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The indirect synthesized method induced relaxor state to ferroelectric characteristics for $Pb_{0.95}La_{0.05}(Fe_{2/3}W_{1/3})_{0.65}Ti_{0.35}O_3$ ceramics

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Abstract

$Pb_{0.95}La_{0.05}(Fe_{2/3}W_{1/3})_{0.65}Ti_{0.35}O_3$ ceramics are synthesized by using the conventional direct oxide synthesized (DS) method and the indirect synthesized (IS) method. The low-field dielectric response is investigated by using the empirical law, two ordering models and the space charge polarization. The temperature-dependent dielectric peak of the samples prepared using the IS synthesized method is obviously increased; the temperature-dielectric constant is changed to sharp and the diffused phase characteristic is decreased. It is concluded that the IS synthesized method can change the dielectric natures from a relaxor like behavior to a sharp ferroelectric state. The space charge polarization is also changed by using the IS synthesized method. According to these results, it is suggested that the 1:1 ordered domain is enhanced based on the random-site type by using the IS synthesized method for $Pb_{0.95}La_{0.05}(Fe_{2/3}W_{1/3})_{0.65}Ti_{0.35}O_3$ ceramics. However, if the sintering temperature is not high enough for some calcined powders, the random-site type can be changed to the space charge type.

Keywords: Diffused phase; Synthesized method; Order: space charge polarizations

1. Introduction

The complex perovskite type relaxor ferroelectric (RFE) materials show the $A(B'B'')O_3$ structure where the B' site and B'' site can be occupied by different metal cations which cause the compositional fluctuation effect. The diffused phase nature is described by Smolensky who suggests that there exists different Curie temperature T_c in the microregions and the broad-peak dielectric permittivity is induced [1,2]. Setter and Cross report that the diffused phase property changes to a sharp ferroelectric phase when the B site ordering degree is increased by thermal treatment in $Pb(Sc_{1/2}Ta_{1/2})O_3$ (PST) ceramics [3,4].

The classical relaxor $Pb(Mg_{1/3}Nb_{2/3})O_3$ (PMN) families have a 1:2 ratio of B-site cations. It is different with the 1:1 ratio of B-site cations for $Pb(Sc_{1/2}Ta_{1/2})O_3$ family ceramic. Currently, there are two models, the space-charge model and the random-site model, to explain the 1:1 ordered phenomenon in PMN family relaxors [5–9]. In the space-charge model, the space charge polarization is easily induced by increasing the 1:1 ordered domain and the 1:1 ordered domain is not easily grew by increasing the sintering temperature [5]. In the random-site model, the space charge polarization is vanished even if the 1:1 ordered domain is increased. Moreover, the 1:1 ordered region can be coarsened by the thermal treatments [6]. Based on these physical concepts, we can use the diffused phase degree to determine the ordering state and use the space charge polarization to determine the ordering type, the space charge type or the random site type, for the relaxor ferroelectric ceramics.

$Pb(Fe_{2/3}W_{1/3})O_3$ (PFW) is one of the classical RFE materials where the dielectric loss is high because of the p type carriers [10–14]. Its dielectric properties can be adjusted

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by mixing other compositions, doping other dopants or changing synthesized methods [12–27]. Szwagierczak and Kulawik [12] and Zhou et al. [13,14] report that the dielectric loss and the second onset of dielectric peak are suppressed when doping manganese in the PFW ceramics. Mitoseriu et al. report that the lattice structure and the dielectric properties can be adjusted by adding $PbTiO_3$ (PT) composition in PFW ceramics [16–19]. Authors also report that the dielectric loss is reduced, the space charge polarization is vanished, the diffused phase characteristic is enhanced, the ordering degree is reduced and the glassy behavior is reinforced when adding MnO in 0.7PFW–0.3PT ceramics [20,21]. Zhou et al. report that the diffused phase characteristics are enhanced by the lanthanum dopants in pure PFW ceramics, $Pb_{1-x}La_x(Fe_{2/3}W_{1/3})O_3$ and $Pb_{1-y}La_y(Fe_{(2+y)/3}W_{(1-y)/3})O_3$ [15]. Furthermore, the dielectric properties of $Pb_{1-x}La_x(Fe_{2/3}W_{1/3})_{0.65}Ti_{0.35}O_3$ ceramics have been investigated by authors [24]. When increasing the amounts of lanthanum dopants, the dielectric characteristics is changed to disorder relaxor state since the 1:1 ordered domain $Pb_{1-x}La_x(Fe_{1/2}W_{1/2})O_3$ is impeded [24]. When increasing sintering temperature for $Pb_{0.95}La_{0.05}(Fe_{2/3}W_{1/3})_{0.65}Ti_{0.35}O_3$ ceramics [25], the diffused phase transition is decreased and the space charge polarization is changed [25].

To obtain stoichiometric perovskite PMN, the columbite precursor method is reported by Swartz and Shrout [11,22]. Zhou et al. also report that the higher dielectric constant, the obvious frequency dispersion and the second onset of dielectric peak are found by the columbite method for the pure PFW ceramics [23]. The IS synthesized method different from the columbite precursor method has been used to synthesize 0.75PFW–0.25PT–MnO and 0.75PFW–0.25PT ceramics by authors [26,27]. The diffused phase nature is reduced and the dielectric property is changed from relaxor like behavior to normal ferroelectric state by using the IS synthesized method. However, the space charge polarization is reduced for 0.75PFW–0.25PT–MnO ceramics and enhanced for 0.75PFW–0.25PT ceramics by the IS synthesized method. The glassy behavior and the freezing process are also changed by the IS synthesized method. It is suggested that the charge balance of nanopolarizations is the response mechanism for the random-site order enhanced by the IS synthesized method, and the local polarizations are affected by the ordering degree and the local field [26,27]. To more understand the effects of synthesized methods, the DS synthesized method and the IS synthesized method are used to fabricate $Pb_{0.95}La_{0.05}(Fe_{2/3}W_{1/3})_{0.65}Ti_{0.35}O_3$ ceramics. The low-field dielectric responses are investigated, the diffused phase degree is estimated by using the empirical law and the space charge polarization is discussed by using two ordering models.

