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Existence of a quadruple point in a binary ferroelectric phase diagram

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In experimentally measured temperature-composition ferroelectric phase diagrams of $BaTiO_3$-based binary systems, a quadruple point where cubic (C), tetragonal (T), orthorhombic (O), and rhombohedral (R) phases converge has been frequently reported in previous work. More interestingly, the quadruple points are experimentally found to behave as a critical point with large enhancement in properties. However, it has remained a fundamental question as to whether a quadruple point in a *binary* ferroelectric system defies the thermodynamic phase rule and whether such a point necessarily goes critical. In this study, it is demonstrated by Landau theory that a C-T-O-R quadruple point in a *binary* ferroelectric system can only exist in the form of *a unique type of critical point* at which two first-order transition lines and two second-order ones meet, and such critical quadruple points do not defy the thermodynamic phase rule. It is further shown that at such a critical C-T-O-R quadruple point, the system exhibits infinitely large piezoelectric coefficients, which agrees with the high piezoelectricity observed at the C-T-O-R quadruple point in a number of $BaTiO_3$-based binary ferroelectric systems and also helps to explain the large piezoelectricity obtained at the morphotropic phase boundaries of these quadruple point based systems.

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I. INTRODUCTION

The Gibbs phase rules set constraints on the maximum number of phases converging at a point in an equilibrium phase diagram of a multicomponent system [1–4]. For example, in the temperature-composition phase diagram of a binary system when other control parameters such as pressure field are fixed, the first phase rule regarding first-order phase transitions limits the maximum number of phases coexisting at equilibrium to three and the second phase rule regarding critical phase transitions limits the maximum number of phases becoming identical at a critical point to two [1–4]. Therefore, it seems that for the temperature-composition ferroelectric phase diagram of a binary $BaTiO_3$-based ferroelectric solid solution with other fields such as electric field and pressure fixed, according to the above phase rules, the maximum number of ferroelectric phases converging at a point (either in the form of first-order transitions or critical ones) could not exceed three.

Despite the above phase rules, it has long been reported in experiments that in the temperature-composition phase diagram of $BaTiO_3$-based binary ferroelectric systems such as $BaTi_{1-x}Zr_xO_3$ [5], $BaTi_{1-x}Sn_xO_3$ [6], $Ba_{1-x}Sr_xTiO_3$, [7], and $(1–x)BaZr_{0.2}Ti_{0.8}O_3$-$xBa_{0.7}Ca_{0.3}TiO_3$ (BZT-BCT) [8], a quadruple point where cubic (C, $Pm\bar{3}m$), tetragonal (T, $P4mm$), orthorhombic (O, $Amm2$) and rhombohedral (R, $R3m$) phases converge always appears. More importantly, it has been illustrated that such C-T-O-R quadruple points always exhibit a *near-critical* ferroelectric transition which are accompanied with high dielectric permittivity [9], high energy-storage density [10], large electrocaloric effect [11], and enhanced electrostrain [12] due to the flattened free energy curves with respect to polarization at the critical transition. Thus, the experimentally reported quadruple point in these binary ferroelectric systems is hard to understand because it seemingly violates the above Gibbs phase rule, not to mention its critical behavior. Clearly a theoretical understanding to the above puzzle not only makes a contribution to the thermodynamics of ferroelectrics, but also may contribute to a better understanding of the properties of this important class of functional materials.

In this work, we use Landau theory to demonstrate that the C-T-O-R quadruple point can exist in a *binary* ferroelectric system *only* in the form of *a unique type of critical point* where two first-order and two second-order transition lines meet; such kind of critical quadruple point does not defy the phase rule, which explains the experimentally observed critical C-T-O-R quadruple point in $BaTiO_3$-based binary ferroelectric systems. We further show that this type of critical quadruple point should be accompanied by infinitely large piezoelectric coefficients, which agrees with the high piezoelectricity obtained at the C-T-O-R quadruple point in some binary lead-free $BaTiO_3$-based ferroelectric systems and allows us to explain the large piezoelectricity at the morphotropic phase boundary (MPB) in systems containing such

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a quadruple point. In addition, we find that for ternary ferroelectric systems the C-T-O-R quadruple point could exist in the form of other types of special points such as near-isotropic points and isolated critical points. This study could stimulate experimental search of critical points in ferroelectric systems.

