Effect of Ba^{2+} substitution on the stability of the antiferroelectric and ferroelectric phases in $(Pb_{1-x}Ba_x)ZrO_3$: Phenomenological theory considerations

Bhadra P. Pokharel* and Dhananjai Pandey

School of Materials Science and Technology, Institute of Technology, Banaras Hindu University, Varanasi-221005, India (Received 14 September 2001; revised manuscript received 29 January 2002; published 6 June 2002)

The relative stability of the ferroelectric rhombohedral (F_R) and antiferroelectric orthorhombic (A_O) phases of ($Pb_{1-x}Ba_x$)ZrO₃ has been investigated as a function of Ba^{2+} concentration (x) using phenomenological theory considerations. It is shown that all the unknown parameters in the free-energy expressions for the F_R and A_O phases can be evaluated using the dielectric and x-ray-diffraction data as a function of temperature. We show that the differences in the energies of antiferroelectric and ferroelectric phases decrease with increasing Ba^{2+} concentration, indicating the gradual destabilization of the antiferroelectric phase. The theoretically predicted critical composition $x=0.17\pm0.0025$, above which no antiferroelectric phase can exist, is found to be in excellent agreement with the experimental observations.

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I. INTRODUCTION

PbZrO₃ (PZ) is a well-known antiferroelectric (AFE) material with orthorhombic structure (A_O) at room temperature.^{1–5} On heating, it transforms to a ferroelectric (FE) phase with rhombohedral structure (F_R) around 225 °C. This F_R phase transforms to a paraelectric (PE) cubic phase (P_C) around 231 °C. Both A_O to F_R and F_R to P_C phase transitions are first order and show a thermal hysteresis of around 10 °C. The relative thermal stability of the A_O and F_R phases with respect to the P_C phase has recently been investigated by Haun *et al.*⁶ using phenomenological theory approach and by Singh⁷ using first-principles total-energy calculations.

The FE and AFE phase transitions in PZ are caused by two competing instabilities in the low-frequency polar modes at the zone center and the zone boundary, respectively.⁸ Depending on the temperature, one of the two types of instabilities dominate giving rise to a pure FE or AFE phase with definite stability fields. Thus the FE mode freezes out around 222 °C followed by the freezing of the AFE mode around 215 °C in PZ.

The relative strengths of the competing FE and AFE instabilities of PZ can be varied continuously by varying the Ba^{2+} concentration in the mixed $(Pb_{1-r}Ba_r)ZrO_3$ (PBZ) system. However, unlike the well-known frustrated systems like $Rb_{1-r}(NH_4)_rH_2PO_4$ (Ref. 9) and $Eu_{1-r}Go_rS$,¹⁰ the competing instabilities and frustration in this system are not being brought over by the two end members, i.e., PbZrO₃ and BaZrO₃, since the latter does not show any FE or AFE instability and remains cubic down to nearly 0 K (mentioned in Ref. 11). Instead, Ba^{2+} substitution modifies the strength of the already existing competing AFE and FE instabilities of the PZ matrix in such a way that when one of them dominates over the other, a pure AFE or FE phase results¹² whereas in the event of the two interactions being comparable, one gets glassy or relaxor FE behavior.¹³ Thus the A_{0} to F_R to P_C sequence of phase transition of PbZrO₃ is observed in PBZ also but only for a restricted composition range of $0 \le x \le 0.15$.¹² But, for $0.20 \le x \le 0.30$, the sequence

of phase transition changes to F_R to P_C (Ref. 12) with the total absence of the A_O phase. Further, for x=0.30, PBZ shows relaxor FE transition^{12,13} whereas for x>0.30, it shows a reentrant relaxor ferroelectric behavior.¹⁴ The difference in the ionic radii of Pb²⁺ (1.17 Å) and Ba²⁺ (1.29 Å) and the polarizabilities of the two ions seems to be playing the most important role in modifying the relative strengths of the AFE and FE instabilities.

