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## Time-dependent ferroelectric transition in $Pb_{(1-x)}(Zr_{0.4}Ti_{0.6})_{(1-x/4)}O_3 - xLa$ system

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Ferroelectric transition involves tiny shift of ions within unit cell, thus being intrinsically a very fast process without apparent time-dependence. Contrary to this conventional wisdom, here we report a time-dependent ferroelectric transition, which occurs in hours. The system studied was  $Pb_{(1-x)}(Zr_{0.4}Ti_{0.6})_{(1-x/4)}O_3 - xLa$  system with relaxor-forming dopant  $La^{3+}$ . The time-dependent ferroelectric transition occurs at the ferroelectric/relaxor crossover composition range of  $0.09 < x \le 0.16$ . In these compositions, *in situ* Raman spectroscopy and transmission electron microscopy reveal very slow growth of ferroelectric transition can be understood as being caused by the slowing-down of the otherwise fast growth of polar nano-domains due to the random local field caused by  $La^{3+}$ , so that long time is needed to achieve long-range order macroscopic ferroelectric phase. © 2013 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4809577]

Ferroelectric transition involves long-range ordering of spontaneous polarization ( $P_S$ ), which is responsive to electric field, applied stress, and temperature.<sup>1</sup> Such multi-responsiveness makes ferroelectric transition the heart of most technologically important properties of ferroelectric materials, including piezoelectricity and pyroelectricity.<sup>2–5</sup>

The elementary atomic-level process of spontaneous polarization formation is the condensation of certain optical phonon mode, which is equivalent to a relative shift of positive and negative ions within a unit cell.<sup>1–3,6</sup> Such a process occurs at an extremely short time-scale of  $10^{-12}$ – $10^{-6}$  s, much faster than experimentally accessible cooling speed.<sup>7</sup> As a result, ferroelectric transition is expected to be independent of time at normal experimental time scale ( $10^{0}$ – $10^{3}$  s) and is merely as a function of temperature (called athermal).

Apart from few exceptions,<sup>8,9</sup> ferroelectric transitions so far reported seem consistent with the above basic notion and do not show appreciable time-dependence. In this letter, we report the kinetics of ferroelectric transition varies with La<sup>3+</sup> concentration in Pb<sub>(1-x)</sub>(Zr<sub>0.4</sub>Ti<sub>0.6</sub>)<sub>(1-x/4</sub>)O<sub>3</sub> – xLa (PZT-xLa in short) system. We found that normal time-independent ferroelectric transition behavior occurs only at low-La<sup>3+</sup> compositions; on the other hand, the ferroelectric transition takes place over an extraordinarily long time-scale of many hours at the crossover composition regime between normal ferroelectric and relaxor ferroelectric. We showed that the abnormal time-dependent ferroelectric transition can be understood as being caused by the slowing-down of the otherwise fast growth of polar nano-domains due to the random local field caused by La<sup>3+</sup>.

The kinetics of ferroelectric transition in PZT-*x*La system as a function of relaxor-forming dopant La<sup>3+</sup> was studied by Raman spectroscopy and dielectric measurement.

Sample exhibiting time-dependent ferroelectric transition was examined by *in situ* transmission electron microscopy (TEM). PZT-*x*La samples were prepared by a modified solid state reaction method, with starting chemicals of PbO (99.99%), La<sub>2</sub>O<sub>3</sub> (99.99%), ZrO<sub>2</sub> (99.9%), and TiO<sub>2</sub> (99.9%).<sup>10</sup> Two percent of excessive PbO and sealed crucibles were used to reduce the loss of Pb.<sup>10</sup> The calcining was performed at 1000 °C for 3 h and sintering was done at 1250 °C for 3 h in Pb atmosphere.

