization, the orientation polarization and the space charge polarization, also depends on the environmental temperature. The Arrhenius law is usually used to explain the relationship of the relaxation time of dipole and the environmental temperature. The equation is shown as [29]:

$$\tau = \tau_0 \exp\left(\frac{E_\tau}{k_B T}\right) \tag{4}$$

where τ is the relaxation time of dipole, τ_0 is the Debye relaxation time, E_τ is the activation energy, k_B is the Boltzmann constant and T is the environmental temperature. The values of τ_0 and E_τ are usually used to determine the characteristic of dipoles [3,6,28,30].

3.3. The space charge polarization

The space charge polarization is usually induced by the charge imbalance in the micropolarization region and the conductive carriers for RFE materials [30,33–44]. Since the relaxation time τ is long at lower temperature, the space charge polarization exhibits a time lag with respect to the applied alternating field and cannot contribute a polarization according to Eqs. (2) and (3). Furthermore, the relaxation time τ is decreased with increase in temperature and the relaxation processes of the space charge polarization are rapid compared with the external field according to Eq. (4). Therefore, the space charge polarization is usually found at higher temperature in the paraelectric region for RFE materials [4,30,33–37]. Moreover, the permittivity contribution is diminished at higher frequency since the space charge polarization exhibits a time lag with respect to the external field. Therefore, the second dielectric peak of the paraelectric region for the RFE materials is usually used to determine if the space charge polarization is induced [4,30,33–37].

4. Results and discussions

4.1. The temperature dependence of dielectric data

Fig. 2 shows the dielectric constant and the dielectric loss as a function of temperature for pure and MnO added 0.9PFW–0.1PT ceramics. In Fig. 2, the space charge polarization is depressed, the broad temperature–dielectric constant is enhanced and the dielectric loss is decreased as adding MnO. It is suggested that the electron compensation and the disorder degree of B-site are induced by the manganese cations [37]. In the paraelectric region of Fig. 2(a), we can easily find the peak dielectric loss at different measurement frequencies. The peak shifts to higher temperature and the peak value is increased as the temperature is higher when increasing the measurement frequency. From Eq. (3), the dielectric loss closes to zero when the frequency of applied field is very fast or slow. Furthermore, the dielectric loss has a peak value as $\omega\tau = 1$. From Eq. (4), the relaxation time τ is decreased with the increase of the environmental temperature T and the relaxation time is longer as the activation energy E_τ is higher. According to these equations, it is concluded that the relaxation time of the space charge polarization is the reciprocal angular frequency ($\tau = 1/\omega$) at certain temperature and the relaxation time is decreased as the temperature is increased. Therefore, the higher temperature involves the shorter relaxation time and the peak dielectric loss occurs at higher frequency. This is the reason why the peak dielectric loss shifts to higher temperature as the measurement frequency is increased. In Fig. 2(b), the peak dielectric loss is depressed by adding MnO additives. Furthermore, it is difficult to examine the peak dielectric loss since the dielectric loss is increased again as the temperature is high enough. It is suggested that the conductive carrier is enhanced at higher temperature and induces another dielectric loss.

4.2. The frequency dependence of dielectric data

In the previous section, it is difficult to examine the peak dielectric loss for MnO added 0.9PFW–0.1PT ceramics since the conductive carrier is induced by increasing the measurement temperature. Avoiding the effect of temperature, we show the dielectric constant and the dielectric loss as a function of frequency at different temperatures in Figs. 3 and 4. According to the Debye theory and the Arrhenius law [29], the static space