II. LANDAU FREE ENERGY MODELS

The Landau free energy, f, of a BaTiO$_3$-based binary ferroelectric system in an unconstrained state can be written as a Landau polynomial of polarization vector $\mathbf{P}$ (P_1, P_2, P_3) truncated at the sixth order:

$$\begin{aligned} f = {} & \alpha P^2 + \beta_1 P^4 + \gamma_1 P^6 + \beta_2\left(P_1^2P_2^2 + P_2^2P_3^2 + P_1^2P_3^2\right) \\ & + \gamma_2\left[P_1^4\left(P_2^2+P_3^2\right) + P_2^4\left(P_1^2+P_3^2\right) + P_3^4\left(P_1^2+P_2^2\right)\right] \\ & + \gamma_3 P_1^2P_2^2P_3^2, \end{aligned} \tag{1}$$

where P is the length of the polarization vector $\mathbf{P}$ (P_1, P_2, P_3); α, β_1, β_2, γ_1, γ_2, γ_3 are the Landau coefficients depending on concentration (c) and temperature (T). The first three terms at the right-hand side of Eq. (1) are isotropic while the last three terms are anisotropic. The Landau polynomial in Eq. (1) has been derived and employed in previous works on Landau theory of ferroelectric materials [13,14]. A sixth-order rather than eighth-order Landau polynomial is employed because it is both necessary and sufficient to describe all four phases (C, T, O, and R) considered in the studied systems and the contributions of higher-order terms such as eighth order to the free energy are rather small when P is small near the Curie temperature (T_C) [13,15]. Equation (1) is written in terms of polarization vector $\mathbf{P}$ (P_1, P_2, P_3) to distinguish different ferroelectric phases (T, O, and R). For simplicity, the free energy in Eq. (1) is first transformed to polynomials containing only scalar P rather than $\mathbf{P}$ (P_1, P_2, P_3). This is possible because for T, O, and R ferroelectric phases, P_1, P_2, and P_3 have the following relationships with P: $P_1 = P$, $P_2 = P_3 = 0$ for T, $P_1 = P_2 = \frac{\sqrt{2}}{2}P$, $P_3 = 0$ for O, and $P_1 = P_2 = P_3 = \frac{\sqrt{3}}{3}P$ for R. The free energy for T, O, and R phases can then be written as a function of P as follows:

$$f_T = \alpha P^2 + \beta_1 P^4 + \gamma_1 P^6, \tag{2}$$

$$f_O = \alpha P^2 + \left(\beta_1 + \frac{\beta_2}{4}\right)P^4 + \left(\gamma_1 + \frac{\gamma_2}{4}\right)P^6, \tag{3}$$

$$f_R = \alpha P^2 + \left(\beta_1 + \frac{\beta_2}{3}\right)P^4 + \left(\gamma_1 + \frac{2\gamma_2}{9} + \frac{\gamma_2}{27}\right)P^6, \tag{4}$$

where f_T, f_O, and f_R are the free energy of the T, O, and R phases, respectively.

III. RESULTS

There are four kinds of phase transitions in the vicinity of the C-T-O-R quadruple point in experiments [5–8], i.e., C-T, C-R, T-O, and O-R. Both the T-O and O-R transitions have to be first order because the symmetry elements of the T, O, and R phases do not have a group-subgroup relationship [14]. On the other hand, the C-T and C-R transitions can be either first order or second order from the symmetry argument [14]. The second-order Landau coefficient in Eq. (1), α [$\alpha = \alpha_0(T - T_0)$, where α_0 is a positive constant and T_0 is the Curie-Weiss temperature], is positive at first-order transitions ($T_C > T_0$) and zero at second-order transitions ($T_C = T_0$) [15]. Thus, from Eqs. (2) and (4), we know that the order of the C-T and C-R transitions at the C-T-O-R quadruple point has to be the same. Therefore, there are two possibilities with regard to the nature of the four phase transitions in the vicinity of the quadruple point: (1) All four transitions (C-T, C-R, T-O, and O-R) are first-order, which is designated as case 1; (2) C-T and C-R transitions are second-order while T-O and O-R transitions are first-order, which is designated as case 2. Note that here we emphasize "in the vicinity" of the quadruple point rather than exactly at it because the order of transition might change on the quadruple point as required by the four-phase convergence.

