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Influence of Mn-doping on phase transition characteristics and relaxor behaviour of lead lanthanum zirconate titanate ceramics

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Abstract

Changes in dielectric response features of lead lanthanum zirconate titanate (PLZT) ceramics by manganese addition are reported in the present work. Both the PLZT relaxor behaviour and the frequency dependence of the room temperature dielectric constant are shown to be suppressed by the addition of manganese. Similar results are obtained by applying a bias external field or by chemical reduction of PLZT samples, thus indicating the presence of an interrelationship between oxygen vacancies and the random 'bias' electric field. Consequently, the defects created by oxygen vacancies appear as the most important factor causing the disappearance of relaxor behaviour in Mn-doped PLZT ceramics. No modifications in the diffuse phase transition with the manganese content are found, which may be due to the persistence of compositional disorder. Additionally, it was verified that the spin glass model cannot be used to describe these observed effects.

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Keywords: B. Defects; C. Dielectric properties; D. Perovskites; D. PLZT; Ferroelectrics materials

1. Introduction

Over the last four decades, lanthanum-modified lead zirconate titanate solid solutions (PLZT) have been extensively investigated for their excellent properties and technologic relevance.[1] PLZT has been shown to be useful in many applications such as dynamical and volatile memory components, transducers, sensors and many other active and passive devices.[2–4] Particularly, $(Pb_{0.91}La_{0.09})(Zr_{0.65}Ti_{0.35})O_3$ ceramics, the so-called PLZT (9/65/35), is well-known for its high optical transparency and good electro-optical characteristics.[5]

The $(Pb,La)(Zr,Ti)O_3$ system has a perovskite-type (ABO_3) structure. These materials are characterised by a ferroelectric–paraelectric diffuse phase transition with relaxor character.[6] Cation vacancies are created to maintain the charge neutrality due to La^{+3} incorporation onto the PZT structure, producing a mixture of both A and B vacant sites. It is very important to elucidate clearly the type of defects involved in a given relaxor material, because the normal-to-relaxor transitions are directly related to the chemical/structural defects that act to break the translational invariance of the polarisation.[7]

Many models have been developed to explain the relaxor behaviour with diffuse phase transition of ferroelectric materials.[8–15] The compositional disorder, i.e. disorder in the arrangement of different ions on crystallographically equivalent sites, is a common feature of relaxors. The relaxor behaviour was first observed in perovskites with non-isovalent ions disorder, e.g. $Pb(Mg_{1/3}Nb_{2/3})O_3$ (PMN).[9] The compositional fluctuation model was developed by Smolenskii et al.[9] This model assumes that polar nano-regions (PNRs) have different chemical compositions as a result of the different location of ions onto A and B sites. In the vicinity of ferroelectric phase transition, a relaxor is characterised by a set of PNRs chaotically arranged in the crystal. Thus, relaxation processes coming from dynamics of PNRs govern crystal properties. Since there is compositional disorder, spatial fluctuations of local Curie temperature appear. Cross[10] extend this model, associating relaxor behaviour to thermally activated super-paraelectric clusters. This model supposes that the dynamics of polar clusters, based on compositional fluctuations, determine the frequency dispersion of the

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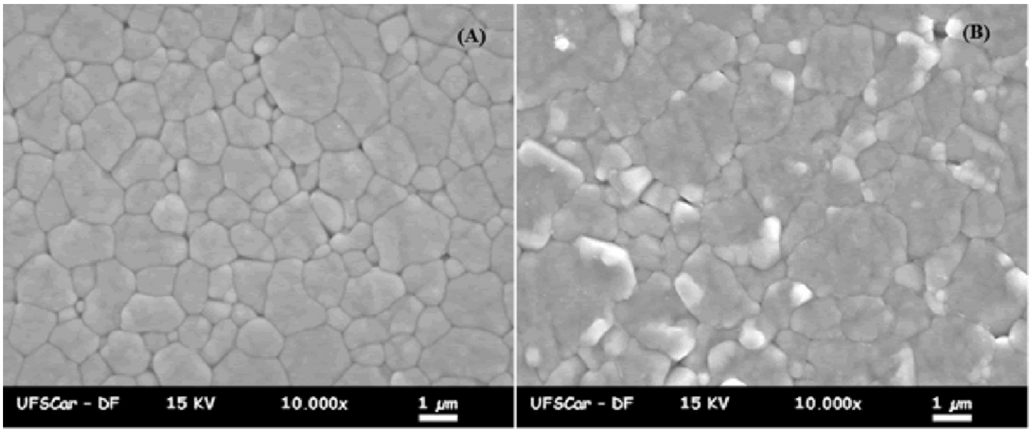

