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Lanthanum dopant induced transition from the ferroelectric to the relaxor state in 0.7PFW-0.3PT ceramics

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Abstract

In this paper, $Pb_{1-x}La_x(Fe_{2/3}W_{1/3})_{0.7}Ti_{0.3}O_3$ ceramics are synthesized by the conventional reaction method and the dielectric properties are investigated with the empirical law and ordering models. The lattice structure changes from tetragonal to pseudocubic after doping with lanthanum and the pyrochlore phase is induced as the amount of lanthanum dopants exceeds 5%. The effects of lanthanum dopants on the resistivity, the diffused phase transition, the space charge polarization and the dielectric loss are investigated. According to the ordering models, the long range order (LRO) ferroelectric is changed to the short range order (SRO) relaxor with the use of lanthanum dopants. It is suggested that growth of the 1:1 ordered domain is impeded by increasing the amounts of lanthanum dopants since the excess positive charge of the 1:1 ordered domain $Pb_{1-x}La_x(Fe_{1/2}W_{1/2})O_3$ is enhanced. Furthermore, the p-type carriers are neutralized by the electron compensation which is induced by the fewer lanthanum dopants.

Keywords: Relaxors; Disorder; Ferroelectric; Phase transformations; Dielectric

1. Introduction

Compared with classical ferroelectrics, relaxor ferroelectric (RFE) materials have the abnormal dielectric properties of a broad dielectric constant and dielectric dispersion. Its general their lattice structure is $A(B'B'')O_3$, in which the B-sites are occupied by different cations [1,2]. When the dielectric constant is considered as a function of temperature, a smoother phase transition is found near T_m, where the dielectric constant reaches its maximum value, but the macroscopic phase transition is not detected in the extended temperature range [1–4]. The physical nature of the diffused phase characteristics due to the compositional fluctuation is described by Smolensky [5]. Furthermore, Setter and Cross reported that the diffused phase transition (DPT) is clearly affected by the ordering degree of the B site cations [6,7]. The general form of the 1:1ordered structure is $A(B'_{1/2}B''_{1/2})O_3$ where the B′-site and the B″-site are the B-sites of the neighboring sublattice and are occupied in an orderly way by two kinds of cations [6–12].

The classical relaxor $Pb(Mg_{1/3}Nb_{2/3})O_3$ (PMN) families have a 1:2 ratio of B-site cations that present different valencies, divalent B^{+2} cations and pentavalent B^{+5} cations. The 1:2 distribution of B-site cations differs from the 1:1 ratio of $Pb(Sc_{1/2}Ta_{1/2})O_3$ family ceramics. Currently, there are two models, the space-charge model and the random-site model, to explain the 1:1 ordering phenomenon in PMN family relaxors [8–12]. In the space-charge model, growth of the 1:1 ordered domain is impeded due to the net charge ordered domain and the opposite charge disordered matrix. If the net negative charge of the 1:1 ordered domain can be decreased, the growth of the 1:1 ordered domain will be easily enhanced [8]. In the random-site model, the 1:1 ordered domain has a neutral charge and has the same composition as the disordered matrix.

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Ttherefore, the space charge polarization is vanished and the 1:1 ordered region can be coarsened by the thermal treatments [9].

$Pb(Fe_{2/3}W_{1/3})O_3$ (PFW) is one of the classical RFE materials that can be easily obtained at lower sintering temperature due to its relatively high tolerance factor (1.007) [13–15]. However, the dielectric loss is high and the Curie temperature is too low (about -90 °) for practical applications [13–24]. With the conductive carriers, many researchers report that the p type carriers can be neutralized by electron compensation [15–19,25]. Furthermore, Mitoseriu et al. reported that the lattice structure and the dielectric properties can be adjusted by adding $PbTiO_3$ (PT) composition in PFW ceramics to form a (1-x)PFW-xPT solid solution [21–24]. Zhou et al. also reported the dielectric properties for pure PFW ceramics doped with lanthanum cations, $Pb_{1-x}La_x(Fe_{2/3}W_{1/3})O_3$ and $Pb_{1-y}La_y(Fe_{(2+y)/3}W_{(1-y)/3})O_3$ [17]. In $Pb_{1-x}La_x(Fe_{2/3}W_{1/3})O_3$ ceramics, the resistivity is decreased and the degree of diffused phase transition is enhanced by doping lanthanum cations. When the amounts of lanthanum dopants are high enough, the resistivity is increased. The pyrochlore phase is the response mechanism and is increased by increasing the amounts of lanthanum cations [17]. In $Pb_{1-y}La_y(Fe_{(2+y)/3}W_{(1-y)/3})O_3$ ceramics, the resistivity is increased and the diffused phase degree is enhanced when doping with lanthanum in pure PFW ceramics. Furthermore, the response mechanism is concluded that the pyrochlore phase does not exist in $Pb_{1-y}La_y(Fe_{(2+y)/3}W_{(1-y)/3})O_3$ ceramics [17].