For case 1, i.e., all four transitions are *first order* in the vicinity of the quadruple point, we can derive a relationship among the Landau coefficients at the quadruple point as shown below. Here C-T, C-O, and C-R rather than C-T, C-R, T-O, and O-R transitions are considered for simplicity. First let us consider a first-order C-T ferroelectric transition at the Curie temperature. Two thermodynamic requirements need to be satisfied at this C-T transition: First, the free energy of the C phase and that of the T phase should be equal; second, the free energy of the T phase should be a local minimum. That is, the first derivative of the free energy of the T phase with respect to P at P_T should be zero (P_T is the polarization length of the T phase at the Curie temperature). With the first requirement, we can obtain an equation, $\alpha P_T^2 + \beta_1 P_T^4 + \gamma_1 P_T^6 = 0$, while with the second requirement, we can obtain another equation, $2\alpha P_T + 4\beta_1 P_T^3 + 6\gamma_1 P_T^5 = 0$. Combining the two equations, P_T can be eliminated and the following relationship among the Landau coefficients at the Curie temperature can be established:

$$\beta_1^2 = 4\alpha\gamma_1. \tag{5}$$

A similar analysis can be performed for the first-order C to R and C to O ferroelectric transitions and thus two more relationships among the Landau coefficients at the C-T-O-R quadruple point can be obtained:

$$\left(\beta_1 + \frac{\beta_2}{3}\right)^2 = 4\alpha\left(\gamma_1 + \frac{2\gamma_2}{9} + \frac{\gamma_3}{27}\right), \tag{6}$$

$$\left(\beta_1 + \frac{\beta_2}{4}\right)^2 = 4\alpha\left(\gamma_1 + \frac{\gamma_2}{4}\right). \tag{7}$$

Equations (5)–(7) contain only the six Landau coefficients α, β_1, β_2, γ_1, γ_2, γ_3 without any other unknown parameters. It is impossible to determine all the values of the six coefficients due to the limited number of equations (i.e., three), but some of them can be determined. For example, it can be deduced from Eqs. (6)–(8) that (see Supplemental Material [16])

$$\beta_2 = \gamma_2 = \gamma_3 = 0, \tag{8}$$

or

$$\alpha = \beta_1 = \beta_2 = 0. \tag{9}$$

Therefore, Eqs. (5)–(7) have two possible mathematical solutions as represented by Eqs. (8) and (9). The first one given by Eq. (8) represents an isotropic case (all anisotropic terms are zero) where the first-order T-O and O-R transitions become barrierless at the C-T-O-R quadruple point while the C-T and C-R transitions are still first order. Note that the transitions among T/O/R cannot be barrierless due to the symmetry argument [14], although the inclusion of eighth-order and/or higher-order terms in Eq. (1) could make the transitions among T/O/R have small barriers. Therefore, Eq. (8) could give a nearly isotropic C-T-O-R quadruple point. The second solution given by Eq. (9) represents a case where the first-order C-T, C-O, and C-R transitions all become critical at the C-T-O-R quadruple point because the fourth-order coefficients in Eqs. (2)–(4) are all zero. Therefore, Eq. (9) represents an isolated critical quadruple point at which four first-order transition lines meet. However, both these cases have a low probability to exit *in a binary ferroelectric system*. This is because the three Landau coefficients (β_2, γ_2, γ_3 or α, β_1, β_2) all depend only on c and T in a binary ferroelectric system. The three equations, $\alpha(c, T) = 0$, $\beta_1(c, T) = 0$, $\beta_2(c, T) = 0$ or $\beta_2(c, T) = 0$, $\gamma_2(c, T) = 0$, $\gamma_3(c, T) = 0$ represent three curves in the c-T space and the probability for them to intersect at a single point is rather low. Nevertheless, these two cases are highly possible in a ternary ferroelectric system because of the sufficient independent variables, i.e., c_1, c_2, and T.

For case 2, i.e., the C-T and C-R transitions are second-order while the T-O and O-R transitions are first order in the vicinity of the quadruple point, we can also deduce a relationship among the Landau coefficients at the quadruple point. From the second-order nature of the C-T and C-R transitions, it can be deduced from Eqs. (2) and (4) that $\alpha = 0$, $\beta_1 > 0$, $\beta_1 + \frac{\beta_2}{3} > 0$, and that the equilibrium polarization at the quadruple point is zero. On the other hand, as the composition moves away from the quadruple point to the C-T and C-R sides, the stable ferroelectric phase below the phase transition points becomes T and R, respectively. It can be deduced that $\beta_2 \approx 0$ at the quadruple point [15]. Therefore, for case 2, the following conditions have to be satisfied: $\alpha = 0$, $\beta_2 \approx 0$, and $\beta_1 > 0$. Such conditions are possible in a binary ferroelectric system because $\alpha(c, T) = 0$ and $\beta_2(c, T) \approx 0$ represent two curves and $\beta_1(c, T) > 0$ represents a region in the c-T space of a binary ferroelectric system and thus the probability of the two curves intersecting at a point in a given region is not low. Specifically, when $\alpha = \beta_2 = 0$ and $\beta_1 > 0$ at the quadruple point, a phase diagram that can be formed is illustrated in Fig. 1, where at the quadruple point, two second-order and two first-order transition lines intersect (see Supplemental Material [16]).

