

# The transitions from glassy state to long-range-ordered state in ferroic glasses

Invited Article

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The field-induced, spontaneous, and isothermal transition from glassy state to long-range-ordered ferroic state in two physically parallel ferroic glasses (relaxor and strain glass) have been reviewed from the aspect of experimental character-

istics. The similarities and differences between these two ferroic glasses from macroscopic to microscopic properties have been summarized. In addition, some interesting phenomena that deserve further investigations have been pointed out.

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**1 Introduction** Ferroic materials possess two or more orientation states of a physical property with the same energy and these orientation states can be switched by an external field [1, 2]. Ferroelastics with spontaneous strain ( $\epsilon$ ), ferroelectrics with spontaneous polarization ( $\mathbf{P}$ ) and ferromagnets with spontaneous magnetization ( $\mathbf{M}$ ) are the three best-known classes of primary ferroics [1, 2]. Quenched randomness or defects in ferroic systems generally give rise to the frustration in a ferroic property such as strain, polarization, or magnetization; and thus result in the disordered glass-like states in ferroic materials, such as strain glass in ferroelastics (shape-memory alloys) [3], relaxor in ferroelectrics [4], and spin glass in ferromagnets [5]. These disordered states are generally termed as “ferroic glass” [6].

There are three distinct states in ferroic materials with respect to their order parameter: a high-temperature parent phase with order parameter equal to zero (austenite or parent phase, paraelectric state, and paramagnetic state), a low-temperature ferroic state with long-range-ordered order parameter (martensite or ferroelastic state, ferroelectric state, and ferromagnetic state), and a low-temperature glassy state (strain glass, relaxor, and spin glass) with a frozen and frustrated local order of the order parameter. The transitions

between the three different states are important as they provide most functionalities of ferroic materials [1–6].

The symmetry-breaking transition from parent phase to long-range-ordered ferroic phase can be induced either by temperature or by external field. The temperature-induced transition is characterized by several main features in the experiments. (i) A frequency-independent peak of susceptibility (magnetic  $\mu = \partial M / \partial H$  and electric  $\chi = \partial P / \partial E$ ) appears at the transition point in ferroelectrics and ferromagnets and a dip of storage modulus ( $\mathbf{S}$ , inverse of mechanical susceptibility  $\partial \epsilon / \partial \sigma$ ) appears at the transition point in ferroelastics/martensite. The storage modulus is used as it is easy to measure experimentally, but for theoretical studies more general variables, such as tensor of elastic constants, should be used. (ii) The Curie–Weiss law describes the susceptibility as a function of temperature in the parent phase of ferroelectrics and ferromagnets, while an elastic softening (elastic constant decreases with temperature approaching the transition temperature) takes place in the parent phase of ferroelastics/martensite. The symmetry-breaking transition results in finite order parameters in the ferroic materials, which are sensitive to the external stimulus such as temperature, stress, electric, or magnetic fields. The field-induced transition from parent

phase to the ferroic phase occurs above transition temperature. The most important feature of such a field-induced transition is its reversibility, resulting in the superelasticity in shape-memory alloys [7] and the double hysteresis polarization–electric field ( $P$ – $E$ ) loop in ferroelectrics [8].

The transition from parent phase to glassy state is known to take place with decreasing temperature. The glass transition features are distinguished by the nonergodic response in their static and dynamic properties [6], for instance, the frequency dispersion of the susceptibility (magnetic  $\mu = \partial M / \partial H$ , electric  $\chi = \partial P / \partial E$ , and storage modulus  $S = \partial \sigma / \partial \epsilon$ ) around a critical glass transition temperature, and the broken ergodicity in the order parameter (spontaneous strain  $\epsilon_s$ , polarization  $\mathbf{P}$ , and magnetization  $\mathbf{M}$ ) below the glass transition temperature. Recent understandings on the glassy behavior of the ferroic glass and its relationship with other states in ferroic materials are as follows [9–15]. When defects are introduced into ferroic systems, kinetic hindrance for its normal transition into long-range-ordered state is produced [12]. The occurrence of glassy state is caused by the competition between the kinetic limitation produced by defects and the thermodynamic driving force toward long-range ordered phase [9]. Above a composition threshold, the kinetic limitation is stronger than the thermodynamic driving force of long-range-ordered state; consequently the transition into long-range-ordered state becomes kinetically forbidden and the glass transition occurs instead [9].