Fig. 1. SEM micrographs for (A) non-doped PLZT and (B) 3 wt.% MnO_2 doped PLZT samples.

permittivity. Moreover, Viehland et al.[11] showed that the cooperative interactions together with super-paraelectric clusters may produce spin-glass behaviour. On the other hand, Westphal et al.[12] linked the diffuseness of the ferroelectric phase transition to quenched random electric fields originating from charged compositional fluctuations. Furthermore, Glinchuk and Farhi[13] showed an order–disorder transition based on the random field theory. These authors conclude that the random polar sites are submerged in a highly polarisable receptor lattice and the dipole–dipole interactions are indirect and random. Meanwhile, Qian and Busill[14] have analysed an arbitrary field influence on dynamics and formation of polar clusters, which may originate in the nanometric chemical defects. The Glazounov and Tagantsev model,[15] called “breathing model”, consider the boundary or limit vibration of the polar nano-regions in terms of the interphase randomly fixed theory, developed for magnetic materials.

It has recently been observed that addition of MnO_2 to PZT solid solution tends to increase the mechanical quality factor and the electromechanical coupling factor, while decreasing the tetragonality. In addition, many interesting modifications in the dielectric response have been reported.[16] Furthermore, it is known that co-doping with softener (La^{3+}) and hardener (Fe^{3+} and Mn^{2+}) ions enhances the dielectric properties of PZT based materials.[17] On the other hand, it is also known that Mn^{2+} addition onto B-site of the PLZT structure produces oxygen vacancies according to the Pauling’s rules.[18]

The relaxor-to-normal dielectric behaviour in the Mn-doped PLZT system still remains unclear. In spite of the many models developed, there is no accurate explanation for the relaxor-to-normal crossover phenomena. In this context, the present work aims to study the influence of manganese addition on phase transition characteristics and relaxor behaviour of PLZT ceramics. The dielectric response for non-doped and Mn-doped PLZT is analysed in the frequency and temperature domain. The changes in the diffuse phase transition and relaxor character by the addition of manganese are discussed.

Table 1
Theoretical, absolute and relative densities of non-doped and Mn-doped PLZT samples.

Samples	Theoretical density (g/cm^3)	Absolute density (g/cm^3)	Relative density (%)
PLZT	7.14	6.85	96.0
PLZT–1Mn	7.58	7.24	95.5
PLZT–2Mn	7.62	7.30	95.8
PLZT–3Mn	7.62	7.28	95.6

2. Materials and methods

$Pb_{0.91}La_{0.09}(Zr_{0.65},Ti_{0.35})O_3 + xMnO_2$ ($x = 0$; 1; 2; 3 wt.%) powders, hereafter referred to as PLZT (for $x = 0$) or PLZT–xMn (for $x \neq 0$), were prepared by the conventional mixed oxide method. The oxides weighed according to the stoichiometry were mixed by ball milling in distilled water for 20 h. The slurry was dried and calcined in a covered alumina crucible at 850 °C for 3.5 h. Ceramic bodies were then formed by isostatic press and fired at 1250 °C for 5 h. Densities were measured according to Archimedes’ method. The obtained values are reported in Table 1. As it can be observed, densities of all fired ceramics were over 95% of their theoretical values. Disk-like ceramic bodies were polished to ensure parallel surfaces on which silver electrodes were deposited by sputtering.