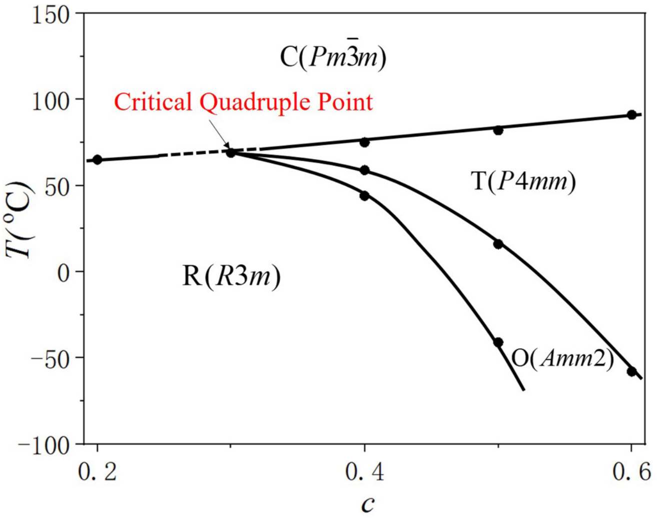

FIG. 1. A binary ferroelectric phase diagram with a unique type of critical C-T-O-R quadruple point where two first-order and two second-order transition lines intersect. It is constructed by a Landau polynomial [Eq. (1)] with $\alpha = \beta_2 = 0$ and $\beta_1 > 0$ at the quadruple point. The solid lines represent first-order transition lines and the dashed lines represent second-order transition lines.

IV. DISCUSSIONS

A. Why do quadruple points in binary BaTiO$_3$-based ferroelectric systems not violate the phase rule?

The above work tells us that although seemingly defying both the first and second phase rule as mentioned in the introduction [1–4], a C-T-O-R quadruple point in the temperature-composition phase diagram of a binary BaTiO$_3$-based ferroelectric system actually does not necessarily violates the phase rule. This is due to the reason that the four different phases appearing in the BaTiO$_3$-based binary systems, i.e., C, T, O, and R, involve symmetry breaking. For "symmetry-breaking" systems, both the first and second phase rules might not apply [17,18].

B. Unique type of critical quadruple point

The above results suggest that a C-T-O-R quadruple point can exist in the temperature-composition phase diagram of a binary BaTiO$_3$-based ferroelectric system only in the form of a unique type of critical point at which two first-order transition lines and two second-order transition lines meet (Fig. 1). This type of critical point differs from the conventional tetracritical point where four second-order transition lines meet [17,18], as well as from the isolated critical quadruple point where four first-order transition lines meet [19,20]. Note that the conventional tetracritical point has been examined thoroughly in previous theoretical studies [17,18,21] and the isolated critical quadruple point has been reported in ferromagnetic systems [22] or liquid crystals [19] and is possible in a ternary ferroelectric system as derived above [Eq. (9)].

C. Comparison with experimental results in BaTiO$_3$-based binary ferroelectric systems

The experimental studies on binary ferroelectric systems such as BaZr$_{0.2}$Ti$_{0.8}$O$_3$-xBa$_{0.7}$Ca$_{0.3}$TiO$_3$ [23,24], BaTiO$_3$-xCaHfO$_3$ [25], and BaTiO$_3$-xBaHfO$_3$ [26] have suggested a C-T-O-R quadruple point closer to an isolated critical point ($\alpha = \beta_1 = \beta_2 = 0$) at which four first-order transition lines meet based on observations that when the composition deviates from the quadruple point composition, the thermal hystereses for the C-T, C-R, T-O, and O-R