Figs. 1(a1)-1(a3) show the variation of transition behavior of PZT-xLa system with increasing defect ( $La^{3+}$ ) concentration x, as manifested by the dielectric permittivity as a function of temperature (with rate of 2 °C/min). In low defect concentration range ( $0 \le x \le 0.09$ ), the system undergoes a normal ferroelectric transition, characterized by a frequencyindependent peak and a sharp drop in dielectric permittivity (as exemplified in Fig. 1(a1)).<sup>1</sup> In high defect concentration range (x > 0.16), the system changes from paraelectric phase to a relaxor ferroelectric state without forming normal ferroelectric phase.<sup>11</sup> The dielectric permittivity peak is rather broad and highly frequency dependent (as exemplified in Fig. 1(a3), which demonstrates that a relaxor transition (polarization freezing) occurs.<sup>11</sup> In the intermediate defect concentration range  $(0.09 < x \le 0.16)$ , the system experiences a spontaneous transition from relaxor to normal ferroelectric phase, which is accompanied by a sharp drop in dielectric permittivity following a frequency dependent broad peak (as exemplified in Fig.  $1(a^2)$ ).<sup>12–15</sup> This composition range is also known as ferroelectric/relaxor crossover range, because it represents the crossover from normal ferroelectric behavior to relaxor behavior.

Raman spectra as a function of temperature and time for the three different composition regimes are shown in Figs. 1(b1)-1(d2). All the samples were first heated up to the parent phase (about 300 °C) and then cooled down with a rate of 10 °C/min to the set temperatures. After the temperature

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FIG. 1. Evidence for time-dependent transition behavior at ferroelectric/ relaxor crossover composition of PZT-0.13La. (a1)-(a3) Dielectric permittivity as a function of temperature in PZT-0.08La, PZT-0.13La and PZT-0.17La during cooling, respectively. The frequency range is from  $10^2$  Hz to  $10^5$  Hz.  $T_c$  is the Curie temperature of ferroelectric transition;  $T_s$  is the critical temperature for the spontaneous transition from relaxor to ferroelectric state;  $T_{\rm f}$  is the glass freezing temperature of relaxor;  $T_{\rm m}$  is the temperature of dielectric maximum. (b1) and (b2): Temperature-dependent Raman spectra and time-independent Raman spectra of PZT-0.08La. (c1) and (c2): Temperature-dependent Raman spectra and time-dependent Raman spectra of PZT-0.13La. (d1) and (d2): Temperature-dependent Raman spectra and time-independent Raman spectra of PZT-0.17La. The ferroelectric transition is characterized by the appearance of four transversal optical (TO) modes at about  $76.37 \text{ cm}^{-1}$ ,  $208 \text{ cm}^{-1}$ ,  $260.5 \text{ cm}^{-1}$ , and  $545 \text{ cm}^{-1}$ . The change of the 3TO peak intensity with time is summarized in the insets of (b2), (c2), and (d2). The peak intensity is defined by the peak height relative to its adjacent valley.

was stable (within 2 min), the Raman spectrum or the isothermal evolution was recorded. In the normal ferroelectric transition regime ( $0 \le x \le 0.09$ ), PZT-0.08La undergoes a normal ferroelectric transition with decreasing temperature as shown by the Raman spectra in Fig. 1(b1),<sup>16,17</sup> while the Raman spectra show no change with time in Fig. 1(b2) and its inset. This suggests that normal ferroelectric transition is a time-independent process. In the relaxor transition regime (x > 0.16), Raman spectra of PZT-0.17La exhibit temperaturedependent change (as shown in Fig. 1(d1)),<sup>18–20</sup> but Raman spectra show no time-dependence (as shown in Fig. 1(d2)); this suggests that relaxor transition is also a time-independent process. The most interesting results can be found in the ferroelectric/relaxor crossover regime  $(0.09 < x \le 0.16)$ . Fig. 1(c1) shows the change of Raman spectra of PZT-0.13La with temperature; this corresponds to the spontaneous relaxor to ferroelectric transition, as expected. The most significant finding is that this transition is time-dependent, as shown in Fig. 1(c2). An abrupt change of intensity can be found after the sample is held for 4h (inset of Fig. 1(c2)). Therefore, Fig. 1(c2) provides direct evidence for a time-dependent relaxor to ferroelectric transition.