2. Experimental procedures

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 $Pb_{0.95}La_{0.05}(Fe_{2/3}W_{1/3})_{1-x}Ti_xO_3$, $x = 0.2$, 0.3, 0.35, 0.4 and 0.5, were synthesized by calcining at 750 °C for 2 h, then followed by pulverization. After that, some different preparative routes were followed as below:

(1) 0.35PTLa: The $Pb_{0.95}La_{0.05}(Fe_{2/3}W_{1/3})_{0.65}Ti_{0.35}O_3$ calcined powders were directly pressed into a disk (called the DS method).
(2) 0.3 + 0.4PTLa: The $Pb_{0.95}La_{0.05}(Fe_{2/3}W_{1/3})_{0.7}Ti_{0.3}O_3$ (0.3PTLa) calcined powders and the $Pb_{0.95}La_{0.05}(Fe_{2/3}W_{1/3})_{0.6}Ti_{0.4}O_3$ (0.3PTLa) calcined powders were mixed again according to the $Pb_{0.95}La_{0.05}(Fe_{2/3}W_{1/3})_{0.65}Ti_{0.35}O_3$ equation and then pressed into a disk (called the IS method).
(3) 0.2 + 0.5PTLa: The $Pb_{0.95}La_{0.05}(Fe_{2/3}W_{1/3})_{0.8}Ti_{0.2}O_3$ (0.2PTLa) calcined powders and the $Pb_{0.95}La_{0.05}(Fe_{2/3}W_{1/3})_{0.5}Ti_{0.5}O_3$ (0.5PTLa) calcined powders were mixed again according to the $Pb_{0.95}La_{0.05}(Fe_{2/3}W_{1/3})_{0.65}Ti_{0.35}O_3$ equation and then pressed into a disk (called the IS method).

All the samples above are synthesized by different methods, but the composition of each sample is the same. Before pressing into a disk, all of the powders were milled with 8 wt.% of a 5% PVA solution. These samples were pressed into a disk of 12-mm diameter and 2-mm thickness. Specimens were sintered isothermally at a heating rate of 5 °C/min at the same sintering temperature 925 °C for 2 h. In order to measure the electrical properties, silver paste is coated to form electrodes on both sides of the samples, and then subsequently fired at 750 °C for 25 min. The dielectric properties of the samples are measured using an impedance analyzer (HP4294A). The phase relations for the sintered samples were identified using an X-ray diffractometer (XRD) and microstructures were observed using a scanning electron microscope (SEM).

3. Experimental results and theoretical interpretations

3.1. Interpretation of the X-ray patterns and the SEM images

Fig. 1 shows the normalized X-ray diffraction patterns of 0.35PTLa, 0.3 + 0.4PTLa and 0.2 + 0.5PTLa ceramics. The maximum intensity peak (0 0 1) is used to normalize the X-ray patterns separately. In Fig. 1, the pure ABO_3 perovskite structure is observed and the pyrochlore phase does not obviously be detected [16–19,24–27]. It is concluded that the pure perovskite structure can be synthesized for $Pb_{0.95}La_{0.05}(Fe_{2/3}W_{1/3})_{0.65}Ti_{0.35}O_3$ by using the DS and IS synthesized methods. This result is similar to that of the previous reports [26,27].

Fig. 2 shows the SEM images of 0.35PTLa, 0.3 + 0.4PTLa and 0.2 + 0.5PTLa ceramics. In Fig. 2, the pyrochlore phase is not obviously found for all samples. This result is corresponding to the X-ray patterns. Comparing Fig. 2(a)–(c), the grain size of the 0.35PTLa ceramic is the largest. When synthesizing by the IS method, the grain size becomes smaller. The average grain size estimated by the log-normal size distribution model is 5.3, 4.48 and 3.89 μm for 0.35PTLa, 0.3 + 0.4PTLa and 0.2 + 0.5PTLa ceramics respectively [28]. This result is different from that of the previous reports [26,27]. In the previous reports, the grain size is enlarged by the IS synthesized

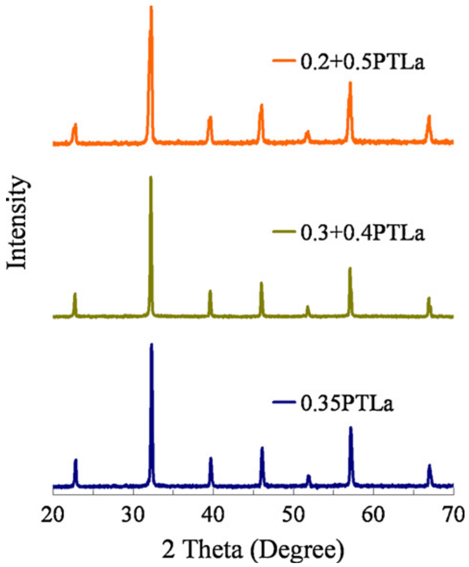

Fig. 1. The Bragg peaks of 2θ in the range between 20° and 70° for 0.35PTLa, 0.3 + 0.4PTLa and 0.2 + 0.5PTLa ceramics.