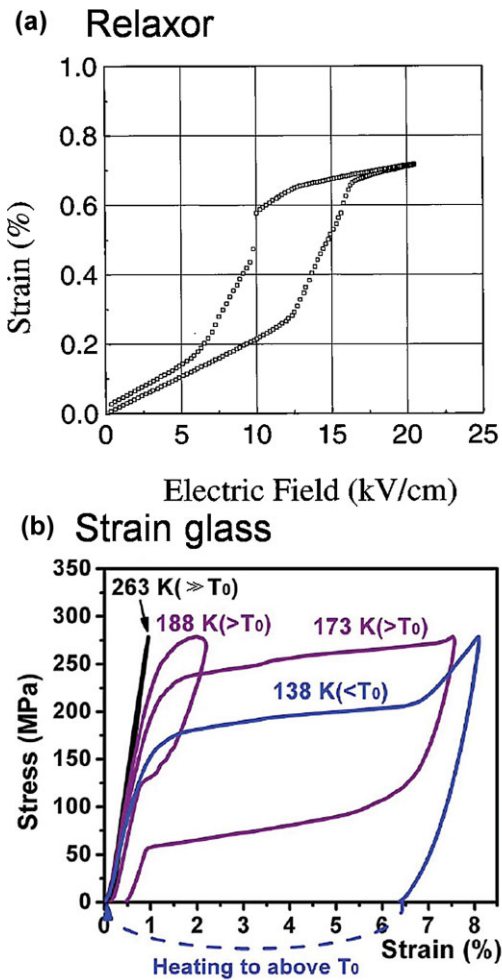
The third type of transition exists between the glassy state to long-range-ordered ferroic state. This type of transition is not always expected as both states can be stable at low temperatures. It has been shown that such a transition can happen in some systems and can be induced by either external field, or temperature, or even time. In the present paper, we are going to review the characteristics of such a transition from glassy to long-range-ordered ferroic state. These experimental characterizations of such a transition demonstrate that the thermodynamic and kinetic factors may take part in a delicate competition in ferroic glasses and such competition dominates its transition behaviors.

## 2 External-field-induced transition from glassy state to long-range-ordered ferroic state

Two kinds of external field induced transitions can take place in relaxor ferroelectrics and in strain-glass alloys. One is that the long-range-ordered state is directly induced from glassy state by an external field at a constant temperature. The other is the external-field-assisted transition from glassy state to long-range-ordered state, that is, the transition takes place upon cooling with the applied external field. In the following subsections, we will show such transitions in a relaxor and a strain glass, respectively.

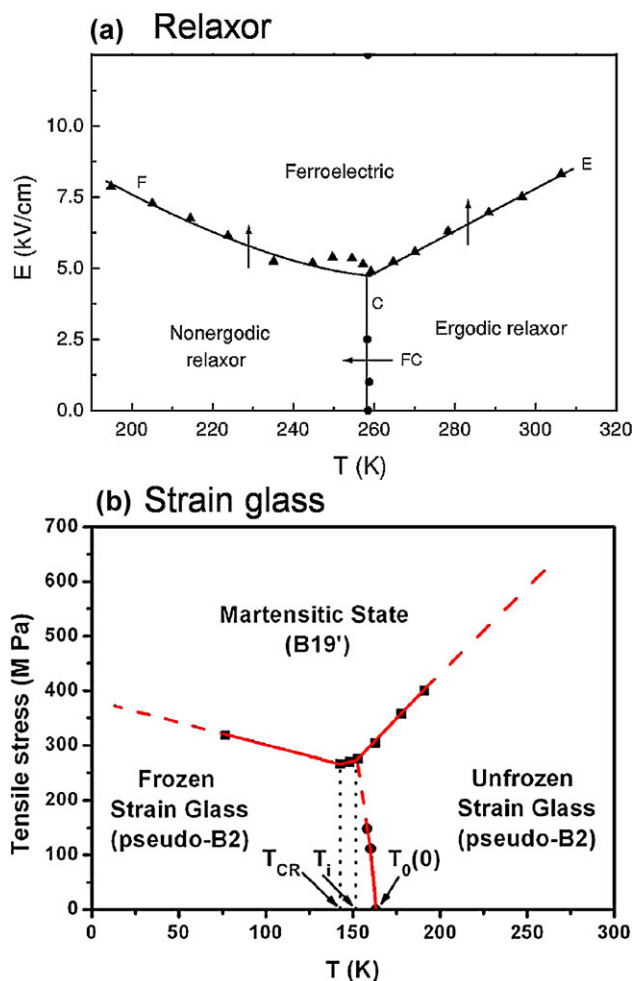
### 2.1 Electric-field-induced relaxor to normal ferroelectric transition