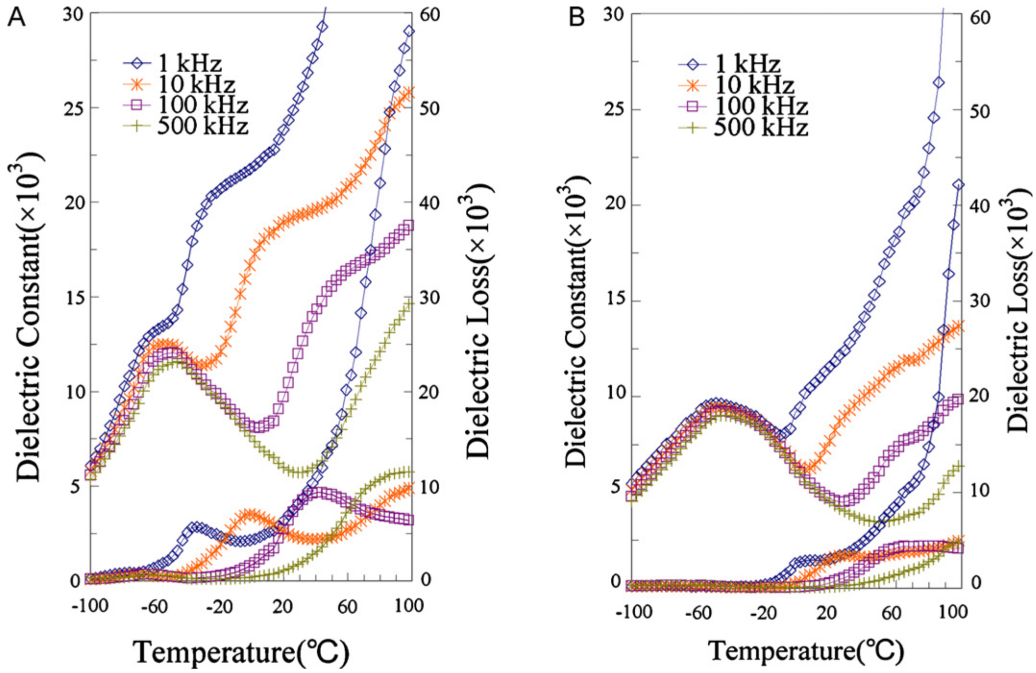

Fig. 2. The dielectric constant and the dielectric loss as a function of temperature at different measured frequencies for (a) pure and (b) MnO added 0.9PFW–0.1PT ceramics.