In this paper, we consider the application of the phenomenological theory developed by Haun et al.⁶ for pure PZ to study the relative stability of the F_R and A_O phases with respect to the high-temperature P_C phase as a function of temperature and Ba^{2+} concentration. For the P_C to F_R transition, all the coefficients in the Landau expansion for free energy can be conveniently determined using the dielectric¹² and high-temperature x-ray-diffraction (XRD) data.¹⁵ The dielectric data given in Ref. 12 provides us the values of Curie point (T_C) , Curie-Weiss temperature (T_O) , and Curie-Weiss constant (C) while the high-temperature XRD data given in Ref. 15 enables us to calculate the anisotropic spontaneous strain as a function of temperature from which one can deduce the temperature-dependent anisotropic spontaneous polarization using electrostrictive coupling. For the AFE transition, the situation is less straightforward since the P_C to A_Q transition is mediated by the F_R phase; as a result one does not know a priori the Néel temperature (T_N) , Curie constant (C_A) , and Curie temperature (θ_0) . Thus the determination of each coefficient in the free-energy expression is not possible. Haun et al.⁶ have resolved this issue in a very ingenious way for understanding the thermodynamics of the P_{C} to F_R to A_O transition in pure PZ. We shall use their approach for studying the P_C to F_R to A_O phase transitions in the PBZ system as a function of Ba²⁺ concentration. We begin this paper with a brief review of the salient aspects of the thermodynamic theory of Haun *et al.*⁶ and then present our results on its application to the PBZ system to predict the absence of the AFE phase for x > 0.17. Our predictions are in excellent agreement observations.^{12,13,15} with the experimental

II. THERMODYNAMIC THEORY

Landau-type phenomenological theories have been used by workers like Kittel,¹⁶ Cross,¹⁷ and Okada¹⁸ to understand the AFE transitions. Whatmore and Glazer¹⁹ used a onedimensional free-energy function containing up to sixthorder terms to model the displacement of Pb ion in PZ. Uchino *et al.*²⁰ determined the hydrostatic electrostrictive coefficients by including the stress terms in the free-energy function. The AFE phase transition in PZ is first order.¹² In the free-energy function of the earlier workers, barring Whatmore and Glazer,¹⁹ terms up to fourth order only were retained which are inadequate to describe the first-order behavior (see, e.g., Refs. 21 and 22). Recently, Haun *et al.*⁶ have developed a thermodynamic theory of PbZrO₃ in which the three-dimensional (3D) free-energy function contains up to sixth-order FE and AFE polarization terms, elastic strain energy terms, and the cross terms due to coupling between the polarization and stress (X_m) consistent with the symmetry of the paraelectric phase (m3m):

$$\Delta G = \{ \alpha_1 (P_1^2 + P_2^2 + P_3^2) + \alpha_{11} (P_1^4 + P_2^4 + P_3^4) + \alpha_{111} (P_1^6 + P_2^6 + P_3^6) + \alpha_{12} (P_1^2 P_2^2 + P_2^2 P_3^2 + P_3^2 P_1^2) + \alpha_{112} [P_1^4 (P_2^2 + P_3^2) + P_2^4 (P_3^2 + P_1^2) + P_3^4 (P_1^2 + P_2^2)] + \alpha_{123} P_1^2 P_2^2 P_3^2 \} + \{ \sigma_1 (p_1^2 + p_2^2 + p_3^2) + \sigma_{11} (p_1^4 + p_2^4 + p_3^4) + \sigma_{111} (p_1^6 + p_2^6 + p_3^6) + \sigma_{12} (p_1^2 p_2^2 + p_2^2 p_3^2 + p_3^2 p_1^2) + \sigma_{112} [p_1^4 (p_2^2 + p_3^2) + p_2^4 (p_3^2 + p_1^2) + p_3^4 (p_1^2 + p_2^2)] + \sigma_{123} p_1^2 p_2^2 p_3^2 \} \\ + \alpha_{12} (p_1^2 p_2^2 + P_2^2 p_3^2 + p_3^2 p_1^2) + \sigma_{112} [p_1^4 (p_2^2 + p_3^2) + p_2^4 (p_3^2 + p_1^2) + p_3^4 (p_1^2 + p_2^2)] + \sigma_{123} p_1^2 p_2^2 p_3^2 \} \\ + \mu_{11} (P_1^2 p_1^2 + P_2^2 p_2^2 + P_3^2 p_3^2) + \mu_{12} [P_1^2 (p_2^2 + p_3^2) + P_2^2 (p_3^2 + p_1^2) + P_3^2 (p_1^2 + p_2^2)] + \mu_{44} (P_1 P_2 p_1 p_2 + P_2 P_3 p_2 p_3 + P_1 P_3 p_1 p_3) - \{ Q_{11} (X_1 P_1^2 + X_2 P_2^2 + X_3 P_3^2) + Q_{12} [X_1 (P_2^2 + P_3^2) + X_2 (P_3^2 + P_1^2) + X_3 (P_1^2 + P_2^2)] + Q_{44} (X_4 P_2 P_3 + X_5 P_3 P_1 + X_6 P_1 P_2) \} \\ - \{ Z_{11} (X_1 p_1^2 + X_2 p_2^2 + X_3 p_3^2) + Z_{12} [X_1 (p_2^2 + p_3^2) + X_2 (p_3^2 + p_1^2) + X_3 (p_1^2 + p_2^2)] + Z_{44} (X_4 p_2 p_3 + X_5 P_3 p_1 + X_6 P_1 p_2) \} \\ - \{ Z_{11} (X_1 p_1^2 + X_2 p_2^2 + X_3 p_3^2) + Z_{12} [X_1 (p_2^2 + p_3^2) + X_2 (p_3^2 + p_1^2) + X_3 (p_1^2 + p_2^2)] + Z_{44} (X_4 p_2 p_3 + X_5 P_3 p_1 + X_6 p_1 p_2) \} \\ - \{ Z_{11} (X_1 p_1^2 + X_2 p_2^2 + X_3 p_3^2) + Z_{12} [X_1 (P_2^2 + P_3^2) + X_2 (p_3^2 + p_1^2) + X_3 (p_1^2 + p_2^2)] + Z_{44} (X_4 p_2 p_3 + X_5 P_3 p_1 + X_6 p_1 p_2) \} \\ - \{ Z_{11} (X_1 p_1^2 + X_2^2 + X_3^2) + 2 S_{12} (X_1 X_2 + X_2 X_3 + X_3 X_1) + S_{44} (X_4^2 + X_5^2 + X_6^2)],$$