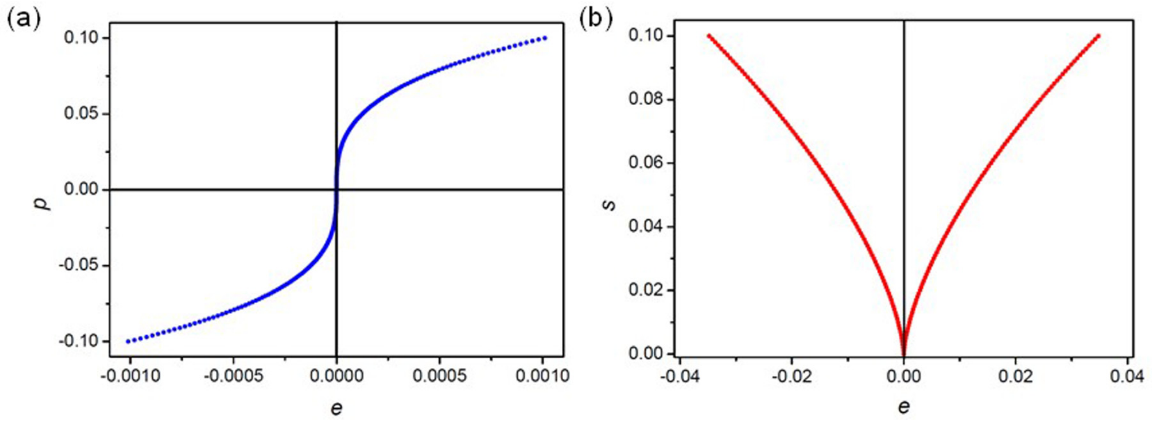

FIG. 2. (a) $p-e$ loop and (b) $s-e$ loop at the unique type of critical quadruple point shown in Fig. 1. p, e, s are reduced polarization, electric field, and strain, respectively. The slopes of both curves at $e = 0$ approach infinity, which indicates infinitely large ε_{33} and d_{33}.

transitions all gradually increase. There could be three possibilities for this disagreement: (a) The coupling between polarization and strain may slightly renormalize the fourth-order term in Eq. (2) and would change the second-order transition near the quadruple point to weak first order [27]; (b) the experimental binary phase diagrams could have a very limited composition range of the second-order transition lines in Fig. 1 (β_1 approaches 0 at the quadruple point), which makes the quadruple point look like an isolated critical point. This is because when β_1 approaches 0 at the quadruple point, the quadruple point on the phase diagram shown in Fig. 1 will asymptotically evolve to an isolated critical point where $\alpha = \beta_1 = \beta_2 = 0$; (c) the quadruple point measured in the experiments may not be a real quadruple point but a quasiquadruple point with two triple points (i.e., C-T-R and T-O-R) close to each other [28].

D. Piezoelectricity at the critical C-T-O-R quadruple point

The criticality of the C-T-O-R quadruple point in a binary ferroelectric system can resolve the controversy on the origin of high piezoelectric property at the MPB (specifically the T-O phase boundary) of the quadruple-point-bearing $BaTiO_3$-based binary ferroelectric systems such as BZT-BCT [23]. The T-O phase boundary in BZT-BCT shows a much larger d_{33} (620 pC/N) than that found at the T-O boundary in pure $BaTiO_3$ (<200 pC/N) [29]. Whether this high piezoelectricity is related to the C-T-O-R quadruple point of the system has been a controversial issue since its discovery [30,31]. Below we will show that d_{33} at this type of critical quadruple point exhibits an infinitely high value and thus the high d_{33} at the T-O boundary of quadruple-point-bearing ferroelectric systems is related to the quadruple point.

We first calculate the polarization (P)-electric field (E) loop, and strain (S)-E loop of the novel type of critical quadruple point. Under the constraint that $\alpha = \beta_2 = 0$ at the quadruple point, the free energy shown in Eq. (1) becomes $f = \beta_1 P^4 + \gamma' P^6$ ($\beta_1 > 0$, $\gamma' > 0$), where $\gamma' = \gamma_1$ for the T phase, $\gamma' = \gamma_1 + \frac{1}{4}\gamma_2$ for the O phase, and $\gamma' = \gamma_1 + \frac{2}{9}\gamma_2 + \frac{1}{27}\gamma_3$ for the R phase. Under an external electric field E along the polarization direction of one ferroelectric phase such as $[001]_C$ of the T phase, a coupling term, $-EP$, enters the free energy and the total free energy becomes $f = \beta_1 P^4 + \gamma' P^6 - EP$. From $\frac{\partial f}{\partial P} = 0$, a relationship between P and E can be obtained: $E = 4\beta_1 P^3 + 6\gamma' P^5$. Defining a reduced electric field e and a reduced polarization p as $e = \frac{E}{4\times(\frac{2}{3})^{3/2}\frac{\beta_1^{5/2}}{\gamma'^{3/2}}}$ and $p = (\frac{3\gamma'}{2\beta_1})^{1/2}P$, we obtain $e = p^5 + p^3$. The p-e loop of the mixed-type critical quadruple point is shown in Fig. 2(a). We then calculate the electrostrain of the critical quadruple point according to $S = QP^2$ (where S is strain and Q is the electrostrictive coefficient) and establish a relationship between S and E, i.e., $E = 4\beta_1(\frac{S}{Q})^{3/2} + 6\gamma'(\frac{S}{Q})^{5/2}$. Defining a reduced strain, $s = \frac{3\gamma'}{2\beta_1}\frac{S}{Q}$, we obtain $e = s^{3/2} + s^{5/2}$. The s-e loop of the critical quadruple point is shown in Fig. 2(b).