method. According to the previous reports [16–21], the sintering temperature of $(1-x)$PFW–xPT based ceramics is increased when the amounts of $PbTiO_3$ compositions are increased since the $PbTiO_3$ ceramics exist higher sintering temperature (about 1200 °C) than that of $Pb(Fe_{2/3}W_{1/3})O_3$ ceramics (about 900 °C). It is concluded that 0.3 + 0.4PTLa and 0.2 + 0.5PTLa behave the higher-sintering-temperature characteristics compared with 0.35PTLa since the sintering temperature of 0.4PTLa and 0.5PTLa is higher. Furthermore, all samples are sintered at the same temperature. Therefore, the grain sizes of 0.3 + 0.4PTLa and 0.2 + 0.5PTLa are smaller than that of 0.35PTLa. Comparing Fig. 2 (b) and (c), the grain size of 0.2 + 0.5PTLa is smaller than that of 0.3 + 0.4PTLa since the sintering temperature of 0.5PTLa is higher than that of 0.4PTLa. In conclusions, it is inferred that 0.4PTLa and 0.5PTLa behave more high sintering temperature compared with 0.35PTLa, and then induce higher sintering temperature and cause smaller grain size for 0.3 + 0.4PTLa and 0.2 + 0.5PTLa. Furthermore, the sintering temperature always affects the dielectric properties for relaxor ferroelectrics [3–6,25]. The higher sintering temperature usually accompanies with the sharper temperature-dielectric constant and the more ordering degree of B-site cations. Regarding the grain structure in Fig. 2, the distributions of grain size of 0.3 + 0.4PTLa and 0.2 + 0.5PTLa are more uniform compared with 0.35PTLa. This result is similar to that of the previous reports [26,27].

According to the X-ray patterns and the SEM images, it is concluded that the solid solution is formed with the pure perovskite structure no matter using the DS synthesized method or the IS synthesized method. Furthermore, the microstructure of the samples is changed by the synthesized method and the sintering temperature [25]. The aim of the present work is investigating the effects of the DS and IS synthesized methods. To avoid the interferences of sintering temperature and exactly investigate the effects of synthesized method, all samples are investigated below at the same sintering temperature.

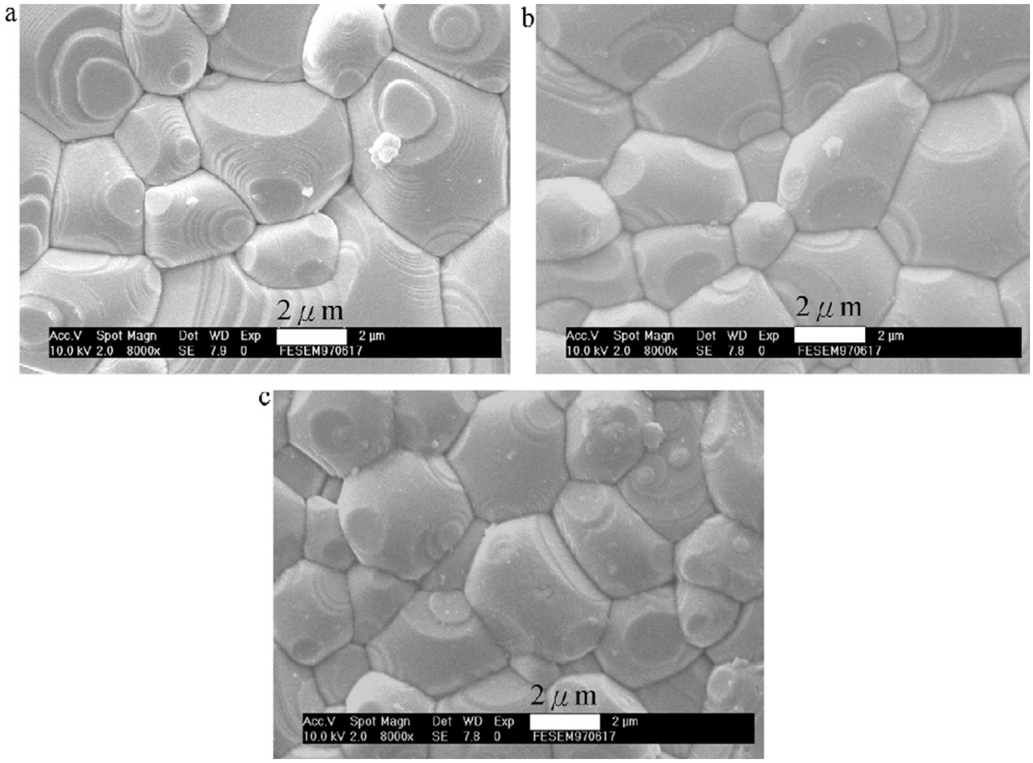

Fig. 2. The SEM images of (a) 0.35PTLa, (b) 0.3 + 0.4PTLa and (c) 0.2 + 0.5PTLa ceramics.