A relaxor can be considered as the conjugate glassy state of the normal ferroelectrics, with



**Figure 1** (a) Reversible electrostrain as a function of electric field for PZN–8PT. The reversibility is due to the field-induced phase transition between a pseudorhombohedral relaxor state and tetragonal normal ferroelectric state (after Durbin et al. [17], Copyright (1999), AIP Publishing LLC). (b) Superelasticity (reversible strain) for  $\text{Ti}_{48.5}\text{Ni}_{51.5}$  strain glass. The reversible elastic behavior is due to the reversible stress-induced transformation from an unfrozen strain glass to long-range strain ordered B19' martensite (after Wang et al. [21], Copyright (2006) by the American Physical Society).

randomly distributed nanosized polar regions [8]. Upon a strong enough external electric field, these nanosized polar regions are expected to align along the external field direction [16, 17]. As a result, a long-range ordered ferroelectric state is obtained. Such a transition between relaxor and long-range ordered ferroelectric state is reversible, giving rise to the double hysteresis loop and the reversible electrostrain. Durbin et al. have proved such a field-induced phase transition between a pseudorhombohedral relaxor state and tetragonal normal ferroelectric state by in situ X-ray diffraction, which is accompanied by a large reversible electrostrain as shown in Fig. 1a [17].



**Figure 2** (a) Electric-field–temperature phase diagram of PLZT 9/65/35 ceramics (after Bobnar et al. [20], Copyright (1999) by the American Physical Society). (b) Tensile stress–temperature phase diagram of  $\text{Ti}_{48.5}\text{Ni}_{51.5}$  strain glass (after Wang et al. [22], with permission from publisher: Elsevier).

As the applied external electric field favors the long-range ordered ferroelectric state, it is expected that transition from relaxor state to long-range-ordered state can take place upon cooling with the applied external field as well. For instance, Yao et al. found that under a electrical field of  $3 \text{ kV m}^{-1}$ , a relaxor (La-modified lead zirconate titanate with  $\text{Ti}/\text{Zr} = 65/35$  and La contents of 8 at.%, abbreviated as PLZT 8/65/35) can be transformed into normal ferroelectric state upon cooling [18]. This transition is often referred to as the field-induced micro- to macrodomain transition in the literature [18, 19]. Bobnar et al. [20] established the electric-field–temperature phase diagram of PLZT 9/65/35 relaxor ceramics, as shown in Fig. 2a. The three lines are the phase boundaries separating the ergodic, nonergodic relaxor, and the normal ferroelectric states. In particular, the lines E and F also indicate the critical bias field ( $E_c$ ), at which the long-range ordered ferroelectric state is induced. By cooling the system with the bias field larger than  $E_c$ , an ergodic relaxor

to ferroelectric phase transition takes place, while by cooling the system in an external field smaller than  $E_c$ , the system will undergo the glassy transition from the ergodic relaxor to the nonergodic relaxor state.

**2.2 Stress-induced strain glass to normal martensite transition** Strain glass was recently found in several ferroelastic/martensite alloys by introducing point defects beyond a critical value [21–26]. This is a glassy state of local strain order, being analogous to the ferroelectric relaxor. Similar to the external-field-induced relaxor to normal ferroelectric transition, a stress-induced transition from strain glass to long-range strain-ordered martensite has also been found in strain-glass alloys [21, 25, 26].

Wang et al. [21] first reported such kind of transition in  $\text{Ti}_{48.5}\text{Ni}_{51.5}$  strain-glass alloy and the associated superelasticity (recovery strain upon unloading) as shown in Fig. 1b. The in situ X-ray diffraction data provided clear evidence that the superelasticity of strain glass is attributed to a stress-induced reversible transition from unfrozen strain-glass state to the long-range strain-ordered B19' martensite [21]. Later, similar superelasticity was reported in  $\text{Ti}_{50}(\text{Pd}_{50-x}\text{Cr}_x)$  and  $\text{Ti}_{50}(\text{Ni}_{50-x}\text{Fe}_x)$  strain-glass alloys [25, 26].

Similar to the case in a relaxor, the applied stress field also assists the transition from strain glass to long-range ordered martensite upon cooling. Wang et al. [22] constructed the tensile stress–temperature phase diagram of  $\text{Ti}_{48.5}\text{Ni}_{51.5}$  strain glass as shown in Fig. 2b. Under a tensile stress lower than the critical stress  $\sigma_c$ , the strain-glass system undergoes a freezing transition from an unfrozen strain glass to a frozen strain glass upon cooling, with the average pseudo-B2 structure unchanged. Under a tensile stress higher than the critical stress  $\sigma_c$ , either the unfrozen strain glass or the frozen strain glass can be transformed into long-range strain-ordered B19' martensite phase.