It is readily seen from Figs. 2(a) and 2(b) that both the p-e and s-e loops of this type of critical quadruple point are hysteresis free. Moreover, the slopes of both curves at $e = 0$ approach infinity, which suggests that a small electric field can induce a large polarization and strain at the critical quadruple point. Therefore, both ε_{33} and d_{33} approach infinity at this unique type of critical quadruple point. It is noted that at a second-order or critical transition infinite dielectric permittivity has been obtained theoretically in previous work [32] while the infinitely large piezoelectric d_{33} has not been predicted. The calculation result of infinitely large piezoelectric d_{33} at the critical quadruple point here can also be understood by the transverse instability mechanism proposed by Ishibashi and Iwata [32] and the polarization extension mechanism proposed by Damjanovic [33]. More importantly, it agrees with experimental observations that maximum d_{33} was found at the quadruple point of several $BaTiO_3$-based binary systems such as $BaZr_xTi_{1-x}O_3$ and $BaSn_xTi_{1-x}O_3$ [34,35].

The T-O phase boundary of BZT-BCT starts from the quadruple point and thus could inherit the vanishing energy barrier and infinitely large d_{33} of the unique type of critical quadruple point. As a result, the T-O boundary composition close to the critical quadruple point of the BZT-BCT system should have small energy barriers between different phases and large d_{33} [23]. This is in sharp contrast to the T-O phase boundary in pure $BaTiO_3$ or $K_{0.5}Na_{0.5}NbO_3$ where no quadruple points exist and a large energy barrier is expected between T and O phases. As a result, the piezoelectricity at the T-O boundary of $BaTiO_3$ or $K_{0.5}Na_{0.5}NbO_3$ is much lower (100–200p C/N) than that (620 pC/N) found at the T-O boundary in BZT-BCT [23,29]. In addition, the theoretically infinitely large d_{33} at the critical quadruple point is in sharp contrast to those at conventional first-order ferrroelectric transitions. It has been calculated that at the first-order paraelectric to ferroelectric transition of pure $BaTiO_3$, d_{33} is enhanced but not an infinite value at the Curie tempreature (T_C) [33].

E. Generality of the criticality of C-T-O-R quadruple point in binary ferroelectric systems

The above derivation is parameter free and, thus, suggests that the criticality of the C-T-O-R quadruple point in a binary ferroelectric system is a system-independent, general phenomenon. This explains why in so many different $BaTiO_3$-based binary ferroelectric systems such as $BaZr_{0.2}Ti_{0.8}O_3$-$x$$Ba_{0.7}Ca_{0.3}TiO_3$ (BZT-BCT) [23,24], $BaTiO_3$-$x$$CaHfO_3$ [25], and $BaHf_xTi_{1-x}O_3$ [26], the C-T-O-R quadruple point is always critical or near critical. Few exceptions have been found so far in experiments for bulk $BaTiO_3$-based ferroelectric systems. Therefore, by designing a C-T-O-R quadruple point in binary ferroelectric systems, we can always expect a critical transition, which is accompanied by superior properties including high dielectric permittivity, high piezoelectric coefficient, high energy density, large electrocaloric effect, and large electrostrain [9–12,34,35]. The generality of criticality of a quadruple point in a binary ferroelectric system demonstrated in this work could stimulate research into finding more quadruple point compositions with critical ferroelectric transitions. In addition, the above derivation also suggests that through designing a C-T-O-R quadruple point in a ternary or even quaternary system, a near-isotropic critical point [Eq. (8)] or an isolated critical point [Eq. (9)] could be achieved, which might also exhibit exceptional properties due to the criticality.

F. Comparison with lead-based binary MPB system

For lead-based binary MPB systems such as $PbZrO_3$-$PbTiO_3$ (PZT) and $PbMg_{1/3}Nb_{2/3}O_3$-$PbTiO_3$ (PMN-PT), normally a C-T-R triple point is observed [36,37]. At the C-T-R triple point, it is not necessary that the triple point has to be a critical point. Instead, it is possible that C-T, C-R, and T-R transitions at the triple point are all first order. This is because for first-order C-T and C-R transitions at the triple point, the number of equations that are required to be satisfied simultaneously is only two [Eqs. (5) and (6)], which does not exceed the number of independent variables in a binary ferroelectric system (c and T). However, in experiments the C-T-R triple point in lead-based systems seems to also exhibit near-criticality [38], the reason of which remains elusive. Theoretically, these critical triple points should also have large piezoelectricity. However, as far as we know experimental data of d_{33} at the C-T-R triple point are lacking in these lead-based MPB systems such as PZT and PMN-PT. On the other hand, it should be noted that the theoretically large piezoelectricity at the critical triple or quadruple point might be diminished by the depoling effect in experiments.