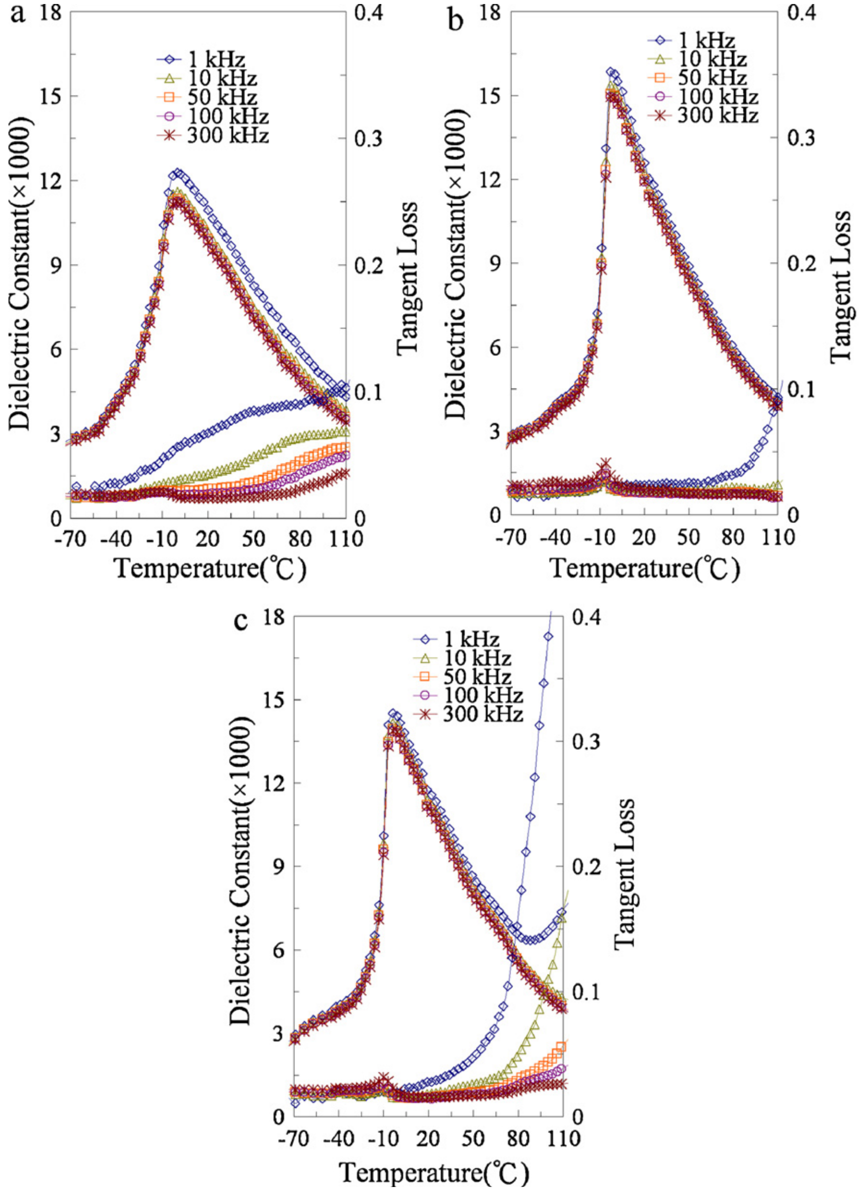

Fig. 3. The dielectric constant and the dielectric loss as a function of temperature for (a) 0.35PTLa, (b) 0.3 + 0.4PTLa and (c) 0.2 + 0.5PTLa ceramics at different frequencies.

3.2. *Interpretation of the dielectric properties and the space charge polarization*

Fig. 3 shows the dielectric constant and the dielectric loss as a function of temperature at different frequencies for 0.35PTLa, 0.3 + 0.4PTLa and 0.2 + 0.5PTLa ceramics. Inspecting Fig. 3, the broad temperature-dielectric constant and the lower maximum-dielectric constant are shown for 0.35PTLa samples, and are changed to the sharper temperature-dielectric constant and the higher maximum-dielectric constant by using the IS synthesized method, 0.3 + 0.4PTLa and 0.2 + 0.5PTLa samples. Furthermore, the 0.35PTLa ceramics exhibit a low dielectric loss and is changed to a more low dielectric loss when using the IS synthesized method for 0.3 + 0.4PTLa samples. On the other one, the dielectric loss of 0.35PTLa ceramics is changed to a more high dielectric loss at low frequency and high temperature when using the IS synthesized method for 0.2 + 0.5PTLa ceramics. The maximum dielectric constant corresponding to the ferroelectric–paraelectric transition is increased by using the IS synthesized method. This result is similar to the previous reports [26,27]. In Fig. 3(c), beside the maxima corresponding to the ferroelectric–paraelectric transition, the dielectric constant is increased again when the temperature is increased in the paraelectric region. The phenomenon is called the second onset of dielectric peak. Its response mechanism is attributed to the dielectric relaxation [12,13]. Zhou et al. [13] and Szwagierczak and Kulawik [12] suggest that the polarization mechanism of the second onset of dielectric peak is relative to the space charge polarization. The space charge polarization is induced from the charge imbalance of nanopolarization [5–9]. Besides, the space charge polarization is also induced from the conductive carriers [12–14,20,21]. When the frequency is increased, the space charge polarization is diminished since the relaxation time (the switching velocity) is too long to exhibit a time lag with respect to the external field [12–14,20,21]. According to the Debye theory ($\varepsilon = \varepsilon_s/1 + (\omega\tau)^2$, ε is the dielectric constant, ε_s is the static dielectric constant, ω is the angular frequency, τ is the relaxation time of dipoles) [29,30], the dielectric constant is decreased with increasing the frequency and is vanished when the frequency is high enough. Comparing Fig. 3(a)–(c), it is concluded that the space charge polarization is obviously induced and the dielectric loss is enhanced by the IS synthesized method for 0.2 + 0.5PTLa ceramics. For the other samples (0.3 + 0.4PTLa), the space charge polarization is not obviously changed and the dielectric loss is decreased by the IS synthesized method for 0.3 + 0.4PTLa ceramics.