where the coefficients α_1 , α_{11} , α_{111} , α_{12} , α_{112} , α_{123} correspond to FE dielectric stiffnesses at constant stress, σ_1 , σ_{11} , σ_{111} , σ_{12} , σ_{112} , σ_{123} to AFE dielectric stiffnesses at constant stress, μ_{11} , μ_{12} , μ_{44} to couplings between AFE and FE polarizations, S_{11} , S_{12} , S_{44} to elastic compliances at constant polarization, Q_{11} , Q_{12} , Q_{44} to electrostrictive coupling between FE polarization and stress, and Z_{11} , Z_{12} , Z_{44} to electrostrictive coupling between AFE polarization and stress.

A. Free-energy expression for the ferroelectric phase

For the FE rhombohedral phase, the solutions of interest to the energy function given by Eq. (1) are $P_1^2 = P_2^2 = P_3^2$ $\neq 0$ and $p_1 = p_2 = p_3 = 0$ under the zero stress condition. This reduces the free-energy function to

$$\Delta G_F = \alpha P_3^2 + \beta P_3^4 + \gamma P_3^6, \tag{2}$$

where $\alpha = 3\alpha_1$, $\beta = 3(\alpha_{12} + \alpha_{11})$, and $\gamma = (3\alpha_{111} + 6\alpha_{112} + \alpha_{123})$. The coefficients β and γ are assumed to be temperature independent. Further, β is positive for second-order phase transition and negative for first-order phase transition.⁶ γ is always positive. The coefficient α_1 is assumed to have the following type of temperature dependence based on the Curie-Weiss law:

$$\alpha_1 = (T - T_O)/(2\varepsilon_O C) = \alpha_O (T - T_O), \qquad (3)$$

where C is the Curie constant, ε_O is the permittivity of free space, and T_O is the Curie-Weiss temperature.