As mentioned above, the lanthanum dopants should improve the electric properties of the PFW-PT ceramics according to the electron compensation [15–19,25] and the ordering phenomenon [6–12]. Although the effects of lanthanum dopants for pure PFW ceramics have been reported by Zhou et al. [17], the effects of lanthanum dopants on the electric properties for PFW-PT ceramics have not been investigated. In the present work, the effects of lanthanum for 0.7PFW-0.3PT (the Curie temperature $T_C \doteqdot 40$ °C) ceramics. The diffused phase characteristic is described using the empirical law, and the 1:1 order domain is explained using the ordering models. Moreover, the space charge polarization, the dielectric loss and the resistivity are examined and the roles of lanthanum dopants in 0.7PFW-0.3PT ceramics are also discussed.

2. Experimental procedure

Raw materials were mixed using pure reagent PbO, Fe_2O_3, WO_3, TiO_2 and La_2O_3 powders (99.5% purity). The materials $Pb_{1-x}La_x(Fe_{2/3}W_{1/3})_{0.7}Ti_{0.3}O_3$, at x = 0, 3, 5 and 8 mol. %, were synthesized by calcining at 750 °C for 2 hours and then pulverizing. The powders were dried and milled with 8 wt.% of a 5% PVA solution. Then the samples were pressed into disks 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 hours. 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 minutes. The dielectric properties of the samples were measured using an impedance analyzer (HP4294A) in the temperature-controlled container. The dc resistivities were determined by using an ohm meter (TOADKK SM-8215 Super Megohmmeter) at room temperature. The phase relations for the sintered samples were identified using an X-ray diffractometer (XRD).

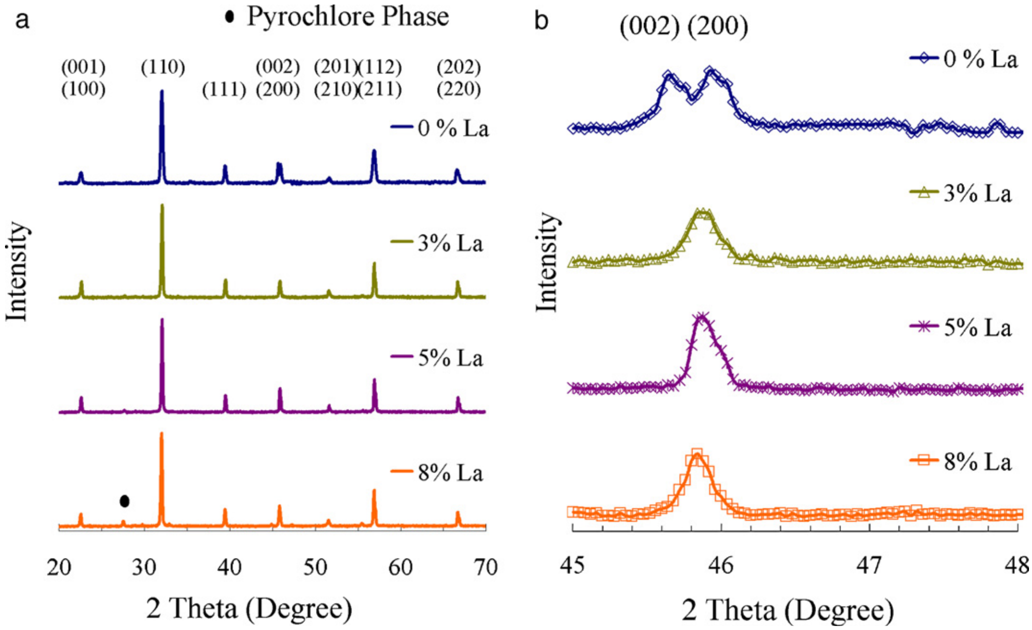

Fig. 1. X-ray patterns of $Pb_{1-x}La_x(Fe_{2/3}W_{1/3})_{0.7}Ti_{0.3}O_3$ compounds with x = 0, 3, 5 and 8%. (a) Diffraction Bragg peaks of 2θ in the range between 20° and 80°. (b) Detailed representation of (002)-(200) Bragg peaks.