3.3. *Interpretation of the dielectric data in the frame of the empirical law*

Within the diffused phase transition (DPT) behavior in relaxors, the heterogenous composition concept is suggested by Smolensky who considers that the Curie temperature T_c distributes following the Gauss law due to the different T_c polarization microregions which are caused by the compositional fluctuation [1]. Smolensky's model well describes the total DPT relaxors, but it is not suitable for the incomplete DPT relaxors. The empirical laws are individually proposed by Burfoot et al. and Eiras et al. who modify the Smolensky's equation according to the experimental results [31,32]. Until now, several researches still employ these empirical laws to successfully discuss the DPT phenomenon of the relaxor [17,31–37]. Recently, authors show that the fitting curves are the same between them and the equation proposed by Eiras et al. is more suitable to describe the behavior of DPT relaxors [38,39]. The equation is shown as below:

$$\varepsilon = \frac{\varepsilon_m}{1 + ((T - T_m)/\Delta)\xi} \tag{1}$$

where ε_m is the maximum dielectric constant corresponding with the temperature T_m. ξ value which denotes diffusive

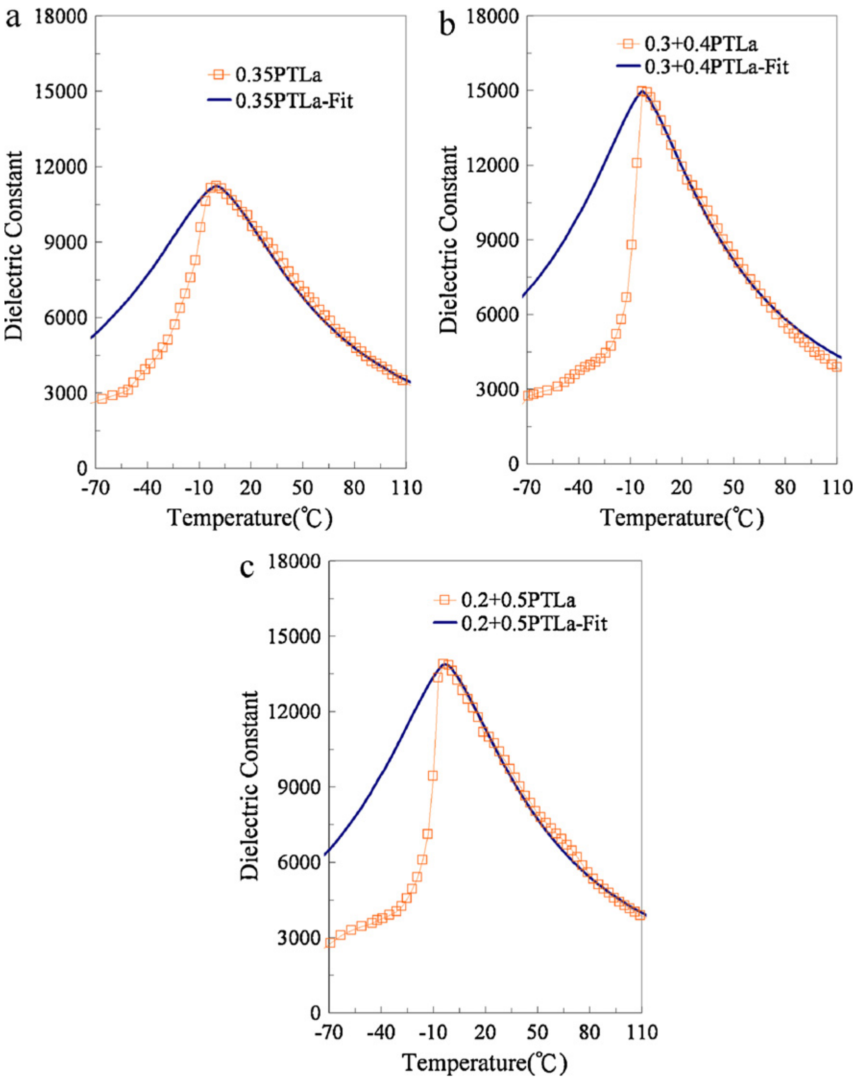

Fig. 4. The experimental data and the fitting result of the temperature-dielectric constant for (a) 0.35PTLa, (b) 0.3 + 0.4PTLa and (c) 0.2 + 0.5PTLa ceramics at $f = 300$ kHz.

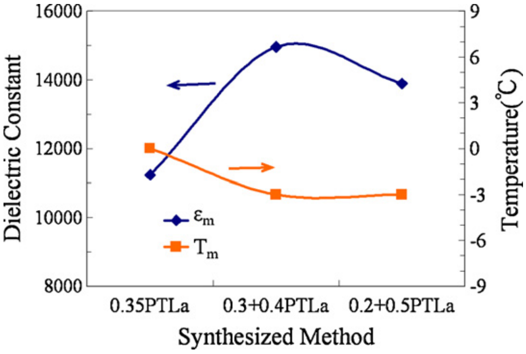

Fig. 5. The dependence of the maximum dielectric constant ε_m and the diffused phase transition temperature T_m for 0.35PTLa, 0.3 + 0.4PTLa and 0.2 + 0.5PTLa ceramics at $f = 300$ kHz.

parameter is in the range between 1 and 2. It shows the normal ferroelectric characteristic as the ξ value nears 1 and shows the total DPT relaxor characteristic as the ξ value nears 2. Δ represents the diffusive extension and the diffusion characteristic is more obvious as Δ value is larger [17,31–39].