Room temperature X-ray diffraction (XRD) patterns for non-doped and Mn-doped PLZT samples were collected using a Rigaku diffractometer with CuKα radiation for 2θ from 20° to 60° at 2°/min. Results revealed single-phase compounds with orthorhombic perovskite structure. Morphological study was performed by scanning electronic microscopy (SEM) with a JEOL instrument model JSM 5800 LV. SEM micrographs of polished and thermally etched surfaces of PLZT and PLZT–3Mn samples are shown in Fig. 1. The results reveal samples with a high density and low porosity. The statistical distribution of grain size was determined from SEM micrograph, for all the studied samples. Grain size as a function of manganese content is displayed in Fig. 2, where no significant differences in grain size are observed. EPR measurements were carried out using a Bruker ESP300E spectrometer operating in the X-band. Results confirm that the majority of manganese behaves like Mn^{2+}, which is in agreement with that reported by Glinchuk et al.[19] for PLZT with different lanthanum concentrations.

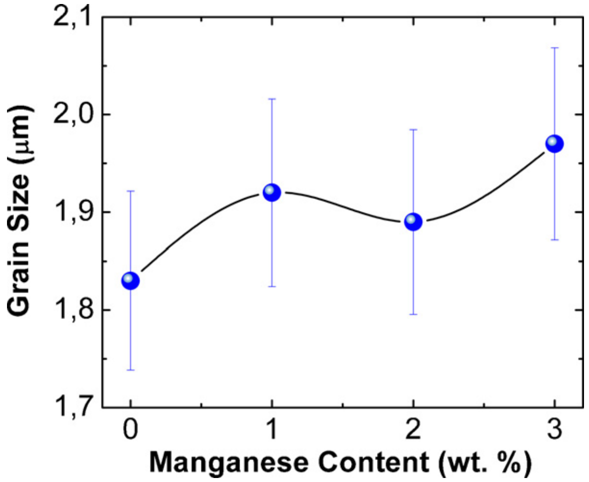

Fig. 2. Grain size as a function of the manganese content for non-doped and Mn-doped PLZT ceramics. The solid line is only a guide for the eye.

The impedance spectroscopy technique was used to obtain the dielectric response of the studied materials as a function of temperature and frequency. Admittance values were obtained from measurements performed in a HP4194A impedance analyzer. The frequency and temperature ranges of the measurements were 100 Hz–10 MHz and 15–700 K, respectively. All measurements were running at a heating and cooling rate of 2 K/min. The real and imaginary parts of dielectric permittivity were computed from the imaginary (susceptance, *B*) and real (conductance, *G*) parts of the complex admittance, respectively.

3. Results and discussion

3.1. Phase transition characteristics

Fig. 3 shows the temperature dependence of the real (ε') and imaginary (ε'') dielectric permittivity for non-doped and Mn-doped PLZT samples. For non-doped PLZT ceramic (Fig. 3(a)), an expected relaxor-like behaviour is observed. The temperature T_m, corresponding to the maximum value of dielectric constant (ε'_m), shifts to higher values, from 389 K to 404 K, in the frequency range from 1 kHz to 1 MHz. On the other hand, the temperature corresponding to the ε'' maximum (ε''_m) shifts to lower values, from 349 K to 380 K. Values of T_m are summarised in Table 2.

