Tetragonal tungsten bronze compounds: relaxor versus mixed ferroelectric–dipole glass behavior

Tetragonal tungsten bronze compounds: relaxor versus mixed ferroelectric–dipole glass behavior

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Abstract

We demonstrate that recent experimental data (Castel *et al* 2009 *J. Phys.: Condens. Matter* **21** 452201) on the tungsten bronze compound (TBC) $Ba_2Pr_xNd_{1-x}FeNb_4O_{15}$ can be well explained in our model predicting a crossover from ferroelectric ($x = 0$) to orientational (dipole) glass ($x = 1$), rather then relaxor, behavior. We show that, since a 'classical' perovskite relaxor like $Pb(Mn_{1/3}Nb_{2/3})O_3$ is never a ferroelectric, the presence of ferroelectric hysteresis loops in the TBC shows that this substance actually transits from ferroelectric to orientational glass phase with x growth. To describe the above crossover theoretically, we use the simple replica-symmetric solution for the disordered Ising model.

(Some figures in this article are in colour only in the electronic version)

Disordered dielectrics and ferroelectrics have been attracting a great deal of attention from scientists for a long time due to additional possibilities (governed by disorder) to control their physical properties which might be useful for applications. The disordered dielectrics can be, in principle, divided into two classes. One of them comprises the compounds like $KTaO_3$:Li (KTL), Nb (KTN) and Na, which undergo a crossover between ferroelectric and orientational (dipole) glass phases [1], while the other class may be related to so-called relaxor ferroelectrics. The latter substances, actually never being ferroelectrics [2, 3], belong to the perovskite family. Their general formulae are $Pb(B_{1/2}B'_{1/2})O_3$ (the so-called 1:1 family) and $Pb(B_{1/3}B'_{2/3})O_3$ (the so-called 1:2 family) with the B ion being Mn, Zn, Sc, Nb or Ta. For example, materials as such $Pb(Sc_{1/2}Nb_{1/2})O_3$ (PSN), $Pb(Sc_{1/2}Ta_{1/2})O_3$ (PST) (1:1 family) or $Pb(Mn_{1/3}Nb_{2/3})O_3$ (PMN), $Pb(Zn_{1/3}, Nb_{2/3})O_3$ (PZN) (1:2 family) are considered in the literature to be 'classical' relaxors.

The main reason for the above relaxors not to become ferroelectrics is the non-stoichiometry of the position of the B ion in their perovskite structure. This non-stoichiometry actually 'spoils' the phonon spectrum inherent in the perovskite structure, destroying the ferroelectrically important soft mode (see [4] and references therein). The latter fact manifests itself in many observable quantities of relaxors, to name a few, the smearing of the ferroelectric phase transition and the appearance of additional low-temperature peaks in dielectric spectra obeying the Vogel–Fulcher law [5]. There are, however, differences between relaxors and disordered dielectrics like KTL. The major difference is that, since the above relaxors do not exhibit macroscopic ferroelectricity, they never have ferroelectric hysteresis, while the substances like KTL exhibit it in their ferroelectric and mixed ferroglass phases, see, e.g., [6]. As the tungsten bronze compound (TBC) $Ba_2Pr_xNd_{1-x}FeNb_4O_{15}$ exhibits ferroelectric hysteresis, which disappears with the growth of Pr content x, it rather shows the crossover between ferroelectric and dipole glass behavior similar to that in the KTL family.

In this paper, on the basis of analysis of the experimental facts about the TBC [7], we come to the conclusion that this substance demonstrates mixed ferroelectric–orientational glass, rather than relaxor, behavior. To investigate this crossover theoretically, we utilize the simple model, based on the replica-symmetric solution for the disordered Ising model. We show that our simple model is able to describe qualitatively both the phase diagram and hysteresis loops in the TBC. Based on our previous results on the KTL family of disordered ferroelectrics, we make predictions about the