3. Results and discussions

3.1. X-ray

Fig. 1 shows the X-ray patterns of $Pb_{1-x}La_x(Fe_{2/3}W_{1/3})_{0.7}Ti_{0.3}O_3$ compounds with x = 0, 3, 5 and 8%. In Fig. 1(a), the pure perovskite structures are obtained and no pyrochlore phase is detected for $Pb_{1-x}La_x(Fe_{2/3}W_{1/3})_{0.7}Ti_{0.3}O_3$ with x = 0, 3 and 5%. With increased lanthanum dopants, the pyrochlore phase is observed. Zhou et al. reported that the pyrochlore phase, $PbWO_4$ and $Pb_2FeWO_{6.5}$, is induced when doping lanthanum cations in pure PFW ceramics, $Pb_{1-x}La_x(Fe_{2/3}W_{1/3})O_3$ [17]. According to the diffraction Bragg angle of the pyrochlore phase in Fig. 1 (a), Zhou et al.'s report and ICDD-PDF (International Center for Diffraction Data-Powder Diffraction File) number 00-008-0476 and 01-070-3986, it is suggested that the pyrochlore phase is $PbWO_4$ or $Pb_{0.99}La_{0.01}WO_4$. In addition, the pyrochlore phase is induced by the excess lanthanum dopants, it is also reasonably suggested that the pyrochlore phase may be other La-included compounds.

Since the lead vacancy and the iron reduction are easily induced, causing the p-type carriers for (1-x)PFW-xPT ceramics [15–19], it is concluded that the pure perovskite structure is obtained when doping with smaller amounts of lanthanum dopants to improve the charge balance for $Pb_{1-x}La_x(Fe_{2/3}W_{1/3})_{0.7}Ti_{0.3}O_3$ ceramics. If the amounts of lanthanum dopants are at 8%, the pyrochlore phase is induced since the charge imbalance is strengthened again by the excess positive charge cation, La^{+3}. Fig. 1 (b) shows a detailed representation of (200) and (002) diffraction Bragg peaks, which can be used to examine the lattice structure according to the reports of Mitoseriu et al. [18,21–24]. In Fig. 1(b), the (002) and (200) Bragg peaks split for pure $Pb(Fe_{2/3}W_{1/3})_{0.7}Ti_{0.3}O_3$ ceramics, indicating that the lattice structure is tetragonal, which is consistent with Mitoseriu et al.'s reports [21–24]. With doping lanthanum in $Pb(Fe_{2/3}W_{1/3})_{0.7}Ti_{0.3}O_3$ ceramics, the (002) and (200) Bragg peaks are merged, which indicates the lattice structure is changed from tetragonal to pseudocubic [18,21–24]. Therefore, it is concluded that the lattice can be changed by doping lanthanum in 0.7PFW-0.3PT ceramics and the pyrochlore phase is induced when the amount of lanthanum dopants is high enough. The pyrochlore phase may be $PbWO_4$ or $Pb_{0.99}La_{0.01}WO_4$ or other La-included compounds.

3.2. DC conductive carriers

Fig. 2 shows the room temperature resistivity for 0.7PFW-0.3PT ceramics with different ratios of lanthanum dopants, indicating lower resistivity for pure 0.7PFW-0.3PT ceramics. According to the reports of Szwagierczak et al., Zhou et al. and Fang et al. [15,16,25], lead- and iron-based relaxors usually induce p-type conductive carriers because of the lead vacancy and the iron reduction. The reaction equations are shown as:

$$V_{Pb} \Leftrightarrow V'_{Pb} + h^{\bullet} \tag{1}$$

$$V'_{Pb} \Leftrightarrow V''_{Pb} + h^{\bullet} \tag{2}$$

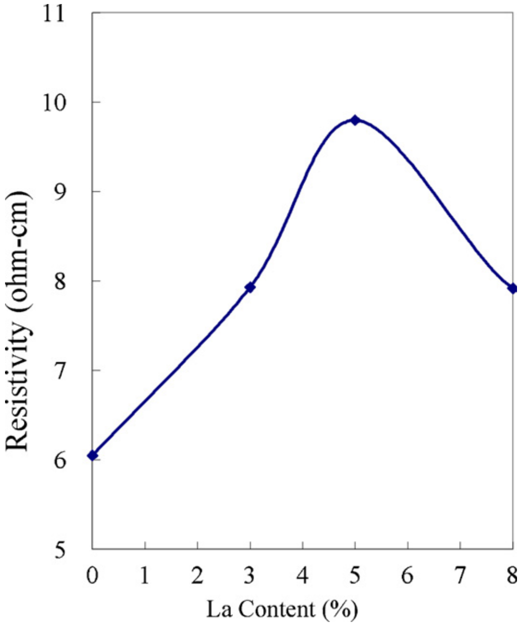

Fig. 2. Room temperature resistivity (log scale) for 0.7PFW-0.3PT ceramics with different amounts of lanthanum dopants.