Now using the minimization conditions $\partial \Delta G / \partial P_3 = 0$ and $\Delta G = 0$ at T_C , we get two simultaneous equations in terms

of even powers of P_3 . Solving them, we obtain the following expressions for the remaining two coefficients:

$$\beta = -3(T_C - T_O)/(\varepsilon_O C P_{3C}^2)$$

and

$$\gamma = 3(T_C - T_O) / (2\varepsilon_O C P_{3C}^4), \qquad (4)$$

where P_{3C} is the value of spontaneous polarization at T_C for a first-order phase transition. T_C is related to T_O in the following manner:

$$T_C = T_O + \beta^2 / (12\alpha_O \gamma). \tag{5}$$

The minimization condition $(\partial \Delta G / \partial P_3)$ mentioned above provides us the following expression for polarization:

$$P_{3}^{2} = [-\beta + \sqrt{\beta^{2} - 3\alpha_{1}\gamma}]/3\gamma.$$
 (6)

Substituting the values of α_1 , β , and γ in this relation, we obtain the following relation for the spontaneous polarization:

 $P_3^2 = \Psi_F P_{3C}^2$,

where

$$\Psi_F = 2/3 [1 + \{1 - 3(T - T_O)/(4(T_C - T_O))\}^{1/2}].$$
(7)

The spontaneous elastic strains $x_i (= \partial \Delta G / \partial X_i)$ under zero stress condition can be obtained from Eq. (1) and are given below:

$$x_1 = x_2 = x_3 = (Q_{11} + 2Q_{12})P_3^2, \tag{8}$$

$$x_4 = x_5 = x_6 = Q_{44} P_3^2. \tag{9}$$

Combining Eqs. (7) and (9), one obtains

$$x_4 = \Psi_F x_{4C}$$
, where $x_{4C} = Q_{44} P_{3C}^2$. (10)

Here x_{4C} is the value of x_4 at $T = T_C$. On substituting from Eq. (10) for P_{3C} into Eq. (4) and using the expression for the coefficients α , β , and γ given by Eqs. (3) and (4) in Eq. (2), one gets the following expression for the free energy:

$$\Delta G_F = [3\Psi_F x_{4C} / (2Q_{44}\varepsilon_O C)][(T - T_O) - 2\Psi_F (T_C - T_O)(1 - \Psi_F / 2)].$$
(11)

Thus ΔG_F as a function of temperature can be calculated from a knowledge of ψ_F , x_{4C} , Q_{44} , T_O , and C which can be determined from the experimental data.

B. Free-energy expression for the antiferroelectric phase

In the orthorhombic AFE phase, polarization can be along any of the $\langle 110 \rangle$ directions of the original pseudocubic unit cell. Thus the solutions of interest to Eq. (1) are $P_1 = P_2$ $= P_3 = 0$, $p_1^2 = 0$, and $p_2^2 = p_3^2 \neq 0$. Hence the Landau freeenergy function for this phase under zero stress condition shall be

$$\Delta G_A = \delta p_3^2 + \zeta p_3^4 + \xi p_3^6, \tag{12}$$

where $\delta = 2\sigma_1$, $\zeta = 2\sigma_{11} + \sigma_{12}$, and $\xi = 2(\sigma_{111} + \sigma_{112})$.

As in the FE case, ζ and ξ are assumed to be temperature independent. Further, for first-order transition, ζ is taken to be negative while ξ is positive.^{21,22} The coefficient σ_1 is assumed to follow the following type of temperature dependence:

$$\sigma_1 = (T - \theta_O) / (2\varepsilon_O C_A) = \sigma_O (T - \theta_O).$$
(13)

Here C_A and θ_O are the AFE analogs of the FE Curie constant and the Curie-Weiss temperature, respectively.

Following the procedure similar to that in Sec. II A for the FE phase, we can express the coefficients ζ and ξ as under

$$\begin{aligned} \zeta &= -2(T_N - \theta_O) / (\varepsilon_O C_A p_{3N}^2) \\ \xi &= (T_N - \theta_O) / (\varepsilon_O C_A p_{3N}^4), \end{aligned}$$

where

$$T_N = \theta_O + \zeta^2 / (8\zeta \sigma_O). \tag{14}$$

Here, T_N and p_{3N} are Néel temperature and AFE polarization at T_N , respectively.

The AFE spontaneous polarization and strain can be expressed in the same way as in Eqs. (7) and (10). Thus

$$p_3^2 = \psi_A p_{3N}^2$$
,

where

$$\psi_A = \frac{2}{3} \{ 1 + [1 - 3(T - \theta_O)/4(T_N - \theta_O)]^{1/2} \}.$$
(15)

Similar to Eq. (10), the following relationships follow:

TABLE I. Curie-Weiss constant and Curie-Weiss temperature for PBZ05 and PBZ10.