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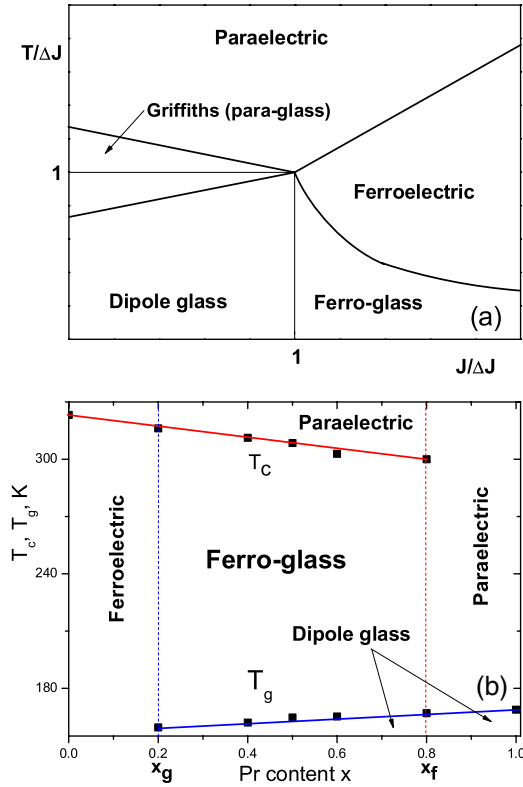[1] http://draco.uni.opole.pl/~stefan/VStephanovichDossier.html.

Figure 1. The phase diagram of the system under consideration. Panel (a) depicts a schematic picture with the Griffiths phase shown. Panel (b) reports the approximations $T_c(x) = 290.95 + 29.05(1 - x)$ K and $T_g(x) \approx 157.2 + 11.57x$ (full lines) and experimental dependences [7] $T_c(x)$ and $T_g(x)$ (squares). Critical x values for glassy x_g and ferroelectric x_f are also shown.

dynamical properties of the TBC as well as about the absence of the Curie–Weiss law in the paraelectric phase of the TBC. The latter fact may be related to the occurrence of a Griffiths (para-glass) phase [8] in this substance. The schematic phase diagram of the TBC and similar substances, where a crossover from ferroelectric to glassy behavior occurs, is reported in figure 1(a). This phase diagram is more or less standard (see, e.g., [1]) except for the region where the Griffiths (para-glass) phase is realized. The boundaries of this region may, of course, vary from substance to substance so that the para-glass phase may penetrate deeper in the paraelectric and/or dipole glass phase. This is because the different strength of the 'glassy interaction' between dipoles leads to the formation of glassy clusters (which is a physical mechanism behind the Griffiths phase) at higher or lower temperatures. Consequently, these clusters merge into an infinite one (signifying the glassy phase onset) at higher or lower temperatures.

To describe theoretically the ferroelectric–orientational glass crossover behavior in the TBC, we should know what kind of dipoles can order ferroelectrically in this material and how many permissible orientations in the crystal lattice do they have. For example, it is well known (see, e.g., [9] and references therein) that Li in KTaO$_3$ forms impurity dipoles due to the off-central position of Li in a host KTaO$_3$ lattice. These dipoles (at $T < T_c(x)$ and at $x > x_{cr}$, where x_{cr} is the Li critical content) can order ferroelectrically and have six

permissible orientations (along the [100] kind of direction) in a host lattice. As this information is absent in the TBC, we describe the thermodynamic properties of this substance by the simplest possible model of two-orientable dipoles. In such a model, to account for interplay between ferroelectric and glassy behavior, we use the replica formalism for a random Ising model. Namely, we consider the Hamiltonian

$$\mathcal{H} = -\tfrac{1}{2} \sum_{ij} J_{ij} S_i^z S_j^z - E \sum_i S_i^z, \tag{1}$$

where $E \equiv E_z$ is an external electric field (in energy units) and the random interactions J_{ij} between pseudospins S_i^z and S_j^z ($S^z \equiv \pm 1$) are distributed according to Gaussian law:

$$P(J) = \frac{1}{\Delta J \sqrt{2\pi}} \exp\left(-\frac{(J - \bar{J})^2}{2(\Delta J)^2}\right), \tag{2}$$

where $\bar{J}$ and ΔJ are, respectively, the mean value (responsible for long-range ferroelectric order formation) and variance (responsible for realization of the glassy order parameter and destruction of long-range order) of random interactions. To describe the dependence of the TBC thermodynamic characteristics on Pr content x, the parameters $\bar{J}$ and ΔJ should be functions of x. Both these quantities will be extracted below from the comparison of temperatures T_c (ferroelectric phase transition temperature) and T_g (glassy freezing transition temperature) with their experimental values.