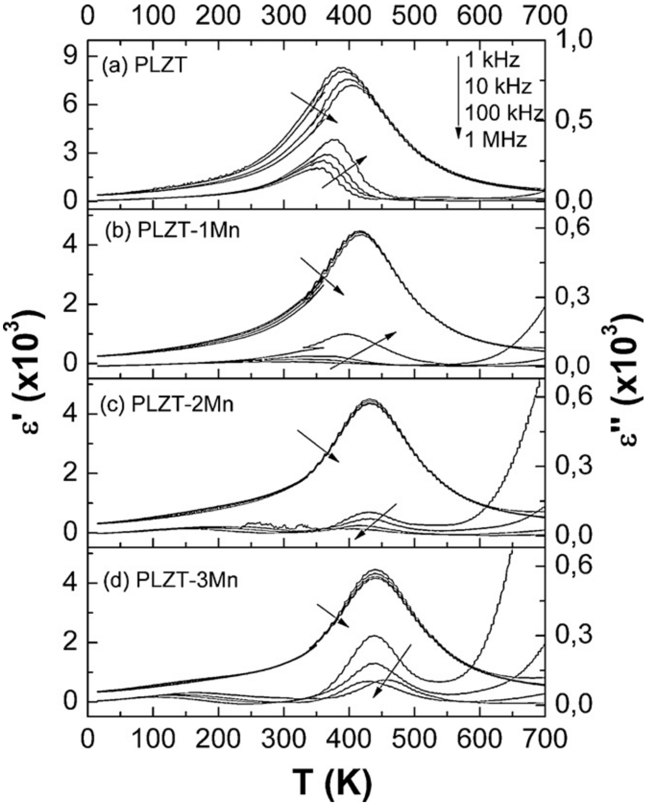

Fig. 3. Temperature dependence of the real ε' and imaginary ε'' parts of the permittivity for non-doped and Mn-doped PLZT ceramics, at several frequencies. Diffuse phase transition is observed for all studied materials. In addition, typical relaxor behaviour is shown for non-doped PLZT.

An evolution in dielectric properties and phase transition temperatures by Mn addition can be verified in Figs. 3(b), (c), and (d) for 1 wt.% Mn-doped PLZT (PLZT–1Mn), 2 wt.% Mn-doped PLZT (PLZT–2Mn) and 3 wt.% Mn-doped PLZT (PLZT–3Mn) ceramics, respectively. Permittivity values and transition temperatures for all studied materials are reported in Table 2. Lower permittivity values are obtained for Mn-doped samples compared with the non-doped sample. The transition temperature shift (ΔT_m) values present no regularity in either ε'_m or ε''_m, although in Mn-doped samples they are lower than in non-doped samples. As may be appreciated, the value of ε'_m for non-doped PLZT is higher than the value reported by Mohiddon et al.[20] ($\varepsilon'_m = 1758$) for PZT (65/35) ceramic. This increase in the dielectric constant can be attributed to the fact that La^{3+} doping increases the dielectric constant by creating A-site vacancies in the PZT lattice, thereby facilitating the motion of the ferroelectric domain walls. When the temperature rises, the lattice vibrations and the interaction between the vacancies also increase, which may be the cause for the increase in ε'_m and the corresponding T_m value.[21] In the same way, it may be observed that room temperature dielectric constant values decrease as manganese content rises, as can be verified in Table 2. This effect can be explained by taking into account

Table 2
Values of some dielectric properties and phase transition parameters obtained from dielectric permittivity versus temperature curves, at 1 MHz.

	PLZT	PLZT–1Mn	PLZT–2Mn	PLZT–3Mn
ε'_m	7204	4348	4342	4170
ε''_m	384	142	30	101
ε'^{a}	2640	1430	1350	1250
ε''^{a}	149	53	25	30
$T_{m\varepsilon'}$ (K)	404	420	432	440
$T_{m\varepsilon''}$ (K)	374	395	425	439
$\Delta T_{m\varepsilon'}$ (K)[b]	14	6	9	5
$\Delta T_{m\varepsilon''}$ (K)[b]	62	12	31	11
T_C (K)	482	491	490	494
C (10^5 K)	3,3	1,3	1,3	1,4

[a] Values at room temperature.
[b] $\Delta T_m = T_m$ (10 MHz)–T_m (100 Hz).

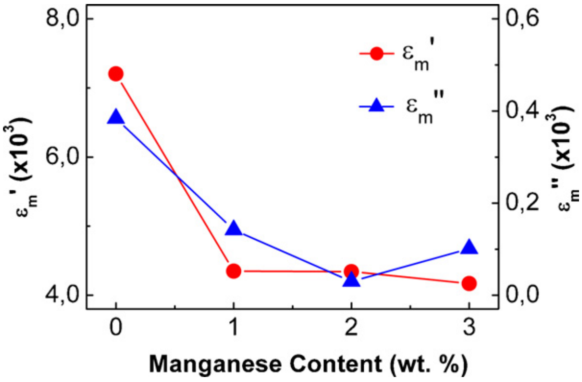

Fig. 4. Real and imaginary dielectric permittivity maximum as a function of manganese content, measured at 1 MHz. Solid lines are only a guide for the eye.

that Mn^{2+} onto B-site substitution provokes oxygen vacancies in the structure. These vacancies are sufficiently mobile to form complex defects to pining the domain walls, thereby reducing their mobility.[22,23] Domain wall motion reduction decreases the extrinsic response, so room temperature dielectric response decreases as manganese content rises. This interpretation has recently been used to explain the stabilisation of the dielectric and piezoelectric responses in Mn-doped PLZT.[24]