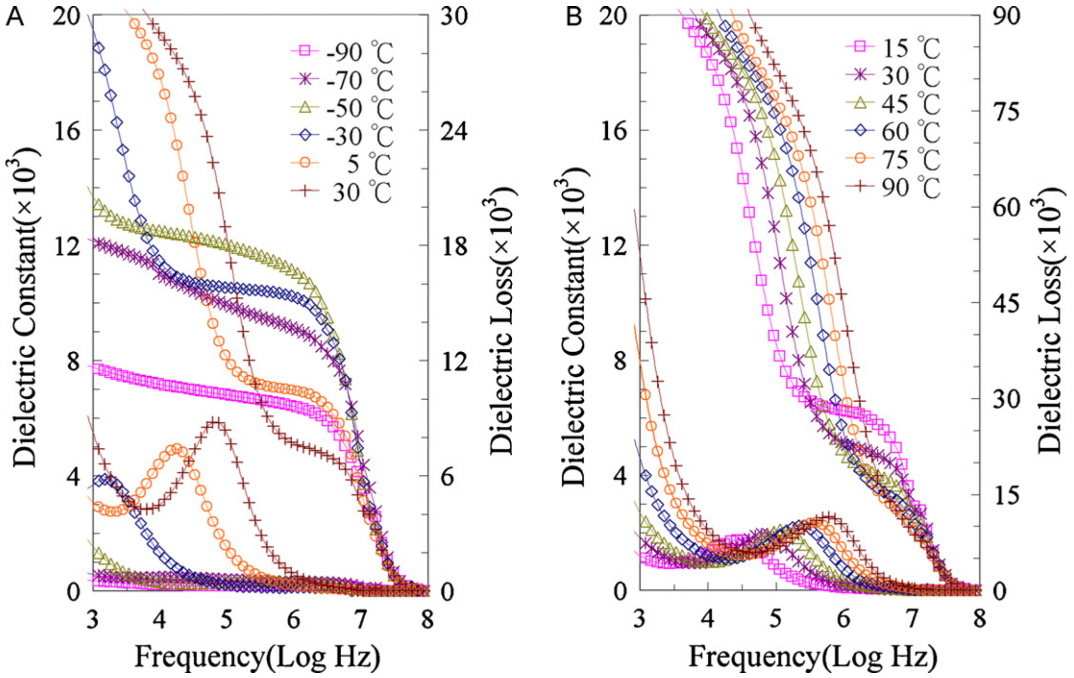

Fig. 3. The dielectric constant and the dielectric loss as a function of frequency at different temperatures of (a) broad temperature range and (b) higher temperature range for 0.9PFW–0.1PT ceramics.

charge polarization and its relaxation time can be found from the value of the peak dielectric loss and its frequency. In Figs. 3(a) and 4(a), the peak dielectric loss is diminished at lower temperature which shows that the space charge polarization exists at higher temperature due to its dipole properties, i.e. the activation energy E_τ and the Debye relaxation time τ_0. Furthermore, this phenomenon is enhanced by adding MnO. In Figs. 3(b) and 4(b), we clearly examine the peak dielectric loss. As increasing the measurement temperature, the peak dielectric loss increases and shifts to higher frequency. According to the Debye theory and the Arrhenius law [29], the static dipole moment of the space charge polarization is increased and its relaxation time is decreased as the measurement temperature is higher. According to the data of Figs. 3 and 4, Fig. 5 shows the value of the peak dielectric loss at different measurement temperatures for pure and MnO added 0.9PFW–0.1PT ceramics.

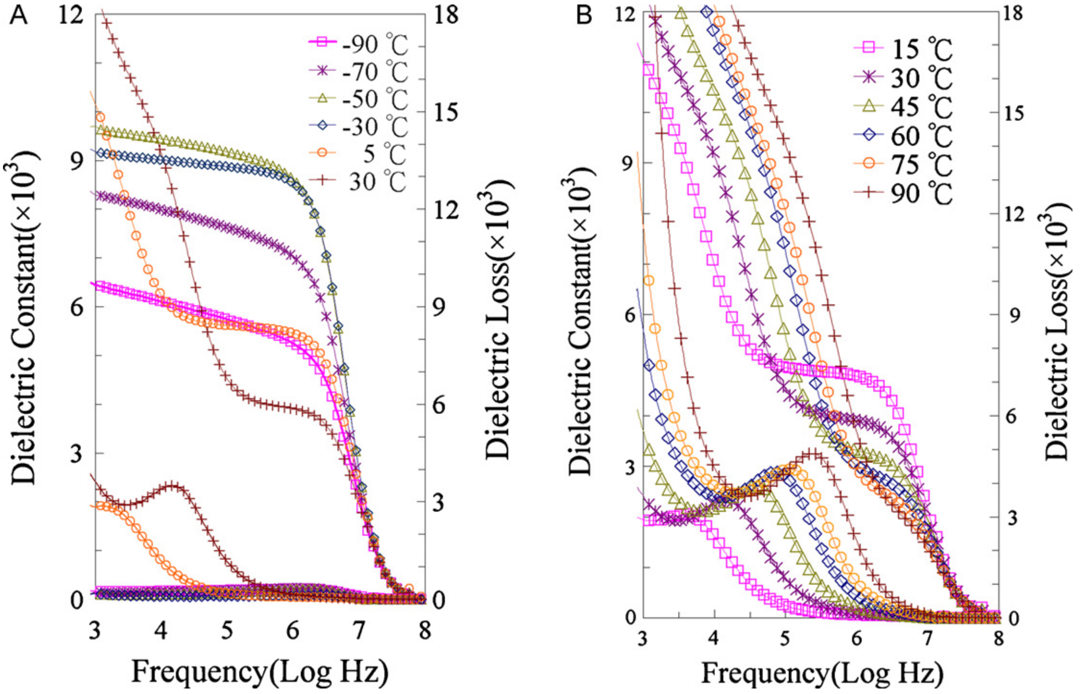

Fig. 4. The dielectric constant and the dielectric loss as a function of frequency at different temperatures (a) broad temperature range and (b) higher temperature range for MnO added 0.9PFW–0.1PT ceramics.