Conventional replica formalism (see, e.g., [12, 13]), being applied to Hamiltonian (1) (with respect to equation (2)) gives the following standard (so-called replica-symmetric [12, 13]) equations for long-range m (dimensionless spontaneous polarization) and glassy q order parameters:

$$m = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} e^{-\frac{y^2}{2}} \tanh\left[\frac{E + \bar{J}m + y\Delta J\sqrt{q}}{k_B T}\right] dy,$$
$$q = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} e^{-\frac{y^2}{2}} \tanh^2\left[\frac{E + \bar{J}m + y\Delta J\sqrt{q}}{k_B T}\right] dy, \tag{3}$$

where k_B is the Boltzmann constant. These equations (along with the corresponding free energy function [13]) define all equilibrium thermodynamic properties of the system under consideration. We note here the well-known fact that the replica-symmetric solution is unstable against replica-symmetry breaking. Under the action of external field E one can draw a borderline, separating the regions of stable and unstable replica-symmetric solutions. For the field-temperature variable plot, this line is known as the de Almeida–Thouless (AT) line [14]. A standard (in replica formalism) but lengthy calculation leads to the following criterion of replica-symmetric solution stability:

$$\frac{(\Delta J)^2}{(k_B T)^2} \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} e^{-\frac{y^2}{2}} \frac{dy}{\cosh^4\left[\frac{E + \bar{J}m + y\Delta J\sqrt{q}}{k_B T}\right]} < 1. \tag{4}$$

To obtain the AT line from equation (4), we should solve it (the equality in equation (4)) simultaneously with equations (3) for order parameters. Our analysis shows that the presence of the

long-range order parameter m plays a role of an additional (to the external one) stabilizing field so that the replica-symmetric solution (3) in our case is stable almost everywhere on the E–T plane except for the very low-temperature region. This result is correct for all x except the point $x = 0$, where the system is ordered. We note that different versions of the above replica formalism had been used to describe the disordered dielectrics like proton glasses [10] and relaxor ferroelectrics (see [11] and references therein).

First we use equations (3) to calculate the T–x (T is a temperature) phase diagram of the system, i.e. the dependences $T_c(x)$ and $T_g(x)$, which should be calculated for $E = 0$ in equations (3). Namely, to find T_c, we put $m \to 0$ in the first equation (3) and expand its integrand at small m up to the first nonvanishing term. This yields

$$\tanh\left[\frac{\bar{J}m + y\Delta J\sqrt{q}}{k_B T}\right] \approx \tanh\left[\frac{y\Delta J\sqrt{q}}{k_B T}\right]$$
$$+ \frac{\bar{J}m}{k_B T}\left(1 - \tanh^2\left[\frac{y\Delta J\sqrt{q}}{k_B T}\right]\right). \quad (5)$$

Substitution of equation (5) into the first equation (3) yields the vanishing of the first term, while the second one gives the equation for T_c:

$$k_B T_c = \bar{J}(1 - q_0(T_c)) \equiv \frac{\bar{J}}{\sqrt{2\pi}}\int_{-\infty}^{\infty} e^{-\frac{y^2}{2}}\frac{\mathrm{d}y}{\cosh^2\left[\frac{y\Delta J\sqrt{q}}{k_B T_c}\right]}. \quad (6)$$

Now we pay attention to the fact that, since $q \equiv 0$ at $T > T_g$, so that $q(T_c > T_g) = 0$, we immediately obtain from equation (6) that $k_B T_c = \bar{J}$. Then, putting $q \to 0$ in the second equation (3), we obtain the expression for $T_g(x)$. Finally, the expressions for both transition temperatures are

$$k_B T_c = \bar{J}, \qquad k_B T_g = \Delta J. \quad (7)$$

To deduce the dependences of $\bar{J}(x)$ and $\Delta J(x)$, we refer to figure 5 from [7], where the experimental dependences $T_c(x)$ and $T_g(x)$ for the TBC are reported. It is seen that there are critical concentrations for glassy $x_g \approx 0.2$ and ferroelectric $x_f \approx 0.8$ order realizations. At all other values of x the dependences $T_c(x)$ and $T_g(x)$ are almost linear. These facts suggest that Pr content dependence of the phase transition temperatures, and hence the above parameters of the interaction distribution, should be chosen in the form of a power series in x:

$$\bar{J}(x) = \begin{cases} 0, & x \geqslant x_f \\ J_0 + a_1 x + a_2 x^2 + \cdots, & x < x_f, \end{cases}$$
$$\Delta J(x) = \begin{cases} \Delta J_0 + b_1 x + b_2 x^2 + \cdots, & x > x_g \\ 0, & x \leqslant x_g. \end{cases} \quad (8)$$