Fig. 4 shows the dependence of the dielectric permittivity maximum (real and imaginary parts) with the manganese content, at $f = 1$ MHz. As can be seen, the dielectric permittivity maximum decreases for Mn-doped PLZT compared to the value for non-doped PLZT. This may be due to two factors: (1) differences in ionic radii between B-site ions and manganese ion; (2) random electric field formation because of charge imbalance in the PLZT structure. The observed increase in the value of ε_m'' for PLZT–3Mn related to PLZT–1Mn and PLZT–2Mn can be explained by taking into account the experimented frequency inversion by imaginary dielectric permittivity for PLZT–3Mn (see Fig. 3).

It is well known that the distance between oxygen ions and the Mn^{2+} ion (1.790 Å) is smaller than the Ti–O distance (1.815 Å) or the Zr–O distance (1.937 Å).[25] So, substitution of Zr^{4+} or Ti^{4+} by Mn^{2+} leads to shrinkage of crystal cells.[26] If the Mn^{2+} content is increased, then the number of shrunk crystal cells in Mn-doped PLZT increases, and ultimately the local shrinkage of 3% Mn-doped PLZT compound is most severe. This crystal cell shrinkage could decrease the dipolar moment magnitude, leading to a decreasing in the maximum permittivity. Furthermore, it is well known that the manganese addition causes an additional charge imbalance, which may generate a strong and randomly distributed dc electric field. Viehland et al.[27] report that with the increment of dc external electric field the PMN dielectric values decrease significantly, while T_m is increased.

To evaluate the influence of the manganese on the phase transition, a modified Curie-Weiss equation is used[26]:

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

where ε_m represents the maximum dielectric constant and T_m the temperature at which this maximum occurs. The

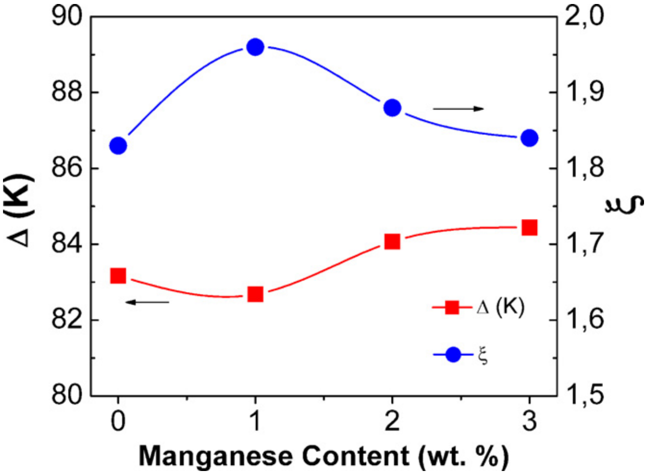

Fig. 5. Diffusivity exponent ξ and diffusivity coefficient Δ as a function of manganese content, calculated at $f = 1$ MHz. Solid lines are only a guide for the eye.

parameter Δ is a measure of the pick width and is considered the diffusivity coefficient. The exponent ξ, called the diffusivity exponent, indicates the character of the phase transition. In fact, $\xi = 1$ indicates a 'normal' ferroelectric phase transition, which is described by the approach proposed in Landau–Devonshire theory for ferroelectric phase transitions (first or second order phase transitions), while the value $\xi = 2$ represents a so-called 'complete' diffuse phase transition (DPT), verified in the theoretical limit of the Kirilov–Isupov approximation. Additionally, a ξ value between these limits ($1 < \xi < 2$) indicates a so-called 'incomplete' DPT, where the interaction between ferroelectric clusters is considered.[28–31]

Fig. 5 shows the dependence of the diffusivity parameters ξ and Δ as a function of manganese content, at $f = 1$ MHz. The parameter Δ shows no significant differences between non-doped and Mn-doped PLZT samples. The values are in the range of 82–85 (a difference of less than 5%). In the same way, the parameter ξ displays no significant difference either (a difference of less than 8%). The ξ values between 1.8 and 2.0 are characteristic of the broadened peaks observed in Fig. 3. Moreover, these values indicate that phase transition should be classified as incomplete DPT for all studied materials.