$$Fe_{Fe}^{+3} \Leftrightarrow Fe_{Fe}^{+2} + h^{\bullet} \tag{3}$$

where V_{Pb}, V'_{Pb}, and V''_{Pb} are neutral, singly, and doubly ionized lead vacancies; $h^{\bullet}$ is the electron hole; and Fe_{Fe}^{+3} and Fe_{Fe}^{+2} are triply and doubly ionized iron ions. Szwagierczak et al., Zhou et al. and Fang et al. suggested that electron holes can be diminished by electron compensation [15,16,25]. In Fig. 2, the resistivity is increased with lower doping ratio of lanthanum cations in 0.7PFW-0.3PT ceramics. According to the reports mentioned above [15–19,25], the p-type carrier is neutralized by electron compensation when substituting lanthanum cations for lead cations. The reaction equation is:

$$La_{Pb}^{+2} \Leftrightarrow La_{Pb}^{+3} + e^{-} \tag{4}$$

where La_{Pb}^{+2} and La_{Pb}^{+3} are doubly and triply ionized lanthanum ions, which substitute for the lead-site (A-site), and e^{-} is the free electron. In Fig. 2, the resitivity is decreased when the ratio of lanthanum dopants is high enough (8%). As mentioned in section 3-1, the pyrochlore phase is induced by a higher ratio of lanthanum dopants and may be $PbWO_4$ or $Pb_{0.99}La_{0.01}WO_4$ or other La-included compounds. If the pyrochlore phase is $PbWO_4$ or $Pb_{0.99}La_{0.01}WO_4$, it is suggested that the lead vacancy and the tungsten vacancy are induced from the pyrochlore phase, $PbWO_4$ or $Pb_{0.99}La_{0.01}WO_4$, thus causing p-type carriers and decreasing resitivity. Eqs. (1) and (2) already show the reaction equation of the lead vacancy on electron hole induction. The reaction equations of the tungsten vacancy are shown as:

$$V_{W} \Leftrightarrow V'_{W} + h^{\bullet} \tag{5}$$

$$V'_{W} \Leftrightarrow V''_{W} + h^{\bullet} \tag{6}$$

$$V''_{W} \Leftrightarrow V'''_{W} + h^{\bullet} \tag{7}$$

$$V'''_W \Leftrightarrow V''''_W + h^\bullet \tag{8}$$

$$V''''_W \Leftrightarrow V'''''_W + h^\bullet \tag{9}$$

$$V'''''_W \Leftrightarrow V''''''_W + h^\bullet \tag{10}$$

where V_W, V'_W, V''_W, V'''_W, V''''_W, V'''''_W and V''''''_W are, respectively, neutral, singly, doubly, triply, tetravalent, pentavalent and hexavalent ionized tungsten vacancies; and $h^\bullet$ is the electron hole. If the pyrochlore phase is not $PbWO_4$ and $Pb_{0.99}La_{0.01}WO_4$, another reasonably suggestion is proposed that the carrier concentration (free electrons, n-type conductivity) increase again by the further increase of La-dopant. At this time, it is assumed that the carrier mobility can not be affected significantly by the doping level or secondary phase.

3.3. Dielectric properties

Fig. 3 shows the dielectric constant and the tangent loss as a function of temperature for $Pb_{1-x}La_x(Fe_{2/3}W_{1/3})_{0.7}Ti_{0.3}O_3$ ceramics with different x ratios. Figs. 3 (a)∼(d) show that the Cuire temperature T_m decreases and the maximum dielectric constant ε_m correspondence of the Curie temperature is reduced with lanthanum dopants in 0.7PFW-0.3PT ceramics, consistent with Zhou et al.'s report [17]. Fig. 4 shows the maximum dielectric constant and the corresponding Curie temperature T_m measured at 300 kHz for $Pb_{1-x}La_x(Fe_{2/3}W_{1/3})_{0.7}Ti_{0.3}O_3$