We further investigated the time-dependent ferroelectric transition in PZT-0.13La by establishing its temperature-timetransformation (TTT) diagram.<sup>21</sup> The PZT-0.13La sample was cooled down from parent phase at 200 °C with rate of 10°C/min to the set temperatures and the dielectric permittivity was recorded as a function of time once the temperature was stable. Fig. 2(a) shows normalized dielectric permittivity  $\varepsilon(t)/\varepsilon(0)$  versus time curves at 100 Hz for different temperatures. It is found that  $\varepsilon(t)/\varepsilon(0)$  decreases with time at all temperatures, and  $\varepsilon(t)/\varepsilon(0)$  shows a faster and larger decrease with time at lower temperature. Since decreasing of dielectric permittivity indicates the increasing of ferroelectric volume fraction, in the simplest approximation, the fraction of ferroelectric phase v may be assumed to be linearly dependent on  $\varepsilon(t)/\varepsilon(0)$ , i.e.,  $\nu = a(x) - b(x)\frac{\varepsilon(t)}{\varepsilon(0)}(b > 0)$ , where a(x) and b(x) are composition-dependent constants, and they can be obtained by the conditions:  $0\% = a(x) - b(x)\frac{\varepsilon(0)}{\varepsilon(0)}$  and  $100\% = a(x) - b(x) \frac{\varepsilon_{SFT}}{\varepsilon(0)}$  ( $\varepsilon_{SFT}$  is the permittivity immediately after the spontaneous ferroelectric transition). The similar way to determine the volume fraction of product phase is also widely utilized in metals by detecting the time-dependence of resistivity.<sup>22</sup> The ferroelectric phase fraction as a function of time is then shown in Fig. 2(b). With lowering waiting temperature from 105 °C to 80 °C, ferroelectric phase fraction is formed from 2.0% to 50% with same waiting time of 9.5 h. It clearly shows that the ferroelectric phase fraction increases with time but the transition is incomplete within 9.5 h (i.e., only a certain fraction of parent phase transforms into ferroelectric phase). The TTT phase diagram is shown in Fig. 2(c). As the system transforms into ferroelectric phase almost instantly below the spontaneous transition temperature  $T_s$  $(79.5 \,^{\circ}\text{C})$ ,<sup>13,14</sup> the lower limit for isothermal transition is the  $T_{\rm s}$ . Incubation time (time for forming 0.2% ferroelectrics) increases with temperature increasing from  $T_{\rm s}$ . With temperature approaching to  $T_{\rm m}(100\,{\rm Hz})$  of  $109\,^{\circ}{\rm C}$  (temperature of dielectric maximum at 100 Hz), it becomes significantly more difficult for the system to transform into ferroelectric phase with time. For instance, time for forming 5% and 10% ferroelectrics at 100 °C and 105 °C well exceeds 9.5 h.

It should be mentioned that in crossover region, ergodic relaxor phase transforms directly to long range ferroelectric phase, without freezing into a non-ergodic relaxor phase.<sup>23</sup> Hence the ideal glass transition temperature  $T_{\rm f}$ , by Vogel-Fulcher fitting, cannot characterize the relaxor transition at crossover regime.<sup>23</sup> Therefore, we use  $T_{\rm m}$  to characterize the relaxor transition in such composition range. And we note that such a significant dielectric relaxation occurs only in the crossover compositions, not in normal ferroelectric ad relaxor compositions. This suggests that such dielectric aging is caused by a time-dependent transition, not by mobile defects.<sup>24</sup>



FIG. 2. Time-dependent characteristics of ferroelectric transition in PZT-0.13La. (a) Normalized dielectric permittivity at 100 Hz as a function of time at different temperatures. (b) Ferroelectric phase fraction as a function of time at different temperatures. (c) TTT phase diagram. Inset enlarges the time scale from 0 h to 1 h in Fig. 2(c). These results show that (1) the ferroelectric phase fraction increases with waiting time; and (2) lowering temperature results in faster and larger increase of the fraction of ferroelectric phase with time.

The above experimental results clearly show several important features of the transition behavior in PZT-*x*La ferroelectric system. First, there indeed exists time-dependent ferroelectric transition in the intermediate defect concentration PZT-0.13La. Second, the transition behavior depends on defect concentration, i.e., PZT-0.13La shows both temperature and time induced transitions, while PZT-0.08La and PZT-0.17La show only time-independent transition.