It has recently been reported for multiferroic perovskite PFW that the value Δ increases with the addition of manganese.[32] However, in our results the addition of manganese causes no changes in the phase transition diffusivity. Likewise, no tendency is observed in either Δ or ξ parameters for Mn-doped PLZT systems. These results suggest that A-site disorders caused by La^{3+} doping are responsible for the diffuse phase transition observed in all evaluated samples.

A diffuse phase transition in ferroelectrics occurs as a consequence of a structural disorder that breaks the translational invariance of the lattice. The type of diffuseness observed depends both on the nature and scale of the structural disorder. Impurities, point defects, extended defects, incomplete or inhomogeneous cation ordering, macroscopic fluctuations in chemical composition, etc., can lead to the smearing of the ferroelectric phase transition.[27] The broadening of the phase

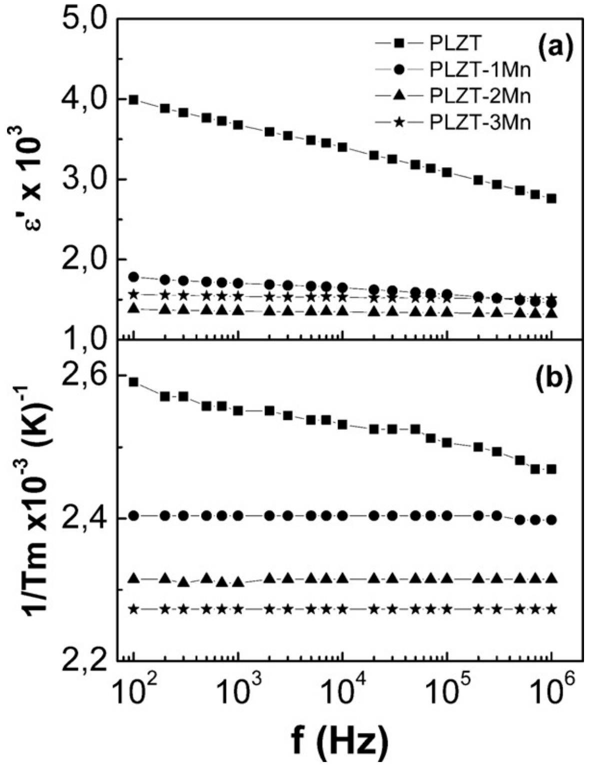

Fig. 6. Frequency dependence of (a) room temperature real permittivity and (b) temperature of the real permittivity maximum, for non-doped and Mn-doped PLZT ceramics.

transition peaks is an important characteristic of a disordered perovskite structure. Here, this effect can be attributed to the disorder in the arrangement of cations at A-site, occupied by Pb^{2+} and La^{3+}, and B-site, occupied by Mn^{2+}, Zr^{4+} and Ti^{4+}, and lattice vacancies, leading to local compositional fluctuations. Thus, a Curie point distribution is generated.[33,34]

3.2. Relaxor behaviour

As can be seen in Fig. 3(a), at temperatures below the transition temperature ($T < T_m$), the real permittivity ε' undergoes a strong frequency dispersion for the PLZT sample. However, at temperatures above the transition temperature ($T > T_m$), no frequency dependence of the ε' is observed. This is typical relaxor behaviour, as has been extensively reported.[35] Moreover, it is possible to observe that frequency dispersion decreases as manganese content rises, disappearing for PLZT–3Mn. Fig. 6(a) shows the frequency dependence of real permittivity for non-doped and Mn-doped PLZT ceramics, at room temperature. It is clearly seen that ε' depends linearly on the logarithmic of the frequency, as has been reported elsewhere.[36] However, dependence decreases significantly as manganese content increases, ε' becoming nearly frequency independent for PLZT–2Mn and PLZT–3Mn compounds, as happens to PLZT at low temperatures.[37] On the other hand, Fig. 6(b) shows the frequency dependence of temperature of the real permittivity maximum. In this case, it is also verified that the frequency dependence of T_m is strongly suppressed as manganese content increases.