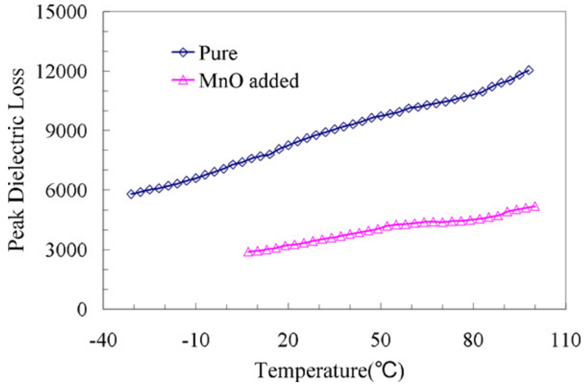

Fig. 5. The peak dielectric loss as a function of temperature for pure and MnO added 0.9PFW–0.1PT ceramics.

Inspecting Fig. 5, the static dipole moment of the space charge polarization is obviously decreased by adding MnO for 0.9PFW–0.1PT ceramics. Furthermore, the peak dielectric loss can be detected at higher temperature for MnO added 0.9PFW–0.1PT ceramics. It is concluded that the relaxation time of the space charge polarization is increased by the MnO additive.

4.3. The fitting results and discussions

To analyze the relaxation properties of the space charge polarization, we calculate the relaxation time τ as a function of temperature according to $\omega\tau = 1$ at the peak dielectric loss which is measured at different temperatures in Figs. 3 and 4. This result is shown in Fig. 6. According to the Arrhenius law [29,30], Fig. 6 is plotted in the form of ln τ as a function of $1000/T$ to estimate the values of the Debye relaxation time τ_0 and the activation energy E_τ. Inspecting Fig. 6, the curve of the reciprocal temperature–relaxation time is not exactly a straight line and bends up at lower temperature. To simplify the discussion, we fit these experimental data with the Arrhenius law at three temperature regions separately. These fitting results are shown in Fig. 6 (solid line) and Table 1. According to the experimental data and fitting results, it is concluded:

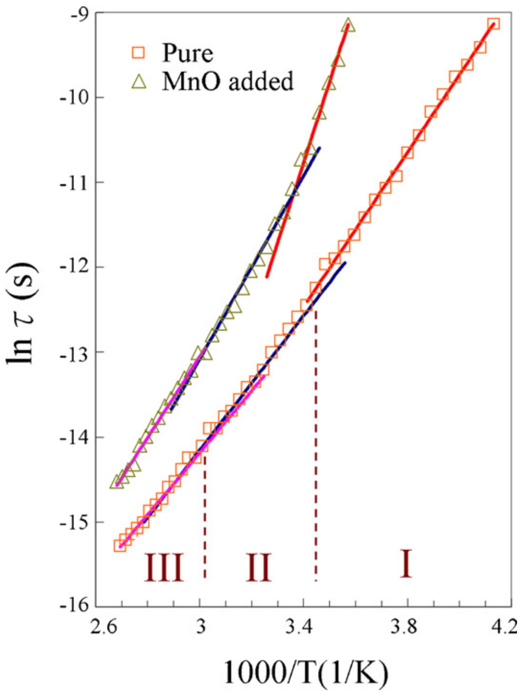

Fig. 6. The nature logarithm of relaxation time as a function of reciprocal temperature for pure and MnO added 0.9PFW–0.1PT ceramics [symbols: experimental data; the solid line: fitting curve].

Table 1
Fitting parameters of pure and MnO added 0.9PFW–0.1PT ceramics.