As mentioned before, the second onset of dielectric peak is only observed in 0.2 + 0.5PTLa ceramics and disappears at higher frequency because the space charge polarization is a time lag with respect to the higher frequency field. To avoid the interference of space charge polarization and exactly investigate the diffused phase degree, only the 300 kHz temperature-dielectric constant is used to discuss the diffused phase phenomenon by using Eq. (1). Fig. 4 shows the experimental data of the dielectric constant as a function of temperature at 300 kHz frequency and their fitting results by using Eq. (1) for 0.35PTLa, 0.3 + 0.4PTLa and 0.2 + 0.5PTLa ceramics. In Fig. 4, the maximum dielectric constant is enhanced and the temperature-dielectric constant is sharper by using the IS synthesized method. However, the diffused phase transition temperature (T_m) corresponding to the maximum dielectric constant (ε_m) is not obviously shifted when changing the synthesized method. This result is similar to the previous reports [23,26,27]. Fig. 5 shows the maximum dielectric constant ε_m and the diffused phase transition temperature T_m for 0.35PTLa, 0.3 + 0.4PTLa and 0.2 + 0.5PTLa ceramics. In Fig. 4, the fitting curves well describe the dielectric behavior at $T > T_m$ but deviate at $T < T_m$. These phenomena are similar with other reports [17,32]. Fig. 6 shows the synthesized dependence of the ξ value and the Δ value of 0.35PTLa, 0.3 + 0.4PTLa and 0.2 + 0.5PTLa ceramics. In Fig. 6, the values of ξ and Δ are decreased when using the IS synthesized methods. The results exhibit that the diffused phase characteristic change from the more DPT relaxor to the normal ferroelectric behavior [17,31–39]. According to many reports, the normal ferroelectric property is always accompanied with the long range order of B-site cations [3–9,17]. Inspecting Figs. 3 and 6, it is found that the values of ξ and Δ are decreased by using the IS synthesized method. Due to the IS synthesized method, the space charge polarization is not evidently changed for 0.3 + 0.4PTLa ceramics and enhanced for 0.2 + 0.5PTLa ceramics. According to the ordering models [5–9], if the ordering degree and the space charge polarization are enhanced at the same time, it can be concluded that this ordering state is attributed the space-charge type. On the other one, the ordering state is attributed the random-site type when the ordering degree is enhanced and the space charge polarization is not obviously changed at the same time.

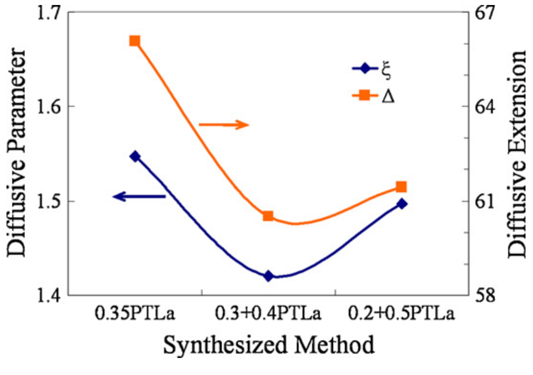

Fig. 6. The dependence of the diffusive parameters and the diffusive extensions for 0.35PTLa, 0.3 + 0.4PTLa and 0.2 + 0.5PTLa ceramics at $f = 300$ kHz.

4. Discussions and conclusions

In the present work, the calcined temperature, the sintering temperature and the composition are the same for all samples. The only difference is 0.3 + 0.4PTLa (0.2 + 0.5PTLa) ceramics are mixed again with $Pb_{0.95}La_{0.05}(Fe_{2/3}W_{1/3})_{0.7}Ti_{0.3}O_3$ and $Pb_{0.95}La_{0.05}(Fe_{2/3}W_{1/3})_{0.6}Ti_{0.4}O_3$ ($Pb_{0.95}La_{0.05}(Fe_{2/3}W_{1/3})_{0.8}Ti_{0.2}O_3$ and $Pb_{0.95}La_{0.05}(Fe_{2/3}W_{1/3})_{0.5}Ti_{0.5}O_3$) calcined powders. The same synthesized processes are also discussed for $0.75Pb(Fe_{2/3}W_{1/3})O_3$–$0.25PbTiO_3$ (0.25PT) and $0.75Pb(Fe_{2/3}W_{1/3})O_3$–$0.25PbTiO_3$–0.15 wt.% MnO (0.25PTMn) ceramics in the previous reports [26,27]. In the previous reports, their X-ray patterns show the pure perovskite structure no matter using the DS synthesized method or the IS synthesized method. This result is similar to the present work mentioned in Fig. 1. But their grain size are enlarged by the IS synthesized method for 0.25PT and 0.25PTMn in the previous reports [26,27]. This result is different from the present work mentioned in Fig. 2. Regarding the dielectric properties, the more ordering degree with the random-site type for 0.25PTMn and the more ordering degree with the space charge type for 0.25PT are enhanced by the IS synthesized method. Therefore, it is concluded that the ordering degree can be enhanced by the IS synthesized method. But the ordering type cannot be determined by the IS synthesized method. Furthermore, it is suggested that the charge balance and the conductive carriers of their calcined powders (IS synthesized method) are the response mechanisms to determine the ordering type, the random-site type or the space charge type [26,27]. In the present work, 0.65PFW–0.35PT doped lanthanum samples are synthesized by the DS and IS synthesized method. Furthermore, the lanthanum dopants can decrease the ordering degree, the space charge polarization, the charge imbalance of nanopolarization and the conductive carriers for 0.65PFW–0.35PT ceramics according to the previous report [24]. It is concluded that the calcined powder of $Pb_{0.95}La_{0.05}(Fe_{2/3}W_{1/3})_{1-x}Ti_xO_3$ are less charge imbalance and conductive carriers. Therefore, it is inferred that the ordering degree with random-site type should be enhanced by the IS synthesized method (resembled as 0.25PTMn ceramics) for $Pb_{0.95}La_{0.05}(Fe_{2/3}W_{1/3})_{0.65}Ti_{0.35}O_3$ ceramics. In the present work, the ordering type of 0.3 + 0.4PTLa is the same as the above inference but the ordering type of 0.2 + 0.5PTLa is different from the above inference caused by the IS synthesized method. According to the previous report [25], the ordering degree with the random-site type can be enhanced by increasing the sintering temperature for $Pb_{0.95}La_{0.05}(Fe_{2/3}W_{1/3})_{0.65}Ti_{0.35}O_3$ ceramics when the sintering temperature is in the lower temperature range. Furthermore, the $(1-x)$PFW–xPT based ceramics behave higher sintering temperature when the $PbTiO_3$ compositions are increased [16–21]. Therefore, it is reasonable inferred that 0.5PTLa exhibits the highest sintering temperature and 0.4PTLa exhibits the second highest sintering temperature in the present work. At the same time, it is suggested that the sintering temperature is too low to induce the ordering state with the space charge type for 0.2 + 0.5PTLa ceramics. The evidence is proved by the microstructure and shown in Fig. 2, the grain sizes of 0.3 + 0.4PTLa and 0.2 + 0.5PTLa are decreased by the IS synthesized method and that of 0.2 + 0.5PTLa is the smallest. According to the previous discussions, it is suggested that the 1:1 ordered domain with the random-site type can be enhanced by the IS synthesized method at the same sintering temperature when their calcined powders are less charge imbalance and conductive carriers. But the ordering type can be changed to the space charge type when their calcined powders behave too high sintering temperature when using the IS synthesized method.