	<i>C</i> (°C)	T_O (°C)	
PBZ05	1.62×10^{5}	188	
PBZ10	1.72×10^{5}	172	

and

where

 $x_4 = \psi_A x_{4N},$

 $x_4 = Z_{44} p_3^2$

$$x_{4N} = Z_{44} p_{3N}^2. \tag{16}$$

The free-energy function ΔG_A given by Eq. (12) for the antiferroelectric (A_O) phase can thus be expressed as follows with the help of relations (14) and (16):

$$\Delta G_A = (\psi_A x_{4N} / \varepsilon_O Z_{44} C_A) [(T - \theta_O) - 2 \psi_A (T_N - \theta_O) (1 - \psi_A/2)], \qquad (17)$$

where the constants $(T_N, p_{3N}, \text{ and } \theta_O)$ can be estimated by a fitting procedure explained in the next section and $Z_{44}C_A$ is determined using the thermodynamic condition $\Delta G_A = \Delta G_F$ at the AFE-FE phase transition temperature (T_{AF}) and is expressed as

$$Z_{44}C_{A} = [2x_{4N}\psi_{A}Q_{44}C/3\psi_{F}x_{4C}]\{[(T_{AF} - \theta_{O}) - 2\psi_{A}(T_{N} - \theta_{O})(1 - \psi_{A}/2)]/[(T_{AF} - T_{O}) - 2\psi_{F}(T_{C} - T_{O})(1 - \psi_{F}/2)]\}$$
(18)

III. RESULTS AND DISCUSSION

A. Evaluation of coefficients for the ferroelectric phase

For the calculation of ΔG_F for the FE rhombohedral (F_R) phase given by Eq. (11), we need to know the unknown parameters T_C , C, T_O , Q_{44} , and x_{4C} . Since the P_C to F_R transition is a first-order transition, there is a thermal hysteresis in the transition temperatures measured during heating and cooling cycles.¹² We have taken the average of the transition temperatures in our dielectric measurements during heating and cooling as the thermodynamic phase-transition temperature (T_C) in our calculations. The Curie-Weiss constant (C) and Curie-Wiess temperature (T_0) were determined from a plot of dielectric stiffness versus temperature given in Ref. 12. For pure PZ, the values of C (1.45 $\times 10^5$ K) and T_O (190 °C) obtained using dielectric data on ceramic specimens¹² compare well with those reported in the literature for single crystals ($C=1.55\times10^5$ K, T_O = 190 °C).²⁰ This suggests that the C and T_O values determined using dielectric data on ceramics specimens for the PBZ series (x = 0.05, 0.10) can be used for calculating ΔG_F given by Eq. (9). For PBZ05 and PBZ10, the values are listed in Table I.

To estimate Q_{44} , we have used the observation of Uchino *et al.*²⁰ that the product of Q_h with the Curie-Weiss constant



FIG. 1. Variation of lattice parameters of orthorhombic (antiferroelectric, A_O), rhombohedral (ferroelectric, F_R), and cubic (paraelectric, P_C) phases of $(Pb_{1-x}Ba_x)ZrO_3$ with temperature for (a) x=0.05 and (b) x=0.10. The inset shows the variation of the rhombohedral angle of ferroelectric phase with temperature. The filled (\bullet) and open (\bigcirc) circles are for heating and cooling cycles, respectively. The vertical arrows show the thermal hysteresis.

(*C*) is nearly constant ($\sim 3 \times 10^3 \text{ m}^{-4} \text{ C}^{-2} \text{ K}$) for all FE and AFE perovskites. Since the electrostrictive data for singlecrystal specimens of PBZ05 and PBZ10 are not available in the literature, we have used the approximation Q_{44} $\sim 2.8095Q_h$ to calculate Q_{44} from a knowledge of Q_h . This relationship holds good for single crystals of PZ with $Q_{44}(0.059)$ (Ref. 6) and $Q_h(0.021)$.²⁰ ψ_F given by Eq. (7) can be easily calculated from a knowledge of the transition temperature (T_C) and Curie-Weiss temperature (T_O). The only unknown parameter in Eq. (11) is now x_{4C} which was evaluated in the manner explained as follows: The spontaneous strain x_4 in the F_R phase is given by the relation

$$x_4 = (90 - \alpha_R / 90), \tag{19}$$

where α_R is the rhombohedral angle of the unit cell of the F_R phase.