Combining these parallel facts, it appears that field-induced transition from glassy state to a long-range-ordered state is a quite general phenomenon in ferroic glasses. However, comparison between the behaviors in a relaxor and a strain glass raises several interesting points. First, the reversible behavior in a relaxor (shown in Fig. 1a) takes place in nonergodic (frozen) relaxor state, while in a strain glass (shown in Fig. 1b) it happens in ergodic (unfrozen) strain-glass state. Secondly, there exist slight difference between the field–temperature phase diagrams of a relaxor and a strain glass (shown in Fig. 2). The three phase boundaries join at one point in a relaxor but not in a strain glass. In addition, the phase boundary between unfrozen and frozen state is field-dependent in a strain glass but not in a relaxor. The clarification of these differences may be helpful for understanding the origin of the field-induced transition from glassy state to long-ordered state.

**3 Spontaneous transition from glassy state to long-range-ordered ferroic state** As shown above, the long-range-ordered state can be induced from glassy state upon cooling with the applied external field. However, it

is also known that the glassy state can transform into long-range-ordered state spontaneously as well (without an applied external field). In the following subsections, we will show such transitions in relaxor and strain-glass systems, respectively.

**3.1 Spontaneous relaxor to normal ferroelectric transition** The spontaneous relaxor to normal ferroelectric phase transition has been observed in a wide range of relaxor systems, including PLZT  $x/40/60$  [4],  $\text{Pb}(\text{Sc}_{1/2}\text{Nb}_{1/2})\text{O}_3$  [27],  $\text{Pb}(\text{Sc}_{1/2}\text{Ta}_{1/2})\text{O}_3$  [28],  $(\text{Pb}, \text{La})\text{TiO}_3$  [29],  $\text{Pb}(\text{Ni}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{-PbTiO}_3\text{-PbZrO}_3$  [30],  $\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{-(Pb,L a)TiO}_3$  [31]. Such a spontaneous transition is always accompanied with various unique characteristics.

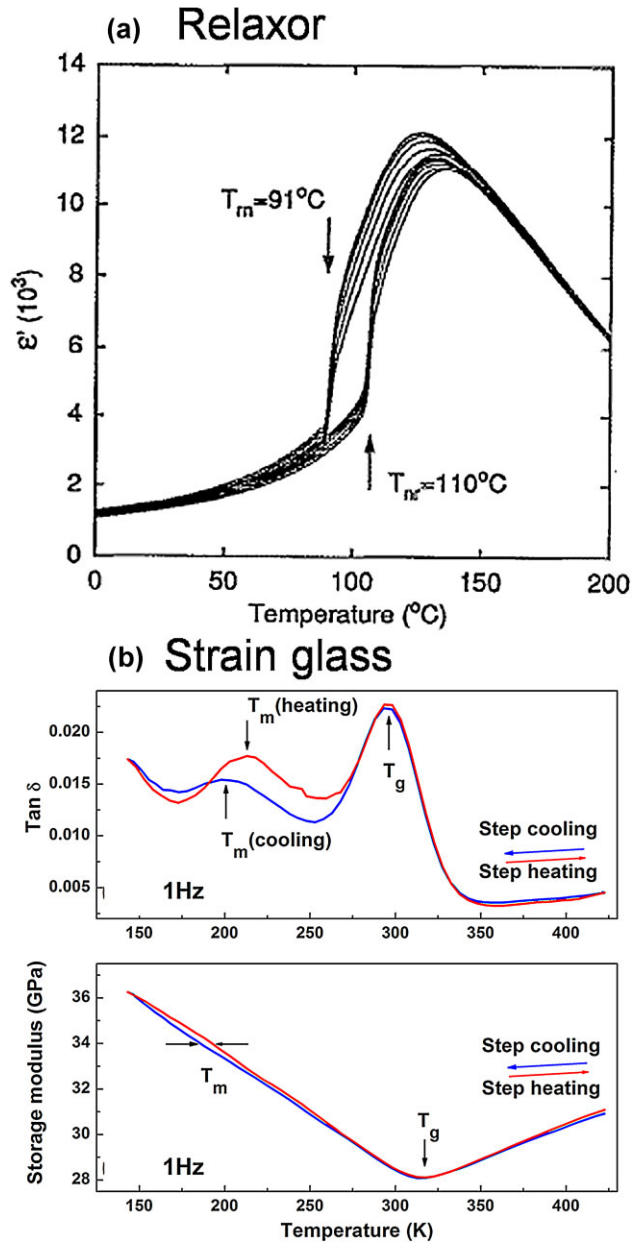
Take the typical relaxor PLZT as an example, Dai et al. [32, 33] showed that when a spontaneous relaxor to normal ferroelectric transition occurs on cooling, the dielectric permittivity exhibits a sharp drop at the transition temperature, as shown in Fig. 3a. The sharp change appears at a critical temperature below the broad frequency-dependent dielectric peak, and it is frequency independent. Most importantly, such a sudden change upon cooling and heating involves a large thermal hysteresis (about 19 K), contrasting with the case for relaxor transition (dielectric permittivity peak) with nearly zero thermal hysteresis.