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References

[1] G.A. Smolenskii, Physical phenomena in ferroelectrics with diffused phase transition, J. Phys. Soc. Jpn. 28 (Suppl.) (1970) 26–37.

[2] V.V. Kirilov, V.A. Isupov, Relaxation polarization of $PbMg_{1/3}Nb_{2/3}$ (PMN) – a ferroelectric with a diffused phase transition, Ferroelectrics 5 (1973) 3–9.

[3] N. Setter, L.E. Cross, The role of B-site cation disorder in diffuse phase transition behavior of perovskite ferroelectrics, J. Appl. Phys. 51 (1980) 4356–4360.

[4] N. Setter, L.E. Cross, The contribution of structural disorder to diffused phase transitions in ferroelectrics, J. Mater. Sci. 15 (1982) 2478–2482.

[5] J. Chen, H.M. Chan, M.P. Harmer, Ordering structure and dielectric properties of undoped and La/Na-doped $Pb(Mg_{1/3}Nb_{2/3})O_3$, J. Am. Ceram. Soc. 72 (1989) 593–598.

[6] M.A. Akbas, P.K. Davies, Domain growth in $Pb(Mg_{1/3}Ta_{2/3})O_3$ perovskite relaxor ferroelectric oxides, J. Am. Ceram. Soc. 80 (1997) 2933–2936.

[7] M.A. Akbas, P.K. Davies, Ordering-induced microstructures and microwave dielectric properties of the BMN–BZ system, J. Am. Ceram. Soc. 81 (1998) 670–676.

[8] P.K. Davies, M.A. Akbas, Chemical order in PMN-related relaxors: structure, stability, modification, an impact on properties, J. Phys. Chem. Solids 61 (2000) 159–166.

[9] Z. Xu, S.M. Gupta, D. Viehland, Dielectric imaging of atomic ordering in undoped and La-doped $Pb(Mg_{1/3}Nb_{2/3})O_3$, J. Am. Ceram. Soc. 83 (2000) 181–188.

[10] G.A. Smolenskii, A.I. Agranovskaya, V.A. Isupov, New ferroelectrics of complex compound, Sov. Phys. Solid State 1 (1959) 907–908.

[11] T.R. Shrout, A. Halliyal, Preparation of lead-based ferroelectric relaxors for capacitors, Am. Ceram. Soc. Bull. 66 (1987) 704–711.

[12] D. Szwagierczak, J. Kulawik, Influence of MnO_2 and Co_3O_4 dopants on dielectric properties of $Pb(Fe_{2/3}W_{1/3})O_3$ ceramics, J. Eur. Ceram. Soc. 25 (2005) 1657–1662.

[13] L. Zhou, P.M. Vilarinho, J.L. Baptista, The characteristics of the diffuse phase transition in Mn doped $Pb(Fe_{2/3}W_{1/3})O_3$ relaxor ceramics, J. Appl. Phys. 85 (1999) 2312–2327.

[14] L. Zhou, P.M. Vilarinho, J.L. Baptista, Effects of annealing treatment on the dielectric properties of manganese-modified $Pb(Fe_{2/3}W_{1/3})O_3$ ceramics, J. Mater. Sci. 33 (1998) 2673–2677.

[15] L. Zhou, P.M. Vilarinho, P.Q. Mantas, J.L. Baptista, E. Fortunato, The effects of La on the dielectric properties of lead iron tungstate $Pb(Fe_{2/3}W_{1/3})O_3$ relaxor ceramics, J. Eur. Ceram. Soc. 20 (2000) 1035–1041.

[16] L. Mitoseriu, P.M. Vilarinho, J.L. Baptista, Phase coexistence in $Pb(Fe_{2/3}W_{1/3})O_3$–$PbTiO_3$ solid solutions, Appl. Phys. Lett. 80 (2002) 4422–4424.

[17] L. Mitoseriu, A. Stancu, C. Fedor, P.M. Vilarinho, Analysis of the composition-induced transition from relaxor to ferroelectric state in $PbFe_{2/3}W_{1/3}O_3$–$PbTiO_3$ solid solutions, J. Appl. Phys. 94 (2003) 1918–1925.

[18] L. Mitoseriu, P.M. Vilarinho, M. Viviani, J.L. Baptista, Structural study of $Pb(Fe_{2/3}W_{1/3})O_3$–$PbTiO_3$ system, Mater. Lett. 57 (2002) 609–614.