In order to clarify the microscopic process of the isothermal transition,<sup>25</sup> we performed an *in situ* TEM observation on the PZT-0.13La sample. *In situ* TEM experiment was carried out on a JEM-2100F microscope. After holding at 200 °C for 5 min, the sample was cooled down to 90 °C with the rate of 10 °C/min and then the isothermal observation started. Figs. 3(a)–3(e) show the formation and growth of ferroelectric phase (characterized by typical ferroelectric domain structure) in PZT-0.13La during isothermal aging at 90 °C. In Fig. 3(a), no ferroelectric domain appears in the whole region at 0 h. When time increases to 4 h, fuzzy inclined domain starts to appear, indicating the appearance of ferroelectric phase, as shown by the dotted circle in Fig. 3(b). With further increasing waiting time to 8 h



FIG. 3. (a)–(e) *In situ* TEM at 90 °C in PZT-0.13La for 0 h, 4 h, 8 h, 12 h, and 16 h, respectively. (f) *In situ* TEM at 25 °C cooled from isothermal aging temperature 90 °C after 16 h. The direction is along [110] zone axis. "Ferro." is short for ferroelectric. Dotted lines show the interface between ferroelectric and parent phase. The increment of ferroelectric domains indicates that the time-dependent motion of the interface gives rise to the isothermal transition behavior.

(Fig. 3(c)) and 12 h (Fig. 3(d)), the ferroelectric domain contrast becomes clearer and the ferroelectric domains become larger. Further aging to 16h (Fig. 3(e)) only increases the ferroelectric domain fraction in a marginal way and the isothermal transition begins to saturate. However, the ferroelectric transition can further proceed to completion when the sample is cooled to 25 °C from the isothermal aging temperature  $(90 \,^{\circ}\text{C})$ , as shown in Fig. 3(f). In Fig. 3(f) ferroelectric domains nearly appear in all area and the maximum domain size is 300 nm, demonstrating that the transition driving force by cooling is stronger as compared with that by isothermal aging. Our in situ TEM observation provides direct evidence for the time-dependent ferroelectric transition behavior in PZT-0.13La, and reveals the isothermal transition proceeds by the motion of the interface between parent phase and ferroelectric phase during aging. Comparison of dielectric permittivity as a function of time in PZT-0.08La, PZT-0.13La, and PZT-0.17La shows that only PZT-0.13La (crossover composition) has dramatic change in dielectric permittivity with time, while change in PZT-0.08La and PZT-0.17La can be neglected. It is noted here that our in situ TEM and Raman results together with the comparison of time dependent dielectric behavior in the three composition regimes can exclude the possibility that the change of dielectric constant with time is caused by mobile charges.<sup>25</sup>

Fig. 4(a) shows the phase diagram of PZT-*x*La system, which is divided into three regions of different transition behaviors: (I) normal ferroelectric region ( $0 \le x \le 0.09$ ), (II) ferroelectric/relaxor crossover region ( $0.09 < x \le 0.16$ ), and (III) relaxor region (x > 0.16). Our results show that



FIG. 4. (a) Phase diagram of PZT-xLa.  $T_c$  is temperature for ferroelectric transition;  $T_m$  is temperature of dielectric maximum at 100 Hz, which does not indicate any phase transition;  $T_f$  is the ideal glass freezing temperature in relaxor, obtained by Vogel-Fulcher fitting. The  $T_f$  of PZT-0.18La and PZT-0.21La in relaxor region is got by Vogel-Fulcher fitting the frequency dependent data in Ref. 15. (b1)–(b2) Schematic of interface motion with time in normal ferroelectric transition region at  $T < T_c$ . (c1)–(c2) Schematic of interface motion with time in crossover region at temperature between  $T_m$  (100 Hz) and  $T_s$ . (d1)–(d2) Schematic of interface motion with time in relaxor ferroelectric region at  $T < T_f$ . Yellow and red colors stand for ferroelectric domains with different orientations, and green stands for parent phase with polar nanodomains. Peak on the plane represents random local fields induced by point defects.

time-dependent ferroelectric transition occurs only in Region II, i.e., the intermediate defect concentration region. No time-dependent ferroelectric transition is found in either low defect concentration regime (I) or high defect concentration region (III). Region I corresponds to normal, time-independent ferroelectric phase transition, and Region III corresponds to normal relaxor transition without further transforming into normal ferroelectric phase.