It should also be mentioned that monoclinic phases (M_A, M_B, and M_C) have been reported in lead-based MPB systems [39], which are supposed to play an essential role in the large piezoelectricity of these lead-based systems. These monoclinic phases cannot be stabilized by a sixth-order Landau free energy and eighth- and higher-order terms are required in the Landau polynomial [14]. However, our recent work has found that the monoclinic phase could be stabilized by long-range elastic and electrostatic interactions in a multidomain state even under a sixth-order Landau polynomial [40,41]. In addition, in the lead-free $BaTiO_3$-based MPB systems, monoclinic phases do not exist in the phase diagrams and the T, O, and R ferroelectric phases in these systems can be well stabilized by a sixth-order Landau polynomial [14]. Therefore, the eighth- and higher-order terms are not considered in this study.

V. CONCLUSIONS

In summary, to theoretically understand the existence of C-T-O-R quadruple points and their criticality in binary $BaTiO_3$-based ferroelectric systems reported experimentally, we have used Landau theory to show that the C-T-O-R quadruple point could *only* occur in the temperature-composition phase diagram of a *binary* ferroelectric system in the form of *a unique type of critical point* where two first-order transition lines (T-O and O-R) and two second-order transition lines (C-T and C-R) meet, and such critical quadruple points do not defy the thermodynamic phase rule. This type of critical quadruple point has been demonstrated to be consistent with the experimentally found criticality of the quadruple point in various binary ferroelectric systems. In addition, theoretically the piezoelectric coefficient d_{33} at this type of critical quadruple point is shown to have an infinitely large value, which is consistent with the experimental observations of the largest d_{33} at the quadruple point in $BaZr_xTi_{1-x}O_3$ and $BaSn_xTi_{1-x}O_3$ systems. It also explains why the MPB of a quadruple-point-bearing ferroelectric system shows a much higher d_{33} value than that found at a polymorphic phase boundary of conventional ferroelectrics not originating from a quadruple point. The criticality of the C-T-O-R quadruple point found in this study is general and holds for any binary ferroelectric systems. For ternary ferroelectric systems, the C-T-O-R quadruple point could exist in other forms of special points such as a near-isotropic point or an isolated critical point. The findings of this study could shed light on future design of high-performance ferroelectrics, including high-piezoelectricity materials, large-electrocaloric materials, high-permittivity capacitors, and high-electrostrain materials and, thus, could motivate experimental studies searching for critical quadruple point based ferroelectric systems.

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[1] J. W. Gibbs, *The Scientific Papers of J. Willard Gibbs, Vol. 1: Thermodynamics* (Ox Bow Press, Woodbridge, CT, 1993).

[2] L. D. Landau and E. M. Lifshitz, *Statistical Physics, Part 1*, 3rd ed. (Pergamon Press, New York, 1980).

[3] D. I. Uzunov, *Introduction to the Theory of Critical Phenomena*, 2nd ed. (World Scientific, Singapore, 2010).

[4] L. Tisza, Ann. Phys. **13**, 1 (1961).

[5] T. Maiti, R. Guo, and A. S. Bhalla, J. Am. Ceram. Soc. **91**, 1769 (2008).

[6] X. Wei and X. Yao, Mater. Sci. Eng. B **137**, 184 (2007).

[7] V. V. Lemanov, E. P. Smirnova, P. P. Syrnikov, and E. A. Tarakanov, Phys. Rev. B **54**, 3151 (1996).

[8] D. S. Keeble, F. Benabdallah, P. A. Thomas, M. Maglione, and J. Kreisel, Appl. Phys. Lett. **102**, 092903 (2013).

[9] J. Gao, X. Hu, Y. Wang, Y. Liu, L. Zhang, X. Ke, L. Zhong, H. Zhao, and X. Ren, Acta. Mater. **125**, 177 (2017).

[10] J. Gao, Y. Wang, Y. Liu, X. Hu, X. Ke, L. Zhong, Y. He, and X. Ren, Sci. Rep. **7**, 40916 (2017).

[11] Z. Luo, D. Zhang, Y. Liu, D. Zhou, Y. Yao, C. Liu, B. Dkhil, X. Ren, and X. Lou, Appl. Phys. Lett. **105**, 102904 (2014).