Here J_0 defines the mean interaction between dipoles in the TBC at $x = 1$, having the physical meaning of a mean electric field (in energy units) acting between the dipoles. In turn, ΔJ_0 defines the maximal (at $x = 1$) variance of random interactions. Comparison of equations (7) and (8) shows the other meaning of the parameters J_0 and ΔJ_0. Namely, J_0

defines the mean-field (i.e. at $x < x_g$, where the system is almost completely ordered) ferroelectric phase transition temperature, while ΔJ_0 measures the maximal (at $x > x_f$) glassy freezing temperature. The situation here is qualitatively similar to that in KTL [1]. Note that dependences (8) reflect the physics of the system under consideration: at $x < x_g$ the width of the distribution function tends to zero so that Gaussian (2) reduces to a δ function. It can be shown [15] that this δ function generates the well-known mean-field equation $m = \tanh(m J_0/k_B T)$ for long-range parameter m in the ordered Ising model. On the other hand, at $x > x_f$ the mean value $\bar{J}$ equals zero so that the distribution function (2) remains Gaussian but with zero mean, which leads to the situation when the system admits only the glassy order parameter, see, for example, [12]. We note here that, while at all x values except critical concentrations the dependences $T_c(x)$ and $T_g(x)$ are almost linear, near $x_{f,g}$ the whole power series (8) comes into play. Actually, in [7], the finite values of phase transition temperatures appear abruptly near $x_{f,g}$. Within the replica formalism, it is possible to obtain the equations for the above critical concentrations $x_{f,g}$. The calculation of $x_{f,g}$, however, involves more subtle analysis than that based on simple equations (3), as below T_g the replica-symmetric solution (3) is unstable. The results of such an analysis will be published elsewhere. In figure 1(b), we show the approximation of experimental points (see figure 5 of [7]) $T_c(x)$ and $T_g(x)$ by linear terms in (8). The fitting linear dependences were obtained in the form

$$T_c(x) \approx 320 - 29.049x \text{ (K)},$$
$$T_g(x) \approx 157.2 + 11.57x \text{ (K)}. \quad (9)$$

From these dependences we can recover the values $J_0 \approx 320\,\text{K}$ and $\Delta J_0 \approx 168.8\,\text{K}$. The comparison of these values shows that $J_0 \approx 1.9\Delta J_0$, which means that the mean value of the interaction is almost two times larger than its dispersion. Such a large ratio $J_0/\Delta J_0$ is actually responsible for the situation when the TBC exhibits ferroelectric long-range order for the majority of Pr contents—from $x = 0$ to 0.8. It is seen that the above linear dependences approximate the experimental points pretty well. This means that our simple replica-symmetric solution captures qualitatively all peculiarities of a crossover between orientational glass and ferroelectricity in the TBC.

Next we use equations (3) for the qualitative description of ferroelectric hysteresis $m(E)$ in the TBC. Figure 2(a) reports the qualitative picture of a hysteresis, described by equations (3). Namely, if $T > T_c(x)$ (paraelectric phase), the curve $m(E)$ is a monotonically growing function so that both directions of electric field variation are the same, i.e. we are on the same curve. At $T < T_c(x)$ the $m(E)$ curve acquired an 's shape' with a central unstable part with $\mathrm{d}m/\mathrm{d}E < 0$. This unstable part yields the hysteretic behavior, namely jumps at $E = \pm E_c$, where E_c is a coercive field. These jumps, as usual, generate the hysteresis loop as shown in figure 2(a). The results of specific calculations for the experimental [7] temperature $T = 280$ K (corresponding to the dimensionless quantity $k_B T/J_0 = 0.875$) are reported in figure 2(b). It is seen that the maximal coercive field is achieved at $x = 0$, where the whole
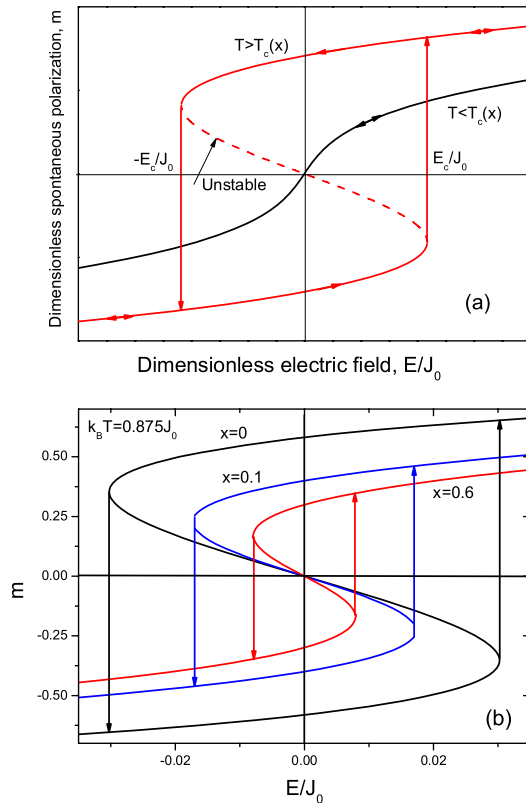
Figure 2. The theoretical hysteresis loops $m(E/J_0)$, obtained from solution of equations (3). Panel (a) shows the qualitative situation. Dashed line corresponds to the unstable part of the $m(E/J_0)$ curve at $T < T_c(x)$. Arrows show the possible directions of sweep around the hysteresis loop. The coercive field E_c is also shown. Panel (b) reports a quantitative solution for $k_B T = 0.875 J_0$ and different x.