[19] L. Mitoseriu, M.M. Carnasciali, P. Piaggio, P. Nanni, Raman investigation of the composition and temperature-induced phase transition in $(1-x)Pb(Fe_{2/3}W_{1/3})O_3$–$x PbTiO_3$ ceramics, J. Appl. Phys. 96 (2004) 4378–4385.

[20] C.-S. Hong, S.-Y. Chu, W.-C. Su, R.-C. Chang, H.-H. Nien, Y.-D. Juang, Effects of the MnO additives on the properties of $Pb(Fe_{2/3}W_{1/3})$–$PbTiO_3$ relaxors: comparison of empirical model and experimental results, J. Appl. Phys. 101 (2007) 054117.

[21] C.-S. Hong, S.-Y. Chu, B.-J. Li, W.-C. Su, R.-C. Chang, H.-H. Nien, Y.-D. Juang, Investigation of the dielectric properties of MnO-additive $Pb(Fe_{2/3}W_{1/3})$–$PbTiO_3$ relaxors using the spin-glass model, J. Appl. Phys. 103 (2008) 094102.

[22] S.L. Swartz, T.R. Shrout, Fabrication of perovskite lead magnesium niobate, Mater. Res. Bull. 17 (1982) 1245–1250.

[23] L. Zhou, P.M. Vilarinho, J.L. Baptista, Synthesis and characterization of lead iron tungstate ceramics obtained by two preparation methods, Mater. Res. Bull. 29 (1994) 1193–1201.

[24] C.-S. Hong, S.-Y. Chu, C.-C. Tsai, C.-C. Hsu, Lanthanum dopant induced transition from the ferroelectric to the relaxor state in 0.7PFW–0.3PT ceramics, Ceram. Int. 37 (2011) 1911–1918.

[25] C.-S. Hong, S.-Y. Chu, C.-C. Hsu, Effects of the sintering temperature on the diffused phase transition and the spin-glassy behavior in $Pb_{0.95}La_{0.05}(Fe_{2/3}W_{1/3})_{0.65}Ti_{0.35}O_3$ ceramics, J. Appl. Phys. 107 (2010) 094110.

[26] C.-S. Hong, S.-Y. Chu, W.-C. Su, R.-C. Chang, H.-H. Nien, Y.-D. Juang, Investigation of the dielectric properties of MnO-additive $Pb(Fe_{2/3}W_{1/3})$–$PbTiO_3$ relaxors prepared by two different methods, J. Alloys Compd. 460 (2008) 658–667.

[27] C.-S. Hong, S.-Y. Chu, C.-C. Tsai, W.-C. Su, C.-C. Hsu, Effects of synthesized method on glassy behavior and freezing process of 0.75PFW–0.25PT ceramics, J. Appl. Phys. 109 (2011) 034106.

[28] M.I. Mendelson, Average grain size in polycrystalline ceramics, J. Am. Ceram. Soc. 52 (1969) 443–446.

[29] K. Uchino, Ferroelectric Devices, Marcel Dekker, New York, 2000.

[30] L.L. Hench, J.K. West, Principles of Electronic Ceramics, Wiley, New York, 1990.

[31] H.T. Martirena, J.C. Burfoot, Grain-size and pressure effects on the dielectric and piezoelectric properties of hot-pressed PZT-5, Ferroelectrics 7 (1974) 151–152.

[32] I.A. Santos, J.A. Eiras, Phenomenological description of the diffuse phase transition in ferroelectrics, J. Phys.: Condens. Matter 13 (2001) 11733–11740.

[33] S. Huang, C. Feng, L. Chen, X. Wen, Dielectric properties of $SrBi_{2-x}Pr_xNb_2O_9$ ceramics ($x = 0$, 0.04 and 0.2), Solid State Commun. 133 (2005) 375–379.

[34] R. Yimnirun, S. Ananta, P. Laoratanakul, Dielectric and ferroelectric properties of lead magnesium niobate–lead zirconate titanate ceramics prepared by mixed-oxide method, J. Eur. Ceram. Soc. 25 (2005) 3235–3242.

[35] R.M. Piticescu, L. Mitoseriu, M. Viviani, V.M. Poladian, Preparation and characterisation of $Pb(Zr_{0.52}Ti_{0.48})_{0.975}Nb_{0.025}O_3$ ceramics modelling the device, J. Eur. Ceram. Soc. 25 (2005) 2491–2494.

[36] L. Cao, X. Yao, Z. Xu, Y. Feng, Research on dielectric and piezoelectric properties of Ta-doped $0.68Pb(Mg_{1/3}Nb_{2/3})O_3$–$0.32PbTiO_3$ ceramics, Ceram. Int. 30 (2004) 1373–1376.

[37] N. Vittayakorn, G. Rujijanagul, X. Tan, M.A. Marquardt, D.P. Cann, The morphotropic phase boundary and dielectric properties of the $xPb(Zr_{1/2}Ti_{1/2})O_3$–$(1 - x)Pb(Ni_{1/3}Nb_{2/3})O_3$ perovskite solid solution, J. Appl. Phys. 96 (2004) 5103–5109.

[38] C.-S. Hong, S.-Y. Chu, W.-C. Su, R.-C. Chang, H.-H. Nien, Y.-D. Juang, Dielectric behaviors of $Pb(Fe_{2/3}W_{1/3})$–$PbTiO_3$ relaxors: models comparison and numerical calculations, J. Appl. Phys. 101 (2007) 054120.

[39] C.-S. Hong, S.-Y. Chu, C.-C. Tsai, W.-C. Su, Investigating the physical meanings of diffused phase transition models, J. Alloys Compd. 509 (2011) 2216–2220.