[12] L. Zhao, X. Ke, W. Wang, L. Zhang, C. Zhou, Z. Zhou, L. Zhang, and X. Ren, Phys. Rev. B **95**, 020101(R) (2017).

[13] M. Porta and T. Lookman, Phys. Rev. B **83**, 174108 (2011).

[14] D. Vanderbilt and M. H. Cohen, Phys. Rev. B **63**, 094108 (2001).

[15] G. A. Rossetti, Jr., A. G. Khachaturyan, G. Akcay, and Y. Ni, J. Appl. Phys. **103**, 114113 (2008).

[16] See Supplemental Material at http://link.aps.org/supplemental/10.1103/PhysRevB.103.085132 for the derivation process from Eqs. (5)–(7) to solution (8) and (9), and the Landau parameters used to produce the phase diagram shown in Fig. 1.

[17] R. B. Griffiths, Phys. Rev. B **12**, 345 (1975).

[18] A. P. Levanyuk and D. G. Sannikov, Zh. Eksp. Teor. Fiz. **60**, 1109 (1971) [Sov. Phys. - JETP **33**, 600 (1971)].

[19] D. G. Sannikov, Zh. Eksp. Teor. Fiz. **75**, 1714 (1978) [Sov. Phys. - JETP **48**, 863 (1978)].

[20] S. M. Allen and J. W. Cahn, Bull. Alloy Phase Diagrams **3**, 287 (1982).

[21] P. B. Vigman, A. I. Larkin, and V. M. Filev, Zh. Eksp. Teor. Fiz. **68**, 1883 (1975) [Sov. Phys. - JETP **41**, 944 (1975)].

[22] M. E. Fisher and D. R. Nelson, Phys. Rev. Lett. **32**, 1350 (1974).

[23] W. Liu and X. Ren, Phys. Rev. Lett. **103**, 257602 (2009).

[24] M. Acosta, N. Novak, G. A. Rossetti, Jr., and J. Rodel, Appl. Phys. Lett. **107**, 142906 (2015).

[25] L. Zhao, X. Ke, Z. Zhou, X. Liao, J. Li, Y. Wang, M. Wu, T. Li, Y. Bai, and X. Ren, J. Mater. Chem. C **7**, 1533 (2019).

[26] J. Gao, Y. Liu, Y. Wang, X. Hu, W. Yan, X. Ke, L. Zhong, Y. He, and X. Ren, J. Phys. Chem. C **121**, 13106 (2017).

[27] S. Yang, X. Ren, and X. Song, Phys. Rev. B **78**, 174427 (2008).

[28] A. A. Heitmann, and G. A. Rossetti, Jr., J. Am. Ceram. Soc. **97**, 1661 (2014).

[29] T. R. Shrout and S. J. Zhang, J. Electroceram. **19**, 185 (2007).

[30] M. Acosta, N. Novak, V. Rojas, S. Patel, R. Vaish, J. Koruza, G. A. Rossetti, Jr., and J. Rodel, Appl. Phys. Rev. **4**, 041305 (2017).

[31] J. Gao, X. Ke, M. Acosta, J. Glaum, and X. Ren, MRS Bull. **43**, 595 (2018).

[32] Y. Ishibashi and M. Iwata, Jpn. J. Appl. Phys. **38**, 800 (1999).

[33] D. Damjanovic, Appl. Phys. Lett. **97**, 062906 (2010).

[34] Y. Yao, C. Zhou, D. Lv, D. Wang, H. Wu, Y. Yang, and X. Ren, EPL **98**, 27008 (2012).

[35] L. Dong, D. S. Stone, and R. S. Lakes, J. Appl. Phys. **111**, 084107 (2012).

[36] D. La-Orauttapong, B. Noheda, Z.-G. Ye, P. M. Gehring, J. Toulouse, D. E. Cox, and G. Shirane, Phys. Rev. B **65**, 144101 (2002).

[37] K. Uchino, *Ferroelectric Devices* (Marcel Dekker, New York, 2000), Chap. 7.

[38] R. S. Solanki, S. K. Mishra, Y. Kuroiwa, C. Moriyoshi, and D. Pandey, Phys. Rev. B **88**, 184109 (2013).

[39] M. Davis, J. Electroceram. **19**, 25 (2007).

[40] X. Q. Ke, D. Wang, X. Ren, and Y. Wang, Phys. Rev. B **88**, 214105 (2013).

[41] X. Ke, D. Wang, X. Ren, and Y. Wang, Phys. Rev. Lett. **125**, 127602 (2020).