Glass-ferroic composite caused by the crystallization of ferroic glass

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We report a glass-ferroic composite (in short “glass-ferroic”) in ferroic materials, an analog of the composite of glassy and crystalline phases (glass-crystal composite, e.g., semicrystalline polymer). The formation of glass-ferroic (i.e., the existence of residual ferroic glass) stems from a time-dependent crystallization of the ferroic glass. Moreover, glass-ferroics show two types of transition characteristics depending on the thermal hysteresis of crystallization transition as exemplified in Ti$_{48}$Ni$_{51.3}$ and Pb$_{0.87}$La$_{0.13}$Zr$_{0.4}$Ti$_{0.6}$O$_{3}$. Based on experimental results, a generic phase diagram is established to include all ferroic states, i.e., ferroic crystal, ferroic glass, and glass-ferroic. Being the third class of ferroic materials, glass-ferroics may open a new avenue for achieving novel properties and designing ferroic phase-change memory devices.

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A crystal or crystalline solid is the archetypal material, which has a long-range ordering of ions, atoms, or molecules through the diffusion. It usually forms from a liquid with cooling (the so-called crystallization transition of liquids). On the other hand, its conjugate state, a structural glass cooling (the so-called crystallization transition of liquids). It usually forms from a liquid with diffusion. It usually forms from a liquid with cooling (the so-called crystallization transition of liquids). Moreover, glass-ferroics show two types of transition characteristics depending on the thermal hysteresis of crystallization transition as exemplified in Ti$_{48}$Ni$_{51.3}$ and Pb$_{0.87}$La$_{0.13}$Zr$_{0.4}$Ti$_{0.6}$O$_{3}$. Based on experimental results, a generic phase diagram is established to include all ferroic states, i.e., ferroic crystal, ferroic glass, and glass-ferroic. Being the third class of ferroic materials, glass-ferroics may open a new avenue for achieving novel properties and designing ferroic phase-change memory devices.

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TABLE I. Three classes of transitions and three classes of resulting structural and ferroic materials, where the existence of the third ferroic materials—glass-ferroic was not clear before.

<table>
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<tr>
<th>Crystallization transition of liquids</th>
<th>Structural materials</th>
<th>Ferroic materials</th>
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<tbody>
<tr>
<td>Structural crystal</td>
<td>Structural crystal</td>
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<td>Structural glass</td>
<td>Structural glass</td>
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<td>Glass transition</td>
<td>Glass-crystal</td>
<td>Glass-ferroic</td>
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<td>Crystallization transition of glasses</td>
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Three classes of transitions are between two of the structural/ferroic liquid, structural/ferroic crystal and structural/ferroic glass. The ferroic case of transition-material correspondence can be further seen in Fig. 5(b).

strain glass [7]. Interestingly, the increase in resistivity after the martensitic transition [Fig. 1(c)] suggests that a residual strain glass (i.e., strain glass-martensite) exists since the resistivity of strain glass increases with decreasing temperature whereas the resistivity of B19’ martensite decreases with decreasing temperature [7].

Then upon heating, an abnormal transition behavior was observed. The storage modulus [Fig. 1(d)] and mechanical loss [Fig. 1(e)] curves first show a typical feature of the strain glass transition, a frequency-dependent behavior, which is similar to the one in the cooling process. Upon further heating, the system undergoes another transition, a frequency-independent one, which is a signature of the normal martensitic transition [7,9]. Around the same temperature range, the resistivity curve suggests the occurrence of a reverse B19’ martensitic transition [Fig. 1(f)]. Therefore, the heating results do not depict an inverse transition sequence of the cooling process, which are different from the most commonly observed transition characteristics [see an example in Fig. 3(a)] [10–18]. This unique transition sequence challenges the previous understanding of ferroic crystallization transition (see below for details) [10–12,16] and indicates the formation of glass-ferroic.