It is known that the canonical relaxors retain the average structure of paraelectric phase (cubic) over the whole temperature range, while the normal ferroelectric phases have different average crystal structure from paraelectric phase; thus an average structural change should be detected during the spontaneous relaxor to normal ferroelectric phase transition. As shown in Fig. 4a, the cubic structure changes into tetragonal structure after the spontaneous transition. Microstructurally, the spontaneous transition is also accompanied with the formation of coarse domains from polar nanoregions [33].

In addition, the evolution of a  $P\text{-}E$  hysteresis loop with temperature can also characterize the spontaneous transition [27]. At high temperatures above the relaxor transition, a slim hysteresis loop appears for paraelectric state. When approaching the spontaneous transition temperature, the double hysteresis loop appears. Below the spontaneous transition temperature, a typical square hysteresis loop of a normal ferroelectric appears.

To sum up, the signatures of spontaneous relaxor to normal ferroelectric transition include the following aspects:

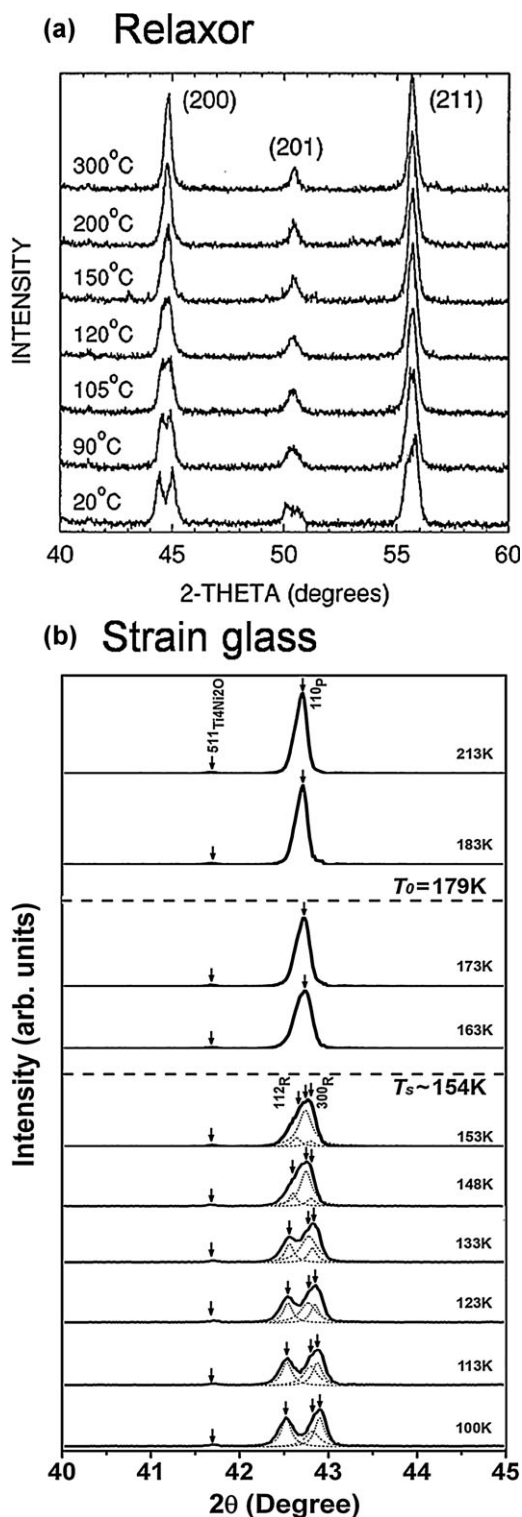
- (1) the frequency independent dielectric permittivity drop at the spontaneous transition temperature;
- (2) large thermal hysteresis associated with the spontaneous transition;
- (3) the average structure change and the formation of the macrodomains;
- (4) the evolution of  $P\text{-}E$  hysteresis loop: upon cooling the hysteresis loop varies from a slim one through a double one to a typical square one.