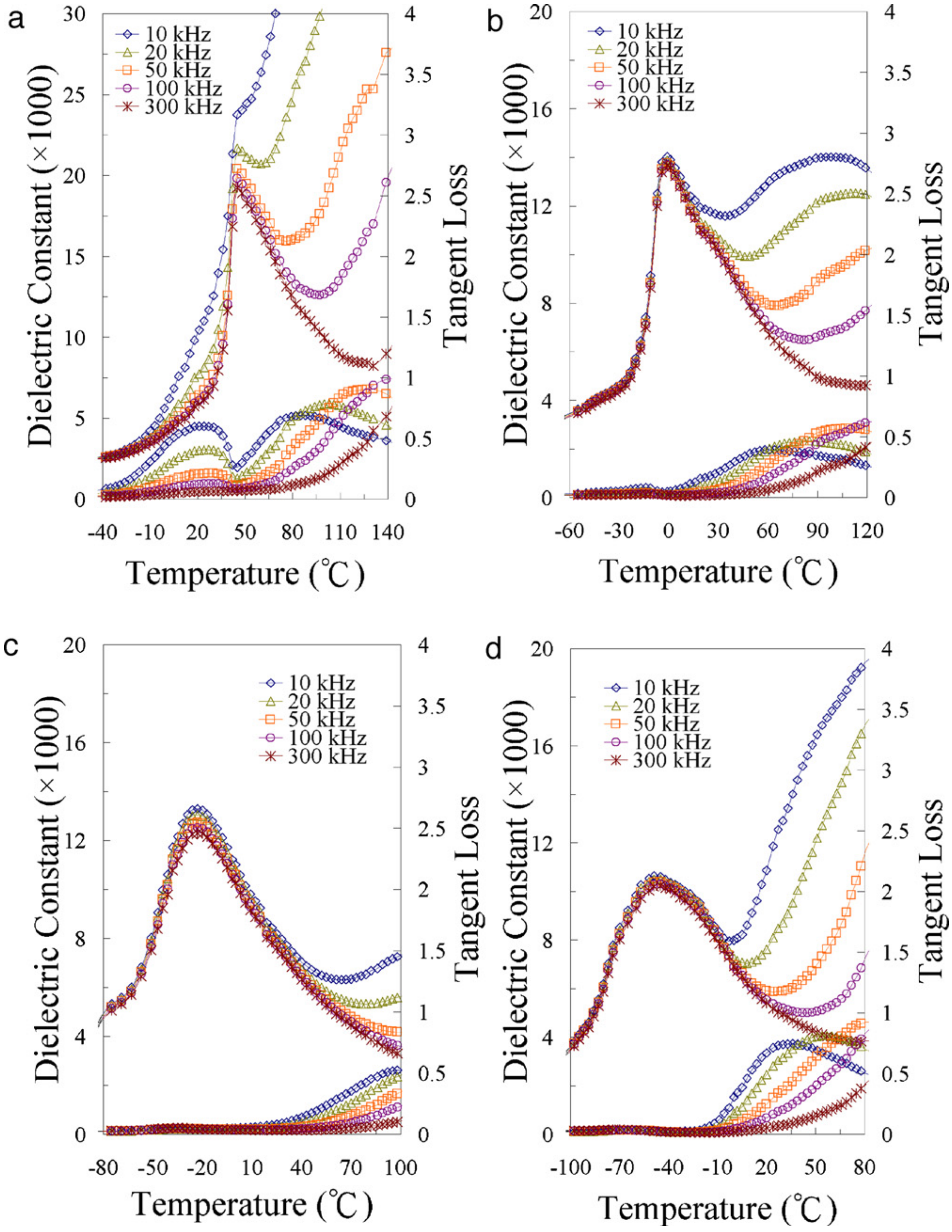

Fig. 3. Dielectric constant and tangent loss as a function of temperature for $Pb_{1-x}La_x(Fe_{2/3}W_{1/3})_{0.7}Ti_{0.3}O_3$ ceramics with x = (a) 0%, (b) 3%, (c) 5% and (d) 8% at different frequencies.

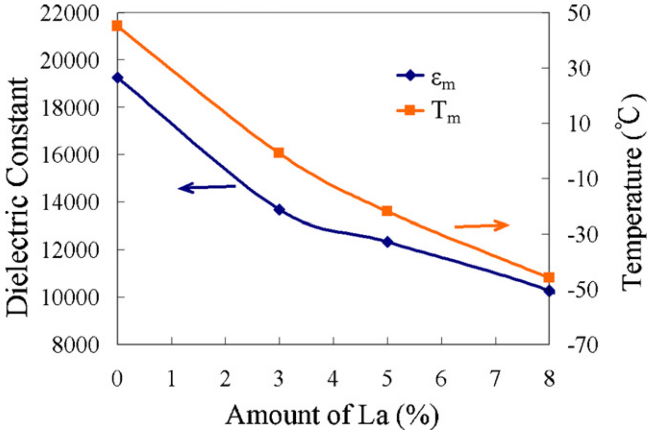

Fig. 4. Dopant dependence of the maximum dielectric constant and the corresponding temperature T_m for $Pb_{1-x}La_x(Fe_{2/3}W_{1/3})_{0.7}Ti_{0.3}O_3$ ceramics at $f = 300$ kHz.

ceramics. Since the Curie temperature T_m and the lattice structure are changed, it is concluded that a solid solution is formed and the dielectric property is changed due to the lanthanum dopants.