We further performed the standard zero-field-cooling (ZFC)/field-cooling (FC) measurements to confirm above abnormal transition behavior. The detailed instructions can be found in previous literature [9]. In order to provide a direct comparison, the same experiments were also conducted in a martensitic Ti49Ni51 alloy and a strain glass Ti48.5Ni51.5 alloy [7]. Figure 2(a) shows ZFC/FC curves of the Ti48.7Ni51.3 alloy. They first exhibit a typical glassy signature of a peak in the ZFC curve and a continuous decrease in the FC curve upon heating as demonstrated in the strain glass Ti48.5Ni51.5 alloy [Fig. 2(b)]. With further heating, both ZFC and FC curves show two inflection points that represent the reverse starting and finishing transition temperatures of B19’ martensite as demonstrated in the martensitic Ti49Ni51 alloy [Fig. 2(c)]. Therefore, these results are fully consistent with Figs. 1(d)–1(f), and we can solidly conclude that: (i) a strain glass-martensite must exist at low temperatures, and (ii) the crystallization transition is irreversible: strain glass → martensite upon cooling and martensite → parent phase upon heating.

Next, we reveal the glass-ferroic formation in a ferro-electric Pb0.37La0.13Zr0.4Ti0.6O3 (PLZT) ceramic. Figure 3(a) represents a typical example of the most commonly observed crystallization transition of ferroic glasses [10–18]. Upon cooling, a relaxor transition occurs by exhibiting a frequency-dependent electric susceptibility peak that also follows the Vogel-Fulcher relation [inset of Fig. 3(a)]. With further cooling, the formed relaxor spontaneously transforms into the FE by showing a sharp decrease in electric susceptibility. Upon heating, the transition sequence shows a reversible characteristic [Fig. 3(a)]. Figure 3(b) shows that after the cooling process an external dc electric field (15 kV cm for 48 h at room temperature) was applied to pole the sample. After this treatment, the decreased susceptibility indicates the existence of a residual relaxor (or relaxor-ferroelectric) because of the lower susceptibility of the FE phase than that of the relaxor (see the sharp susceptibility decrease in crystallization transition upon cooling).

Moreover, the heating curves in Fig. 3(b) further clarify the transitions in Fig. 3(a) and confirm the relaxor-ferroelectric formation after the forward crystallization transition. The whole transitions in Fig. 3(a) can be depicted either (i) by PE ↔ relaxor ↔ FE (i.e., a reversible glass transition and a reversible crystallization transition) [10–12,16], or (ii) by PE ↔ relaxor ↔ FE upon cooling, FE → PE and relaxor (residual) → PE upon heating (i.e., a reversible glass transition and an irreversible crystallization transition). The difference between the two depictions can be simplified to identify the reactant of reverse relaxor transition upon heating, the formed relaxor from the FE or the residual one. After dc polling to eliminate the residual relaxor [Fig. 3(b)], upon heating only a reverse ferroelectric transition, exhibiting a frequency-independent peak of electric susceptibility at \( T_C \), was observed. The fact...
Note that at low frequencies the product of forward crystallization transition is a relaxor-ferroelectric. The direct transition from the FE phase to the PE phase (i.e., a spontaneous ferroelectric transition), whereas upon heating the reverse crystallization transition occurs from the ferroelectric (FE) component of relaxor-ferroelectric to paraelectric (PE) phase (see below for the reason). The relaxor component is responsible for the reverse relaxor transition. (b) After the dc electric-field poling at room temperature, the susceptibility at low temperatures decreases, indicating the existence of residual relaxor. Upon heating the appearance of reverse ferroelectric transition can be only explained by the irreversible crystallization transition (i.e., FE → PE instead of the relaxor), otherwise a peak (reverse relaxor transition) should be found at $T^+_C$ (as the dashed pink line shows in inset) according to the reversible crystallization transition (i.e., FE → relaxor). Accordingly, the reverse relaxor transition in (a) should originate from the residual relaxor, which also indicates that the product of forward crystallization transition is a relaxor-ferroelectric. Note that at low frequencies $T^+_C$ is lower than $T^+_g$ (as the dashed pink line shows in inset), which cannot be used to exclude the reversible transition scenario.