**Figure 3** (a) Dielectric permittivity as a function of temperature shows two features of spontaneous transition in a relaxor: sudden drop of dielectric permittivity and large thermal hysteresis (after Dai et al. [32], Copyright (1993) AIP Publishing LLC). (b) Dynamic mechanical properties ( $\tan \delta$  and storage modulus) as a function of temperature show two features of spontaneous transition in a strain glass: internal friction peak and large thermal hysteresis (after Vasseur et al. [34], Copyright (2012) by the American Physical Society).

**3.2 Spontaneous strain glass to normal martensite transition** The spontaneous strain glass to normal martensite transition has been found in three kinds of strain-glass alloys,  $\text{Ti}_{50}(\text{Ni}_{44.5}\text{Fe}_{5.5})$ ,  $\text{Ti}_{50}(\text{Pd}_{40}\text{Cr}_{10})$ , and  $\text{Ni}_{45}\text{Co}_{10}\text{Mn}_{20}\text{Ga}_{25}$  [34, 36, 37]. Such a spontaneous





**Figure 4** (a) X-ray diffraction patterns of PLZT 12/65/35 relaxor ceramic upon cooling (after Dai et al. [35], Copyright (1996) AIP Publishing LLC). (b) X-ray diffraction patterns of  $Ti_{50}(Ni_{44.5}Fe_{5.5})$  strain-glass alloy upon cooling (after Zhang et al. [36], Copyright (2012) by the American Physical Society). Obvious peak splitting with decreasing temperature can be detected, indicating an average structure change after the spontaneous transition.

transition in strain-glass alloys is accompanied by several unique experimental characterizations as well, including dynamical mechanical properties, average structures, and microstructures.

Vasseur et al. [34] showed the signatures of spontaneous transition for the  $Ti_{50}(Pd_{40}Cr_{10})$  alloy. Upon cooling there appears a frequency-dispersive internal friction peak and a storage modulus dip that correspond to a strain-glass transition. On further decreasing temperature, a frequency-independent internal friction peak appears, indicating a spontaneous strain glass to martensite transition, as shown in Fig. 3b. Being similar to the case in a relaxor, the spontaneous strain glass to martensite transition involves a large thermal hysteresis about 10 K, which suggests a first-order transition.

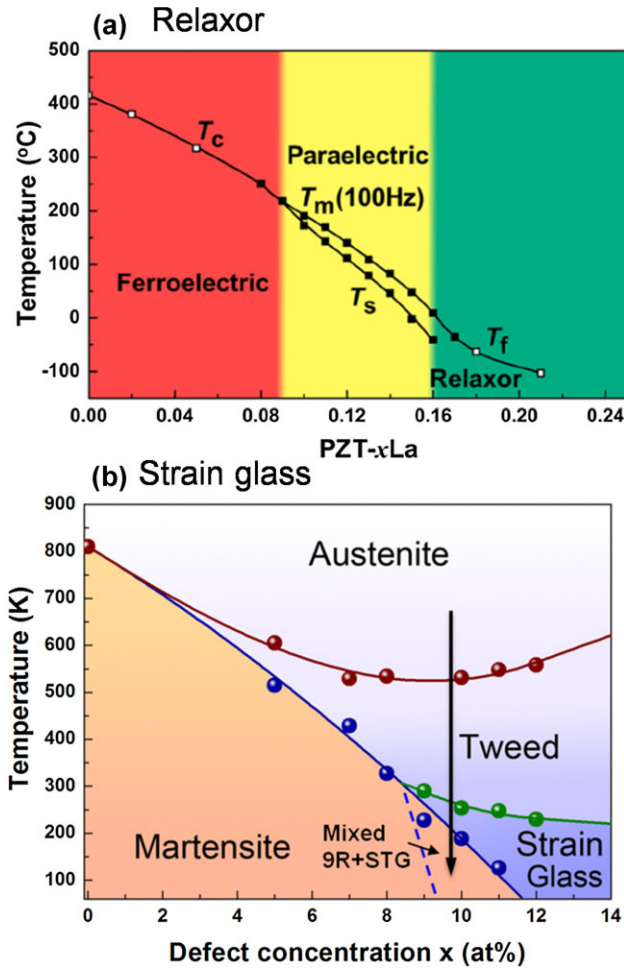
The formation of normal martensite phase after the spontaneous transition should be able to be detected by various diffraction measurements. Zhang et al. [36] performed in situ conventional X-ray diffraction measurement upon cooling for  $Ti_{50}(Ni_{44.5}Fe_{5.5})$  strain-glass alloy, and the result (Fig. 4b) shows that the  $(110)_{B2}$  parent phase peak keeps a singlet with slight broadening from 213 to 163 K, spanning the strain-glass transition temperature ( $T_0 = 179$  K). When the temperature is further lowered, the  $(110)_{B2}$  peak splits into  $(112)_R$  and  $(300)_R$  peaks characterizing the R martensite phase. Vasseur et al. [34] also checked the microstructure evolution in  $Ti_{50}(Pd_{40}Cr_{10})$  by in situ TEM. In the strain-glass state, contrast from nanodomains can be seen; however, when the sample is cooled below the spontaneous transition temperature, parallel martensite domains are visible in addition to the nanodomains. Clearly, such evolution of average structure and microstructure is analogous to that of relaxors, as discussed above.