The variation of α_R as a function of temperature along with the other lattice parameters is shown in Figs. 1(a) and (b) for PBZ05 and PBZ10, respectively. From a knowledge of α_R at various temperatures, the variation of spontaneous strain x_4 as a function of temperature was calculated. This is shown in Figs. 2(a) and 3(a) for PBZ05 and PBZ10, respectively. x_{4C} was determined from the best fit to the plot of x_4 versus ψ_F [see Eq. (10)] as shown in Figs. 2(b) and 3(b) for PBZ05 and PBZ10, respectively. Table II lists the value of x_{4C} so obtained for PBZ05 and PBZ10 along with the value of other constants required for calculating ΔG_F . For comparison we have also given the constants used by Haun *et al.*⁶ for pure PZ in Table II.



FIG. 2. Variation of ferroelectric rhombohedral strain x_{4F} with (a) temperature and (b) ψ_F defined by Eq. (7); variation of antiferroelectric orthorhombic (c) strain x_{4A} and (d) $(x_4 - 2/3x_{4N})^2$ with temperature for PBZ05.

B. Evaluation of coefficients for the antiferroelectric phase

The Néel temperature (T_N) and the associated constants C_A and θ_O in Eq. (17) correspond to the transition between the AFE (A_O) and PE (P_C) phases. In pure PZ as well as in PBZ05 and PBZ10, this is a metastable transition since it occurs in the FE rhombohedral phase field. Thus the constants C_A , T_N , and θ_O are not determinable using dielectric measurements. This is in marked contrast to the FE to PE transition discussed in the preceding section. Since T_N is not known, x_{4N} is also not measurable. In order to determine T_N , θ_0 , and x_{4N} , we have therefore used the fitting proce-



FIG. 3. Variation of ferroelectric rhombohedral strain x_{4F} with (a) temperature and (b) ψ_F defined by Eq. (7); variation of antiferroelectric orthorhombic (c) strain x_{4A} and (d) $(x_4 - 2/3x_{4N})^2$ with temperature for PBZ10.

TABLE II. Values of constants obtained in the present work for the evaluation of the free energies of the FE and AFE phases of $(Pb_{1-x}Ba_x)ZrO_3$ with x=0.05 and 0.10. For x=0 (i.e., PZ), the constants are taken from Ref. 6.

Parameters	PZ	PBZ05	PBZ10
$\overline{x_{4C}}$	1.203×10^{-3}	1.950×10^{-3}	2.561×10^{-3}
$P_{3c} (C/m^2)$	0.1428	0.1901	0.2250
$Q_{44} (m^4/C^2)$	0.059	0.053	0.049
$\alpha_0 (m/C)$	3.766×10^{5}	3.487×10^{5}	3.285×10^{5}
$\beta (m^5/C^2F)$	-4.655×10^{9}	-1.281×10^{9}	-7.498×40^{8}
$\gamma (m^9/C^4F)$	1.143×10^{11}	1.798×10^{10}	7.528×10^{9}
T_N (°C)	226	168.2	112.1
θ_0 (°C)	216.5	145.7	85.0
X_{4N}	2.630×10^{-4}	5.057×10^{-4}	7.501×10^{-4}
$Z_{44}C_A$	683.35	670.88	661.96
$(m^4 \circ C/C^2)$			

dure described below. This procedure is similar to that employed by Haun *et al.*⁶ for pure PZ.

The spontaneous strain associated with the A_O phase can be determined from a knowledge of the pseudocubic lattice parameters given by Whatmore and Glazer:¹⁹

$$a_{P} = 1/2(1/4b_{0}^{2} + a_{0}^{2})^{1/2},$$

$$c_{P} = 1/2c_{O},$$

$$\gamma_{P} = 2 \tan^{-1}(2a_{O}/b_{O}),$$
(20)

where a_O , b_O , and c_O are the orthorhombic cell parameters of the A_O phase and a_P , c_P , and γ_P are the cell parameters of the equivalent monoclinically distorted elementary perovskite cell. The strain x_4 in Eq. (16) can be defined with respect to the PE cubic phase as under

$$x_4 = (90 - \gamma_P)/90. \tag{21}$$

The spontaneous strain x_4 was calculated from the hightemperature XRD data on PBZ05 and PBZ10 presented in Figs. 1(a) and (b), respectively (taken from Ref. 15). The variation of x_4 with temperature *T* as per Eq. (16) can be expressed in the following form:

$$(x_4 - 2/3x_{4N})^2 = -[x_{4N}^2/3(T_N - \theta_O)]T + [4x_{4N}^2/9 + x_{4N}^2\theta_O/3(T_N - \theta_O)].$$
(22)