Upon cooling PLZT undergoes a relaxor transition and then a forward crystallization transition (i.e., a spontaneous ferroelectric transition), whereas upon heating the reverse crystallization transition occurs from the ferroelectric (FE) component of relaxor-ferroelectric to paraelectric (PE) phase (see below for the reason). The relaxor component is responsible for the reverse relaxor transition. (b) After the dc electric-field poling at room temperature, the susceptibility at low temperatures decreases, indicating the existence of residual relaxor. Upon heating the appearance of reverse ferroelectric transition can be only explained by the irreversible crystallization transition (i.e., FE → PE instead of the relaxor), otherwise a peak (reverse relaxor transition) should be found at $T^+_C$ (as the dashed pink line shows in inset) according to the reversible crystallization transition (i.e., FE → relaxor). Accordingly, the reverse relaxor transition in (a) should originate from the residual relaxor, which also indicates that the product of forward crystallization transition is a relaxor-ferroelectric. Note that at low frequencies $T^+_C$ is lower than $T^+_g$ (as the dashed pink line shows in inset), which cannot be used to exclude the reversible transition scenario.

$T^+_C$ is lower than $T^+_g$ (inset of Fig. 3(b)) indicates that the crystallization transition is irreversible, otherwise a reverse relaxor transition should appear according to the reversible transition scenario (as the dashed pink line demonstrates). The direct transition from the FE phase to the PE phase without an intermediate relaxor upon heating suggests that: (i) the product of forward crystallization transition is a relaxor-ferroelectric instead of a fully transformed FE phase [12]; (ii) the crystallization transition is irreversible: relaxor $\rightarrow$ FE upon cooling and FE $\rightarrow$ PE upon heating. More discussions on the previous understanding can be seen in Ref. [19].

From the results of Ti$_{48.7}$Ni$_{51.3}$ and PLZT, it can be concluded that the crystallization transition of ferroic glasses produces the glass-ferroic. It originates from a time-dependent crystallization process, which can be understood in the context of a classical free-energy landscape containing multiple minima (basins) separated by local barriers [1,20,21]. The associated microstructure evolution upon continuous cooling and heating was simulated by the phase field modeling [19]. Upon cooling, the system, which in the parent phase can continuously explore different configurations [Fig. 4(a1)], will gradually trap into specific basins. Because of the low kinetic energy ($k_B T$), some local barriers caused by disorder (e.g., point defects [7,20,21] and nano-sized precipitates [9]) cannot be overcome, thereby leading to “frozen” configurations (a glass state) [Fig. 4(b1)]. The heterogeneity of disorder in the glass state [1] gives rise to a distribution of the time-dependent formation of the stable ferroic phase (i.e., crystallization). Upon further cooling, the driving force increases, and thus some configurations with low local barriers [Fig. 4(c1)] or domains with low disorder [Fig. 4(c2)] can undergo a crystallization transition in a much shorter time. Yet others with high disorder cannot crystallize immediately because they are trapped among high local barriers and need sufficient time to overcome their local barriers, thereby keeping a glass state. This time dependence explains why the crystallization transition of ferroic glass produces the glass-ferroic instead of the ferroic crystal.

Upon heating, the ferroic phase component first keeps the stability due to a high-energy barrier [Fig. 4(e1)]. When it transforms, the driving force from the ferroic phase to the parent phase is larger than the local one to ferroic glass. Meanwhile, the kinetic energy is also high to overcome local barriers [Fig. 4(f1)]. Therefore, the increase in both driving force and kinetic energy upon heating (i.e., a cooperation relationship) supports the transition directly from the ferroic phase to the parent phase [Fig. 4(f1)], which is different from the situation upon cooling that the driving force increases whereas the kinetic energy decreases (i.e., a competition relationship) [Fig. 4(c1)].