system is ferroelectric. As Pr content x grows, the coercive field decays so that at x corresponding to the T_c value, the unstable part of the $m(E)$ curve degenerates in a vertical line and $E_c = 0$. At x values corresponding to $T > T_c$, we have the paraelectric phase with a monotonic $m(E)$ curve similar to that from figure 2(a). We note that saturation polarization diminishes as x grows. This is because at larger x the dilution of the system grows so that there are less (than at $x = 0$) ferroelectrically active dipoles, which gives smaller saturation polarization.

The comparison of our theoretical hysteresis loops from figure 2 with experimental ones from [7] shows their different shapes in theory and experiment. While both theory and experiment give the decay of saturation polarization as x grows, the coercive field in the experiment and theory have different behaviors. Namely, the experimental coercive field depends on x only weakly, while the theoretical one depends strongly. The latter fact gives the different shapes of theoretical and experimental hysteresis loops. To calculate the above shape more precisely, the consideration of repolarization of the domain structure of the TBC in the external electric field is necessary. This problem requires experimental investigations of the character of the ferroelectric domain structure in the TBC. The theoretical approach dealing with domain structure characteristics in disordered ferroelectrics have been put

forward earlier [16]. Another way of (less physical) calculation of hysteresis loops in the TBC is to use the Preisach model [17]-like approach (see, e.g., [18] and references therein), where the loops $m(E)$ from figure 2(b) (we recollect that these are actually the solutions of equations (3) at $T < T_c(x)$) can be considered as elementary hysterons. As those hysterons are functions of T and x, the resulting loop would also depend on these parameters.

To conclude, in the present paper we have shown that the tungsten bronze compound (TBC) $Ba_2Pr_xNd_{1-x}FeNb_4O_{15}$ undergoes a crossover between ferroelectric and orientational (dipole) glass phases rather then exhibits 'classical' (i.e. that adopted in the literature) relaxor behavior. To demonstrate that, we use the replica-symmetric solution of the disordered Ising model which permits us to derive the dependences of the phase transition temperatures T_c and T_g on Pr content x. We note here that the above replica formalism permits us to obtain the equations for critical concentrations for ferroelectric x_f and glassy order x_g appearance. This issue can be elaborated by considering the nonequilibrium (like frequency-dependent dielectric susceptibility) properties of the system under consideration; it is outside the framework of the present paper.

The same replica-symmetric equations (3) have been used to calculate the dependence $m(E)$, determining qualitatively the ferroelectric hysteresis in the system. We have shown that hysteresis behaves according to the system phase diagram. Namely, as (at given x) T approaches T_c or $x \to x_f$, the loops monotonically shrink, giving smaller coercive field values. At $T = T_c$ or $x = x_f$ the loop has zero width and coercive field $E_c = 0$. Although our theory describes the decay of saturation polarization at Pr content growth, we were not able to explain the enhancement of E_c (the 'width' of the hysteresis loop) in the TBC at $x = 0.6$, see figure 6 of [7]. The explanation of this puzzling behavior requires (even on the level of the replica-symmetric solution (3)) more exquisite approaches (than the above simple model) like the supposition that there are additional defects (interacting with ferroelectrically active dipoles) in the system such that, at certain x (e.g. at $x = 0.6$ in [7]), they enhance the spontaneous polarization and consequently coercive field. The experimental fact [7] that the paraelectric phase of the TBC does not follow the Curie–Weiss behavior can be explained in terms of the Griffiths (para-glass) phase realization in the substance [8], see figure 1(a). Although the dynamics of order parameters cannot be calculated with the help of the above replica-symmetric solution, its qualitative description can be made similar to that in ferroelectric polymers [19]. Such calculations are outside the framework of the present work and will be published elsewhere. We emphasize once more that to elucidate the interplay between ferroelectric and orientational glass behavior in nonperovskite disordered ferroelectrics, additional experimental investigations are highly desirable.

Acknowledgment

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