To summarize, the signatures of spontaneous strain glass to normal martensite transition include the following aspects:

- (1) the frequency-independent internal friction peak at the spontaneous transition temperature;
- (2) large thermal hysteresis associated with the spontaneous transition;
- (3) the average structure change and the formation of the macrodomains.

### 3.3 Phase diagrams including spontaneous strain glass to martensite transition

For the spontaneous relaxor to normal ferroelectric transition, several explanations considering either the strain effect or the vacancy effect have been proposed [31, 32, 36–39]. For instance, Dai et al. [32] attributed the spontaneous transition to the large tetragonal strain of PLZT  $x/40/60$ ; while Kim and Jang [38], Bidault et al. [39], and Deng et al. [31] showed that A site vacancies, B site vacancies and oxygen vacancies of the  $ABO_3$  structure can influence the spontaneous relaxor to normal ferroelectric transition. For the spontaneous strain glass to martensite transition, the explanation is in



**Figure 5** (a) Phase diagram of PLZT relaxor system (after Sun et al. [40], Copyright (2013) AIP Publishing LLC). (b) Phase diagram of the ternary ferroelastic strain-glass alloy  $\text{Ti}_{50}(\text{Pd}_{50-x}\text{Cr}_x)$  (after Vasseur et al. [34], Copyright (2012) by the American Physical Society). The two phase diagrams both contain the crossover region showing the spontaneous transition.

a phenomenological way. Wang et al. [37] and Zhang et al. [36] showed that the competition between the thermodynamic driving force (favors long-range order) and kinetic limitation (favors short-range order) determines the spontaneous transition behavior.

Here, we show some clues for understanding the spontaneous transition in both the relaxor and strain-glass systems. Figure 5a shows the phase diagram of a PLZT relaxor system that includes the spontaneous transition from relaxor to normal ferroelectric state [40]. The transition behavior varies with defect concentration, and the spontaneous transition takes place in the regime with medium defect concentration ( $0.09 < x < 0.16$ ), as indicated in yellow in Fig. 5a. Figure 5b shows the phase diagram of  $\text{Ti}_{50}(\text{Pd}_{50-x}\text{Cr}_x)$  strain-glass system where a crossover composition regime indicating the spontaneous transition is included [34]. When the defect concentration is low

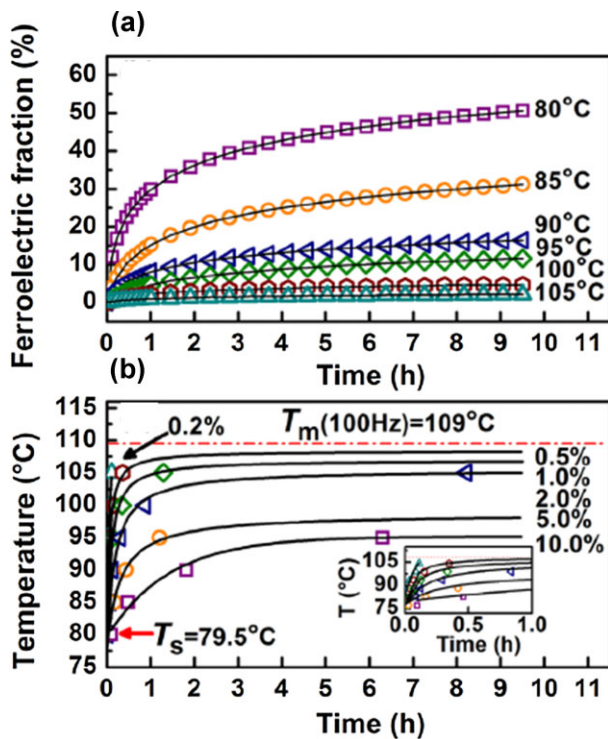
( $x < 8.5$ ), the system undergoes a martensitic transformation. In contrast, a strain-glass transition occurs when the defect concentration exceeds the critical value ( $x > 11.5$ ). In the crossover region ( $8.5 < x < 11.5$ ), the system undergoes the spontaneous strain glass to martensite transition.