In the paraelectric region of Fig. 3, in addition to the dielectric-constant maxima corresponding to the ferroelectric-paraelectric transition, a second dielectric peak is observed and the dielectric loss is enhanced at higher temperature, which is attributed to the dielectric relaxation [15,16,25]. Zhou et al. suggested that the polarization mechanism of the second onset of the dielectric peak is relative to the space charge polarization and the electron hole dc conduction [16]. As the frequency increases, the second dielectric peak, which is due to the relaxation time of the space charge polarization and the dc conduction, vanishes since these dipoles can not follow with the external field [15,16]. According to previous reports, space charge polarization is induced by the net positive charge nanopolarizations and the net negative charge nanopolarizations [8–12,26,27]. Comparing Figs. 3 (a), (b) and (c), it can be seen that the space charge polarization is clearly reduced by the use of lanthanum dopants. Therefore, it is concluded that the charge nanopolarizations, both positive and negative, are eliminated by the lanthanum dopants. According to the space-charge ordering model [8–12], a positive charge nanopolarization can be induced by enhancing the 1:1 ordered domain $Pb(Fe_{1/2}W_{1/2})_{0.7}Ti_{0.3}O_3$, and the negative charge nanopolarization exist in the disordered Fe-rich matrix. However, the 1:1 ordered domain $Pb_{1-x}La_x(Fe_{1/2}W_{1/2})_{0.7}Ti_{0.3}O_3$ is reduced by increasing the ratio of lanthanum dopants since its excess positive charge is enhanced, impeding the growth of the 1:1 ordered domain. In conclusion, the disorder state is enhanced since the 1:1 ordered domain is diminished by the lanthanum dopants and then the space charge polarization is decreased. Moreover, the second dielectric peak is also induced by the electron hole, which can be neutralized by the electron compensation as mentioned above in section 3-2 [15–19,25]. Fig. 3 (d) shows that the second onset dielectric peak and the dielectric loss are further enhanced with additional lanthanum dopants. Referring to Figs. 1 and 2, the pyrochlore phase is induced and the resistivity is decreased with excess lanthanum dopants. Therefore, it is suggested that the pyrochlore phase and the conduction carriers induce the second dielectric peak as the amount of lanthanum dopants becomes in excess.

3.4. Discussion of the diffused phase characteristic in terms of empirical law

Many reports note that the diffused phase transition characteristics of RFE are relative to the ordering degree of cations [6–12,18,19,22]. The diffused phase transition property for relaxors is introduced by Smolensky with the hetrogenous composition in the micro region [5,28]. Moreover, the phase transition temperature T_c is different in the individual micro region, and the T_c probability distribution has normal distribution. Although Smolensky's equation effectively describes the total DPT relaxor dielectric behaviors, it is not suitable for the incomplete DPT relaxor. Therefore, Burfoot et al. and Eiras et al. propose a modified equation to describe the total DPT relaxor and the incomplete DPT relaxor [29,30]. Recently we have shown that the fitting curves are the same using either the equations of Burfoot et al. or Eiras et al. [31]. Eiras et al.'s equation can be written as below:

$$\varepsilon = \frac{\varepsilon_m}{1 + \left(\frac{T - T_m}{\Delta}\right)^{\xi}} \tag{11}$$

where ε_m and T_m are the maximum dielectric constant and corresponding temperature, respectively. The ξ value ranges between 1 and 2, the dielectric material is the normal ferroelectric characteristic as the ξ value is near 1 [18,22,29–37], and the dielectric material is the total DPT relaxor characteristic as the ξ value is near 2. The Δ represents the diffusive extension, and is larger when it is more diffused [18,22,29–37].

As mentioned above in the section 3.3, a second dielectric peak is observed in the paraelectric region for $Pb_{1-x}La_x(Fe_{2/3}W_{1/3})_{0.7}Ti_{0.3}O_3$ ceramics, though it disappears at higher frequency because the space charge polarization can not be switched under the higher frequency field. In order to avoid the effect of space charge polarization, the fit of the degree of the diffused phase transition is limited to the frequency $f = 300$ kHz. At a lower temperature range $T < T_m$, the dielectric behavior is not well described by Eq. (11) in many reports on relaxor ferroelectrics [18,22,30–37]. Therefore, the fitting data is limited to the higher temperature range of $T > T_m$. Fig. 5 shows the 300 kHz dielectric constant as a function of temperature experimental data and the fitting results using Eq. (11) for $Pb_{1-x}La_x(Fe_{2/3}W_{1/3})_{0.7}Ti_{0.3}O_3$ with x = 0, 3, 5 and 8%. In Fig. 5, the fitting curves effectively describe the dielectric behavior at $T > T_m$ but deviate at $T < T_m$, consistent with previous reports [18,22,30–37]. Furthermore, the dielectric behavior deviates from the fitting curve (Eq. (11)) again as the temperature is high enough in the paraelectric region. The deviation is because that the space charge polarizations can switch under the external field when the external temperature is high enough. The response mechanism is that the relaxation