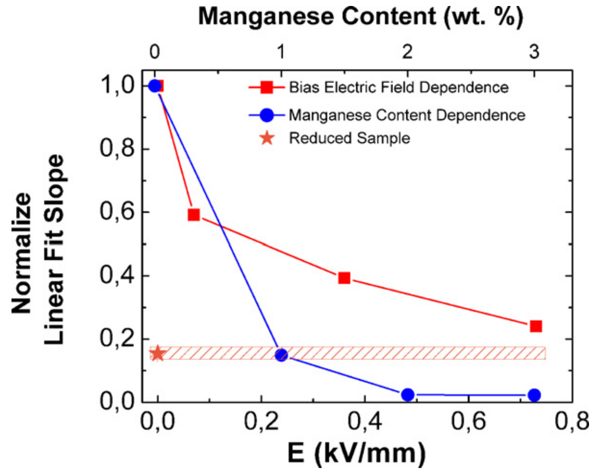

Fig. 7. Linear fit slope as a function of an external 'bias' electric field and as a function of the manganese content for non-doped and Mn-doped PLZT ceramics, respectively. The value for a reduced PLZT sample is also shown. Linear fit slope values were obtained from room temperature real permittivity versus frequency logarithm plots.

The observed behaviour indicates a possible lack of the PLZT relaxor character by manganese doping. It is well known that the PLZT relaxor behaviour degree depends on the La content.[38] For PLZT systems, the ferroelectric long-range order (LRO) is broken by La^{3+} ions with excess of A-site vacancies, which results in the formation of polar nano-regions (PNRs) rather than the establishment of the LRO ferroelectric state. Structural disorder and charge imbalance are regarded as being the origin of the relaxor properties. Thus, from the appearance of dynamic local PNRs, it becomes evident that PNRs are generally related to the origin of the relaxor properties.[38] However, the disappearance of the frequency dispersion seems to be caused by the manganese content in the Mn-doped PLZT ceramics. A possible explanation of this effect is the appearance of a random 'bias' electric field due to the presence of manganese in the PLZT structure. Hence, the potential barrier that can be overcome by the dipoles is enhanced. Since the relaxation time of many dipoles is equal to or higher than the 'observation' time, they become slow or frozen dipoles. These dipoles therefore do not contribute to the dielectric response. When the 'bias' electric field is increased, the slow dipole proportion also increases. As a consequence, the PNRs became macroscopic regions and the polarisation orientation mechanisms of the relaxor are shut down, as is reported for other relaxors.[39] Furthermore, the 'bias' electric field generated by the manganese addition may exert an influence on the domain wall mobility, thereby decreasing its contribution to the ac electric field dielectric response. Additionally, it is well known that substitution of Mn^{2+} onto B-site creates oxygen vacancies, which results in the formation of complex defects. These defects act as pinning centre leading to reduce domain wall motion, which in turn influences the relaxor behaviour.[40] The increase of oxygen vacancy by Mn doping in PLZT could also contribute to the random-field effect.

Fig. 7 shows the manganese content and 'bias' electric field dependences of the linear fit slope, computed from the dependence of ε' with the frequency logarithm (Fig. 6(a)). The linear fit slope for non-doped PLZT sample is assumed as a reference, and all other values are normalised in accordance to this slope. As can be observed, the linear fit slope values decrease with manganese addition in the PLZT structure. In the same way, a decrease in the linear fit slope values as 'bias' electric field increases is verified for a non-doped PLZT samples. This fact is in agreement with the hypothesis that an additional electric field, generated by manganese addition, causes the disappearance of the permittivity dispersion in PLZT–xMn system.

A non-doped PLZT sample was placed in high vacuum, at 700 °C, for 5 h in order to obtain a reduced sample. A heating rate of 30 °C/min and a cooling rate of 10 °C/min was applied. The room temperature dielectric constant in terms of the frequency was evaluated, thereby determining the linear fit slope for this dependence. The normalised linear fit slope value for reduced non-doped PLZT sample is displayed in Fig. 7. As can be observed, a significant decrease in the normalised linear fit slope is verified, similar to the obtained values from Mn-doped samples. This result indicates that there is an interrelationship between oxygen vacancies and the random 'bias' field generated by manganese addition. It is therefore possible to affirm that defects created by oxygen vacancies seem to be responsible for the disappearance of the relaxor characteristic in PLZT–xMn ceramics.