The experimentally observed variation of x_4 with temperature is shown in Figs. 2(c) and 3(c) for PBZ05 and PBZ10, respectively. The constants T_N and θ_O were determined from a least-squares fitting procedure from a plot of $(x_4 - 2/3x_{4N})^2$ versus temperature T using Eq. (22). In the fitting, minimum variance criterion was used for selecting the optimum value of x_{4N} . Figures 2(d) and 3(d) depict the bestfit straight line for the constants x_{4N} , T_N , and θ_O given in Table II along with other important constants used in the calculation of the free energies of PBZ10, PBZ05, and PZ. Haun *et al.*⁶ in their work on PZ approximated T_N by taking the average of the P_C to F_R phase-transition temperature

 (T_C) and the F_R to A_O phase-transition temperature (T_{AF}) . The value of T_N (168.2 °C and 112.1 °C for PBZ05 and PBZ10, respectively) determined by us using the fitting procedure agrees well with the value (167.5 °C, 111.5 °C) obtained by averaging T_C and T_{AF} . Due to the first-order nature of the $P_C - F_R$ and $F_R - A_O$ phase transitions and the associated thermal hysteresis, it is not possible to measure T_C and T_{AF} . We have taken the average of the transition temperatures obtained during heating and cooling cycles as the equilibrium transition temperatures T_C and T_{AF} . For PBZ10, due to the irreversibility of the F_R - A_O transition during cooling,¹² one cannot measure T_{AF} during cooling. To resolve this, we estimated the T_{AF} (cooling) from the extrapolation of the values known for PZ and PBZ05 during cooling, i.e., by taking a decrease in T_{AF} (cooling) at the rate of 27 °C/mol % of BaZrO₃ added.¹²

Now all constants in Eq. (17) except C_A and Z_{44} are known. C_A cannot be determined experimentally for reasons already explained. However, C_A occurs as a product $C_A Z_{44}$ in Eq. (17). This product $(C_A Z_{44})$ can be evaluated using Eq. (18) in which all the parameters on the right-hand side have already been determined. Having determined all the unknown parameters in Eq. (17), we calculated the free energy ΔG_A of the AFE phase as a function of temperature.

C. Relative free energies of the antiferroelectric and ferroelectric phases

Having determined all the unknown parameters in Eqs. (11) and (17), we have calculated the relative free energies ΔG_F and ΔG_A of the FE and AFE phases, respectively, as a function of temperature for PZ, PBZ05, and PBZ10. Figures 4(a)-(c) depict the variation of ΔG with temperature (T) for both FE and AFE phases of PZ, PBZ05, and PBZ10, respectively. It is evident from this figure that the $\Delta G_F(x,T)$ and ΔG_A (x,T) curves intersect at T_{AF} below which the AFE phase has got lower free energy than the FE phase. Further, the difference in the energies between the AFE and FE phases is decreasing with increasing Ba²⁺ content at all temperatures below the AFE-FE phase transition temperature (T_{AF}) . This clearly indicates that the AFE phase is getting gradually destabilized with increasing Ba²⁺ content. To determine the critical composition (x_C) above which $\Delta G_A(x,T)$ is always higher than $\Delta G_F(x,T)$, we have analyzed the trend of composition dependence of the free-energy difference $\Delta G_A - \Delta G_F$ using the values for x = 0, 0.05, and 0.10 at several temperatures below the T_{AF} (=30 °C) for x =0.10. This is shown in Fig. 5 for T=20, 0, -20, and -50 °C in the inset and for T = -110, -120, -150, and -175 °C in the main figure. It is interesting to note that for all temperatures, the free-energy difference follows linear composition dependence whose extrapolation for x > 0.10gives a critical composition $x_c = 0.17 \pm 0.0025$ above which $\Delta G_A - \Delta G_F$ becomes positive, i.e., $\Delta G_A > \Delta G_F$. Although we have shown the results for only eight temperatures in Fig. 5, we have verified that $\Delta G_A > \Delta G_F$ for all temperatures below T_{AF} for x=0.10 so long as $x>0.17\pm0.0025$. Since Ba^{2+} substitution is known¹² to decrease the T_{AF} at the rate of 19 °C per mole percent of BaZrO₃ added, the T_{AF} for x