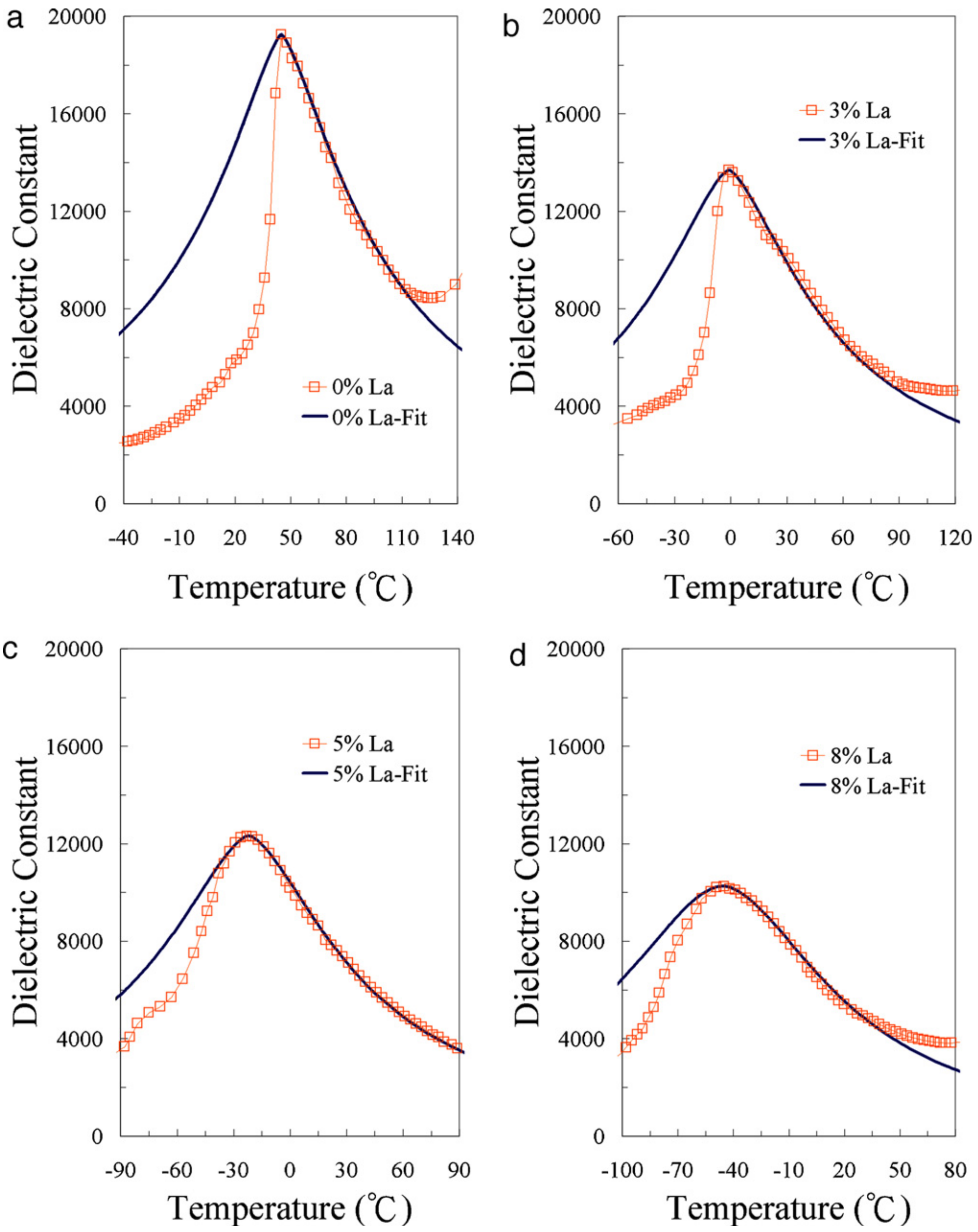

Fig. 5. Experimental data and fitting results of the dielectric constant-temperature dependence for $Pb_{1-x}La_x(Fe_{2/3}W_{1/3})_{0.7}Ti_{0.3}O_3$ ceramics with x = (a) 0%, (b) 3%, (c) 5% and (d) 8% ceramics at 300 kHz.