Recent phase field modeling of ferroelectric transitions as a function of point defect or dopant concentration<sup>26</sup> may provide useful insight into the appearance of isothermal or time-dependent ferroelectric transition in Region II. It has been shown that point defects induce local field (either strain field or dipole field)<sup>27,28</sup> and the local field creates "ruggedness" to the otherwise smooth free energy landscape.<sup>26,29–31</sup> As a result, the kinetics of the transition becomes dramatically sluggish with increasing defect concentration and eventually the kinetics becomes so slow that ferroelectric domains remain polar nano-regions (PNRs) and the system becomes a relaxor.<sup>23,32–34</sup> Here we can infer from this picture that there should exist an intermediate defect concentration range where the transition kinetics is not too fast to catch up like a normal ferroelectric, nor too slow like a relaxor; this concentration range shows transition kinetics comparable with conventional experimental time window  $(10^0-10^3 \text{ s})$  and will appear as a "time-dependent ferroelectric transition."

Figs. 4(b1) and 4(d2) show schematically how the transition kinetics changes with increasing point defect concentration and how time-dependent ferroelectric transition happens. In region I ( $0 \le x \le 0.09$ ), low concentration of point defects induces sparse and weak local fields to the system, as shown in Fig. 4(b1). The hindrance from those local fields to the growth of the ferroelectric domains is inappreciable. This corresponds to a small barrier for interface motion. Consequently, the transition finishes in negligible time scale and no time dependence can be observed in conventional experimental time window  $(10^{0}-10^{3} \text{ s})$ , as shown from Figs. 4(b1) to 4(b2). In region III where defect concentration is very high (x > 0.16), point defects result in numerous and large local fields, as shown in Fig. 4(d1). This induces large energy barriers for interface motion. Thus, at  $T \leq T_{\rm f}$ , PNRs cannot grow into large ferroelectric domains within the experimental accessible time and the transition appears to be time-independent also, as schematically shown from Figs. 4(d1) to 4(d2). For regime II where the defect concentration is intermediate  $(0.09 < x \le 0.16)$ , the defect induced local fields give rise to intermediate local energy barriers for interface motion. As the result, the ergodic PNRs can gradually grow up into ferroelectric phase in experimentally accessible time (seconds to hours) and appear time-dependent, as shown from Figs. 4(c1) to 4(c2).

It is noted that the spontaneous transition temperature  $T_s$  shows clear defect concentration dependence. This fact can be understood by the competition between thermodynamic driving force, which favors long-range ordering (i.e., ferro-electric phase), and local energy barriers caused by random field of dopants (La<sup>3+</sup> here), which favor local ordering or relaxor.<sup>35,36</sup> With increasing dopant La<sup>3+</sup> content, the latter force gradually dominates and thus it becomes harder to form a ferroelectric phase. As the result,  $T_s$  decreases with increasing La<sup>3+</sup> content.

Apparently, the kinetics of the above-mentioned timedependent relaxor to ferroelectric transition is strongly affected by temperature, as lowering temperature can provide additional thermodynamic driving force to speed up the growth of PNRs in the relaxor state.<sup>37,38</sup> This explains why the kinetics of this isothermal transition becomes faster with decreasing temperature (Fig. 2(c)). Below the spontaneous transition temperature  $T_s$ , the transition is too fast and cannot be detected within experimentally accessible time scale and thus appears time-independent. The temperature dependence of the transition kinetics explains the TTT diagram of Fig. 2(c). Practically, as transparent PZT-xLa ceramics and films have been widely used for the interplay between electrical polarization and optical properties,<sup>39,40</sup> we also expect some applications by introducing the function of time, such as time-electro-optic switch and deflector. In the meantime, slowing down of transition kinetics provides an opportunity to study the detailed process of ferroelectric transition.

In summary, we showed that with increasing  $La^{3+}$  concentration the PZT-*x*La ferroelectric system shows three regions of different transition behaviors, (I) normal

time-independent ferroelectric transition, (II) time-dependent relaxor to ferroelectric transition, and (III) normal relaxor transition. Such a change is ascribed to the local field of point defects that alters the ruggedness of the free energy landscape and thus changes the kinetics of interface motion. Time-dependent ferroelectric transition introduces "time" as a controlling parameter of the system properties and may provide possibilities of time-controlled ferroelectric devices.

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