The above two similar phase diagrams seem to suggest that the spontaneous transition exists in the crossover compositions for both relaxor and strain-glass systems. It has been shown that point defects induce local field (either strain field or dipole field) and the local field creates the rugged free-energy landscape [41, 42]. Here, we try to infer from this picture that there exists an intermediate defect concentration range where spontaneous transition happens. In the low defect concentration region, the created local fields from defects are sparse and weak. The hindrance from those local fields to the long-range ordering is not large, thus the normal ferroic state can be achieved upon cooling. In high defect concentration regime, numerous and large local fields are created and they give rise to large enough hindrance to the long-range ordering. As a result, the normal ferroic phase cannot be formed and a glassy state with local order appears. For the crossover regime with medium defect concentration, the defect-induced local fields give rise to intermediate local fields, which result in the glassy state at high temperature. However, with the help of a thermodynamic driving force to overcome the intermediate local fields, such a glassy state can gradually transform into long-range-ordered state on further decreasing the temperature. Interestingly, we will show in the following that such a spontaneous transition can also occur within the experimentally accessible time by keeping the temperature, i.e., isothermal transition.

#### 4 Isothermal transition from glassy state to long-range-ordered ferroic state

Contrary to this conventional wisdom that a ferroelectric transition is intrinsically a very fast process without an apparent time dependence, Sun et al. [40] reported a time-dependent ferroelectric transition, which transforms from relaxor state to normal ferroelectric state within hours in the PLZT system. It is shown that the time-dependent ferroelectric transition occurs at the crossover composition range of  $0.09 < x < 0.16$ . As shown in Fig. 6, the ferroelectric phase fraction increases with waiting time and the temperature–time–transformation curve shows the typical feature of an isothermal transition. Furthermore, in situ Raman spectroscopy and transmission electron microscopy also reveal very slow growth of ferroelectric phase. Thus, the isothermal relaxor to normal ferroelectric transition indeed exists in the crossover regime. Such an interesting phenomenon is considered to result from the slowing-down of the otherwise fast growth of polar nanodomains due to the random local fields caused by point defects, so that a long time is needed to achieve long-range ordered macroscopic ferroelectric phase.

To date, such a kind of time-induced spontaneous transition from glassy state to long-range-ordered state has been reported only in relaxor systems. A similar time-



**Figure 6** (a) Ferroelectric phase fraction as a function of time at different temperatures. (b) Temperature–time–transformation phase diagram. The inset enlarges the time scale from 0 to 1 h. These results show that the ferroelectric phase fraction increases with waiting time (after Sun et al. [40] with permission, Copyright (2013) AIP Publishing LLC).

induced transition from strain glass to martensite transition is highly expected in the crossover regime of strain-glass systems.

**5 Summary** In summary, we reviewed the main characteristics of three kinds of transitions from glassy state to long-range-ordered state in ferroic glasses, including the field-induced one, the temperature-induced (spontaneous) one and the isothermal one. The former two types are well studied in both relaxor and strain-glass systems. The last one is recently reported in relaxor systems and is expected in strain-glass systems. It seems that most of these transitions occur in the crossover regime with medium defect concentrations, suggesting that the delicate balance between the thermodynamic driving force (favors long-range order) and kinetic limitation (favors short-range order) gives rise to the transitions from glassy state to long-range-ordered state. As for the other ferroic glass, i.e., spin glass, such transition from a spin-glass state to a long-range ordered ferromagnetic state is seldom reported in the literature. It is worthwhile to study the transition behaviors at the crossover regime between spin glass and ferromagnets. Detailed comparison of such a transition in these three ferroic glasses might be helpful for further understanding the physical mechanisms of this interesting transition behavior.

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