Other possible explanation for the disappearance of the relaxor behaviour in PLZT due to manganese addition could be the effect of domain interactions on the PLZT structure. This effect can be evaluated by using the Sherrington and Kirkpatrick model to determine the local order parameter. In the following equation[41,42]:

$$\chi = \frac{C\left[1-q(T)\right]}{T-T_C\left[1-q(T)\right]} \tag{2}$$

$q(T)$ is an order parameter which corresponds to the fraction of PNRs effectively frozen at a given time t and temperature T, based in the spin glass model.[11] The parameters C and T_C are the Curie-Weiss constant and the Curie-Weiss temperature, respectively. The values of C and T_C have been computed by fitting $\varepsilon'(T)$ data to Curie-Weiss law, and are reported in Table 2. The parameter $q(T)$ plays an important role in determining the dielectric properties of relaxor materials, and represents the correlation degree of the neighbouring cluster-sized moment.[33]

Fig. 8 shows the order parameters calculated as a function of the temperatures at different manganese contents. The $q(T)$ values are calculated from Eq. (2) using the dielectric permittivity experimental data and the obtained C and T_C values. As can be observed, the parameter $q(T)$ is approximately a linear function at temperatures below 450 K. The value of $q(T)$ is greater at lower temperatures, but tails to zero at temperatures close to 530 K for PLZT–2MN and PLZT–3Mn, while $q(T) = 0$ near to 550 K for PLZT and PLZT–1Mn. From the $q(T)$ definition, it is possible to identify the temperature at which the PNRs are frozen. Here the tailed effect is greater, which indicates that the freezing process is slower.[43] The independence of the tailed effect and the shape of the curves over the whole temperature range may be due to the fact that manganese addition does not modify PNR interactions. This may in turn be because the spin glass model could not be used to describe the frequency dispersion and the decrease in the relaxor character. In any case, the independence of domain interactions with manganese content does not mean that the domain-wall dynamics is not affected by manganese additions.

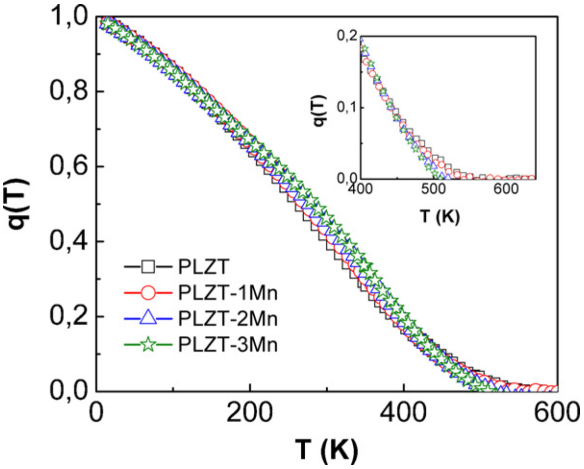

Fig. 8. The local order parameter as a function of temperature for different manganese content by using the spin-glass model for non-doped and Mn-doped PLZT ceramics.

4. Conclusions

The influence of manganese addition on dielectric properties and phase transition characteristics of lead lanthanum zirconate titanate (PLZT) ceramics is investigated. Expected relaxor behaviour is verified in PLZT ceramics. However, several changes in dielectric response features are obtained by manganese addition. The decrease of room temperature permittivity as manganese content rises seems to be a consequence of the extrinsic effect reduction by the domain wall pinning effect.

Dielectric responses of non-doped and Mn-doped PLZT samples are studied in terms of a modified Curie-Weiss. No appreciable difference in the diffusivity parameters is obtained for any of the studied compounds. Compositional disorders due to the presence of different ions onto both the A- and B-site of the perovskite structure seem to be responsible for the observed diffuse phase transition in these materials. Nevertheless, manganese addition reduces the frequency dependence of the temperature of the permittivity maximum until the relaxor character of PLZT system is removed. An additional electric field, caused by the defects arising from manganese addition, may account for the observed results. This hypothesis is confirmed by applying a dc electric field to a non-doped PLZT sample. In a chemically reduced PLZT sample, the temperature of the permittivity maximum is also shown frequency independent indicating an interrelationship between oxygen vacancies and the random 'bias' electric field. On the other hand, neighbourhood domain interactions are not modified by manganese additions. Thus, the spin-glass model can not be used to explain the observed behaviour.

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