Next, we will explain why the glass-ferroic shows two types of transition characteristics as demonstrated in Ti$_{48.7}$Ni$_{51.3}$ and PLZT. The difference involving the sequence between the reverse glass transition (at $T^+_m$) and the reverse crystallization (“melting”) transition (at $T^+_g$) (i.e., $T^+_g < T^-_m$ or $T^+_g > T^-_m$) can
FIG. 5. (Color online) (a) Rough classification of glass-ferroics based on the thermal hysteresis and lattice deformation of crystallization transitions: the abnormal observation only occurs when the thermal hysteresis (or lattice deformation) is large enough, such as in Ti48Ta3Ni51O3, whereas the reversible (normal) one occurs when the thermal hysteresis is much smaller. The data of Ti-Ni and PLZT are from the present study, Ni-Co-Mn-Ga (Ni52Co40Mn12Ga2) is from Ref. [15], Ti-Pd-Cr (Ti46Pd44Cr10) is from Ref. [17], PSN (PbSc0.5Nb0.5O3) is from Ref. [16], 0.6Pb(Nb0.5Ti0.5)O3-0.37PbTiO3-0.03PbZrO3 is from Ref. [11], PST (PbSc0.5Ta0.5O3) is from Ref. [13], and the others are from Ref. [22]. (b)–(d) Generic temperature vs defect-concentration ferroic phase diagram upon cooling, upon heating (Tg > Tm), and upon heating (Tg < Tm), respectively. Tg and Tm denote the reverse glass transition and reverse crystallization (melting) transition temperatures. Three classes of ferroic states, i.e., ferroic crystal, glass-ferroic, and ferroic glass, are produced by three corresponding classes of transitions, i.e., ferroic transition, crystallization transition, and glass transition, respectively. Besides four states in (b), the phase diagram upon heating of (c) and (d) shows an additional composite state transition, respectively. The dotted line, purple and pink dots in (c) and (d) represent the ferroic and crystallization transition curves upon cooling, the state which has the potential application of reversible field-induced properties (RFIP, e.g., large electrostriction with low hysteresis [24]) and ferroelectric phase-change memory (F-PCM) devices (similar to PCM in chalcogenide glass [5]), respectively.

be attributed to the scale of thermal hysteresis (the difference between forward and reverse transition temperatures) of crystallization transitions because of the lack of thermal hysteresis of glass transitions [7,9]. Thermal hysteresis is known to strongly depend on the stability of the ferroic phase: The more stable a ferroic phase is, the larger the thermal hysteresis is, and the higher Tm is [22,23]. Moreover, the stability can be further estimated by the magnitude of lattice deformation since the entropy change is proportional: (i) to the lattice deformation for ferroelectric and ferromagnetic systems [22] and (ii) to the square of the lattice deformation for ferroelastic systems [23]. For example, a large lattice deformation (∼10%) of Ti48Ta3Ni51O3 [23] explains a large hysteresis (∼45 K) whereas a small lattice deformation (∼2%) of PLZT [10] gives rise to a small hysteresis (∼16 K). Therefore, the reason why all previously reported transition characteristics of glass-ferroics appear reversibly (Tg > Tm) is due to the small thermal hysteresis (or lattice deformation) [Fig. 5(a)]. The abnormal observation (Tg < Tm) only occurs when the thermal hysteresis is large enough, such as in Ti48Ta3Ni51O3. Note that the transition sequence in structural glasses (Tg > Tm) can also be understood under the same criterion, a large thermal hysteresis (i.e., the large difference between Tm and Tcrystallization).

The finding of glass-ferroic may lead to many important consequences. First, as the third ferroic state besides ferroic crystal and ferroic glass (Table I), the glass-ferroic universally exists in the phase diagram [Figs. 5(b)–5(d)], which is a fundamental improvement over previously reported phase diagrams [7,18,25] that show two ferroic states corresponding to three classes of phase transitions. Second, glass-ferroics may open a new field to develop functional materials and devices as glass-crystals have proved in structural materials [3,4]. For example, the large reversible field-induced physical property [in the purple dot of Fig. 5(e)] can be expected, and this is confirmed by our ongoing study [24]. Moreover, the F-PCM device [in the pink dot of Fig. 5(d), given that it is at room temperature] can be designed: By applying a heat pulse, it can be switched between a relaxor state (through a natural cooling after applying intense pulse of heat to increase temperature over Tm) and a ferroelastic state (through a time-induced crystallization of the relaxor after applying a lower-intensity heat pulse of longer duration below Tm), thereby changing dielectric and optical (e.g., birefringent) properties and allowing the storage of information. The same diffusionless transformation process with ferroelectric random access memory (F-RAM) [26] indicates some expected advantages of F-PCM, such as low power usage, fast read/write performance, and overcoming the degradation problem of traditional PCM. In addition, the PCM principle of F-PCM could also overcome the destructive reading problem of F-RAM [26]. In short, the phase diagram in Fig. 5 will be a fundamental guiding for where to find glass-ferroics and how to design glass-ferroic properties.

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