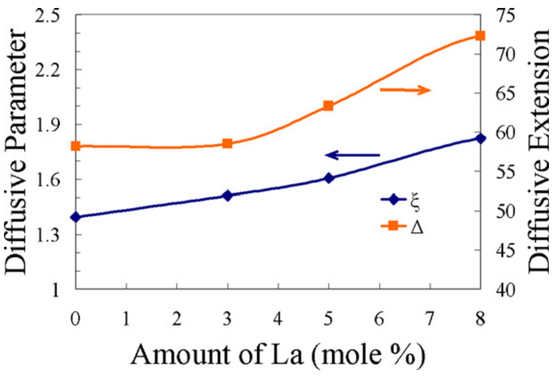

Fig. 6. Dopant dependence of the diffusive parameters and diffusive extensions for $Pb_{1-x}La_x(Fe_{2/3}W_{1/3})_{0.7}Ti_{0.3}O_3$ ceramics at $f = 300$ kHz.

behavior of the space charge polarizations affected by the surrounding temperature. When the surrounding temperature is lower, the relaxation time of the space charge polarizations is longer and the space charge polarizations can not follow with the 300-kHz-frequency field. Therefore, the space charge polarizations can not contribute the polarization effect and can be filtered under the field of high frequency. When the surrounding temperature is increased, the relaxation time of the space charge polarizations is decreased. As the relaxation time is short enough, the space charge polarization can follow with the 300 kHz frequency field again. Therefore, the dielectric behavior of the relaxor ferroelectric and diffused phase transition is interfered by the space charge polarizations. According to the fitting results of Fig. 5, the values of ξ and Δ can be captured. Fig. 6 shows the ξ and Δ values of

$Pb_{1-x}La_x(Fe_{2/3}W_{1/3})_{0.7}Ti_{0.3}O_3$ samples with x = 0, 3, 5 and 8%. In Fig. 6, the values of ξ and Δ increase with increasing lanthanum dopants, indicating that the diffused phase characteristic is enhanced by the lanthanum dopants. According to the reports of Setter et al. and Mitoseriu et al. [6,7,22], the 1:1 ordered domain is reduced and the LRO normal ferroelectric behavior is changed to the SRO relaxor state for more diffused phase transition characteristics. Therefore, it is concluded that the 1:1 ordered domain is reduced by the lanthanum dopants for 0.7PFW-0.3PT ceramics since the diffused phase transition is enhanced. According to the space-charge ordering model [8–12], the 1:1 ordered domain has net charge and is embedded in the opposite charge disordered matrix. Therefore, growth of the 1:1 ordered domain can be reduced by increasing the net charge of the 1:1 ordered domain. On the other hand, growth of the 1:1 ordered domain can be enhanced by decreasing the net charge of the 1:1 ordered domain. Chen et al. reported that the ordering degree is increased by doping lanthanum in PMN ceramics since the net charge of the 1:1 ordered domain, $Pb_{1-x}La_x(Mg_{1/2}Nb_{1/2})O_3$, is reduced [8]. In the present work, the chemical formula of the 1:1 ordered domain is $Pb_{1-x}La_x(Fe_{1/2}W_{1/2})_{0.7}Ti_{0.3}O_3$. When the lanthanum dopants is increased, the positive net charge of the 1:1 ordered domain, $Pb_{1-x}La_x(Fe_{1/2}W_{1/2})_{0.7}Ti_{0.3}O_3$, is increased. Therefore, growth of the 1:1 ordered domain is impended by the lanthanum dopants.

4. Conclusion

In this paper, the lattice structure, the insulated resistivity and the low field dielectric response are investigated for $Pb_{1-x}La_x(Fe_{2/3}W_{1/3})_{0.7}Ti_{0.3}O_3$ ceramics. The diffused phase characteristic is discussed according to the empirical law and the ordering model. Furthermore, the roles of lanthanum ions are suggested. After doping with lanthanum, the diffused phase degree is enhanced and the SRO relaxor state is increased. With increasing lanthanum dopants, the space charge polarization is reduced and then enhanced, while the resistivity is increased and then decreased. It is therefore suggested that the 1:1 ordered domain $Pb_{1-x}La_x(Fe_{1/2}W_{1/2})_{0.7}Ti_{0.3}O_3$ is diminished according to the space-charge ordering model since its charge imbalance is enhanced with increasing lanthanum dopants. Moreover, the p-type carriers are neutralized by the electron compensation with fewer lanthanum dopants and the conduction carriers (holes or electron) are induced again by the lead vacancy, the tungsten vacancy, or the free electron with more lanthanum dopants and the pyrochlore phase, $PbWO_4$ or $Pb_{0.99}La_{0.01}WO_4$.

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