Regions	Temperature range	MnO added		Pure	
		τ_0 (s)	E_τ (eV)	τ_0 (s)	E_τ (eV)
I	~17(°C)	2.09×10^{-19}	0.820	7.20×10^{-13}	0.394
II	18–58 (°C)	1.89×10^{-13}	0.467	4.95×10^{-12}	0.342
III	~59 (°C)	1.33×10^{-12}	0.412	1.21×10^{-11}	0.316

(1) In Fig. 6, it is found that the relaxation time is shorter and the slope is smaller for pure 0.9PFW–0.1PT ceramics. Its physical meaning is that the space charge polarization is easily induced and switched under an alternating electric field. Furthermore, the smaller slope represent the lower activation energy E_τ (see Table 1) and indicates that the relaxation time can be easily decreased with the increase of temperature. When adding MnO, the relaxation time τ and the activation energy E_τ are obviously increased, so the properties of the space charge polarization are changed by adding MnO additives.

(2) In Fig. 6, the curve of the reciprocal temperature–relaxation time is likely to be a straight line for 0.9PFW–0.1PT ceramics. It means that the values of the Debye relaxation time τ_0 and the activation energy E_τ are similar at three temperature regions I, II and III (see Table 1). Its physical meaning is that the response mechanisms of the space charge polarizations are similar at all temperature regions for 0.9PFW–0.1PT ceramics. However, the curve of the reciprocal temperature–relaxation time obviously bends up for MnO added 0.9PFW–0.1PT ceramics at lower temperature region I. It means that the values of τ_0 and E_τ are similar between the temperature regions II and III and different at the temperature region I, suggesting that the response mechanisms of the space charge polarization are similar between the temperature regions II and III and different at temperature region I for MnO added 0.9PFW–0.1PT ceramics.

(3) From Fig. 6 and Table 1, at the temperature region I the values of the Debye relaxation time τ_0 and the activation energy E_τ are changed from 2.09×10^{-19} s and 0.82 eV to 7.2×10^{-13} s and 0.394 eV by the MnO additives. The change degree is obvious compared with the temperature regions II and III. It seems that some polarization mechanism is vanished as adding MnO. Therefore, it is assumed that the response mechanism of the space charge polarization is of two types. One is the charge imbalance in the micropolarization region which induces positive and negative charge nanopolarizations [38–44]. Another is the conductive carriers, electrons and electron holes [30,33–36]. As applying alternating field, these carriers move in opposite direction and induce the space charge polarization.

In conclusions, the space charge polarization has two different response mechanisms, the charge imbalance in the micropolarization regions and the conductive carriers, which exist at any temperature region for pure 0.9PFW–0.1PT ceramics. Table 1 suggests that the space charge polarization has only one response mechanism at temperature region I for MnO added 0.9PFW–0.1PT ceramics since the space charge polarization properties, the Debye relaxation time τ_0 and the activation energy E_τ, are obviously different.

5. Conclusions

The dielectric relaxation of the space charge polarization has been discussed using the Debye theory and the Arrhenius law for pure and MnO added 0.9PFW–0.1PT ceramics. When adding MnO, the static polarization ε_s and the Debye relaxation time τ_0 are decreased and the activation energy E_τ is increased. Especially, the Debye relaxation time τ_0 and activation energy E_τ are obviously different at the lower temperature region I for MnO added 0.9PFW–0.1PT ceramics. Therefore, it is inferred that the space charge polarization has two type response mechanisms, the charge imbalance and the conductive carriers, in pure and MnO added 0.9PFW–0.1PT ceramics. In our previous report [37], it was found that the resistivity, the degree of the diffused phase transition and the disorder degree of B-site cations are enhanced by adding MnO additives for 0.9PFW–0.1PT ceramics. Therefore, it is suggested that the charge imbalance and the conductive carriers are reduced by adding MnO since the compositional fluctuation is restrained and the electron compensation is induced.

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