FIG. 4. Variation of relative free energies for FE and AFE phases of $(Pb_{1-x}Ba_x)ZrO_3$ with temperature for (a) x=0 (PZ), (b) x=0.05 (PBZ05), and (c) x=0.10 (PBZ10). The inset in (a) is on an expanded scale to enable the identification of A_O to F_R (T_{AF}) and F_R to P_C (T_C) transition temperatures.

=0.17±0.0025 will be lower than T_{AF} for x=0.10. In fact, the estimated T_{AF} for $x=0.17\pm0.0025$ is -101 °C which is higher than the temperatures considered in Fig. 5. This clearly confirms that the AFE phase cannot occur for $x > 0.17\pm0.0025$ in the PBZ system since ΔG_A will always be greater than ΔG_F . The structural¹⁵ and dielectric studies¹² have shown that the P_C to F_R to A_O sequence of phase transitions is observed up to x=0.15 only. For $x \ge 0.20$, the F_R phase once formed is stable and does not transform into the A_O phase on further cooling. Thus the experimental observation predicts the crossover composition (x_C) to lie in the range $0.15 \le x \le 0.20$ which is in excellent agreement with the value of $x_C \sim 0.17 \pm 0.0025$ determined by the phenomenological theory calculations described in the present work.



FIG. 5. Variation of $(\Delta G_A - \Delta G_F)$ as a function of Ba^{2+} content at 20 °C (\Box), 0 °C (\blacksquare), -20 °C (\bigcirc), and -50 °C (\bigcirc) shown in the inset, and at -110 °C (\bigcirc), -120 °C (\bigcirc), -150 °C (\blacksquare), and -175 °C (\Box) shown in the main figure.

Before we close, a comparison of the behavior of the PBZ system with the well-known perovskite system $Pb(Zr_{1-x}Ti_x)O_3$ (PZT) (Ref. 23) will be in order. Ti⁴⁺ substitution at the Zr⁴⁺ site for $x \ge 0.06$ in the PZT system also stabilizes a ferroelectric rhombohedral $[F_R^{LT}]$ phase in which the oxygen octahedra are antiphase rotated about the [111] direction in the neighboring perovskite cell.²³ This doubled cell rhombohedral phase of PZT is similar to the ferroelectric F_R phase of the PBZ system.^{13,15} The phenomenological theory consideration of the present work in principle can be applied to the PZT problem also for determining the relative stability of the FE and AFE phases as a function of Ti⁴⁺ content in the PZT system. Having said this, we would like to emphasize the important differences between the two systems. The end member PbTiO₃ of the PZT system is a wellknown ferroelectric with tetragonal structure at room temperature in contrast to BaZrO₃ of the PBZ system which has a cubic structure and does not exhibit any FE or AFE instability. As a result of this, the phase diagram of the PZT system is much more complex with a variety of ferroelectric phases with tetragonal (F_T) , rhombohedral (F_R^{HT}) , doubled cell rhombohedral (F_R^{LT}) , $^{23}_{T}$ monoclinic (F_M^{HT}) , 24 and doubled cell monoclinic (F_M^{LT}) (Ref. 25) phases appearing in different composition and temperature ranges of the phase diagram.

IV. CONCLUSIONS

We have calculated the free energies of the ferroelectric rhombohedral (F_R) and antiferroelectric orthorhombic (A_O) phases of ($Pb_{1-x}Ba_x$)ZrO₃ as a function of Ba^{2+} concentration using a phenomenological theory approach. Our calculations show that the A_O (AFE) phase is gradually destabilized with increasing Ba^{2+} content and for concentrations $x > 0.17 \pm 0.0025$, only the FE phase should exist. These theoretical predictions are found to be in excellent agreement with those observed experimentally.

^{*}Permanent address: Physics Department, Pulchowk Campus, Institute of Engineering Tribhuvan University, Kathmandu, Nepal.

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