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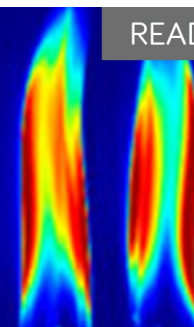
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ABSTRACT

In about twenty years, the temperature-misfit strain phase diagrams have become valuable tools to describe ferroelectric thin film properties. The background theoretical approach consists in searching for the position of the global minimum of the potential landscape and deducing the thermodynamically stable phase. In temperature-misfit strain phase diagrams, lines separate the stable phase regions, and the analysis of the polarization continuity properties across these lines allows us to determine the order of phase transition. This work revealed additional important information relative to the properties of first order phase transitions; we determined the limit of stability of the metastable phases and plotted the corresponding lines in the traditional temperature-misfit strain diagrams. These one dimensional boundaries are the analog to the superheating and supercooling temperature points in the context of bulk ferroelectric crystal. We highlight two dimensional coexistence regions adjacent to first order thermodynamic transition lines. The location and the shape of these regions are strongly dependent on the set of parameters used to describe the bulk crystal. We illustrate the interest in the revelation of coexistence regions, showing that the corresponding multi-stability properties could be used to design non-binary memory cells by using barium titanate thin films.

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I. INTRODUCTION

The key concept of phase has been introduced to describe a thermodynamic system in which the states of matter have similar physical properties. As consequence, the knowledge of phase boundary and related properties allows us to describe the changes in the system behavior. Ehrenfest classifications distinguish between two kinds of phase transitions with specific properties, such as first and second order phase transitions.

In the context of ferroelectricity, the properties of phase transitions of the bulk prototypical BaTiO₃ (BTO) ferroelectric are a subject of permanent interest from theoretical and experimental viewpoints. As an example, the description of the paraelectric-ferroelectric phase transition in the bulk BTO crystal, which is of the first order, is characterized by supercooling and superheating temperatures, and the polarization-temperature dependence exhibits a hysteresis loop presented in ferroelectricity textbooks.^{1,2}

For BTO thin films, the issues concerning the knowledge of the phase properties and their transitions are just as important as for bulk, especially with regard to potential applications in integrated electronics. Despite a large number of theoretical studies, the description of these phenomena is not complete. The reference tool, which is the temperature-misfit strain phase diagram introduced by Pertsev *et al.*,^{3,4} is made up of the lines of thermodynamic transition. For second order transitions, the knowledge of the thermodynamic transition line allows us to describe all of the properties of the transition. On the contrary for first order phase transition, this line is of limited interest because the effective transitions usually occur in the vicinity of this line. Further investigations are required to provide a complete description of physical properties.

Before Pertsev *et al.* works, Desu *et al.*⁵ considered three different values for the thermal expansion coefficient of the substrate and determined the phase of deposited thin film between the zero absolute and 300 °C. The corresponding one dimensional temperature diagrams, with critical temperature points, exhibited many

ranges of temperatures for which phase coexistence analog to that observed in the bulk crystal reference exists. Such behavior suggests the existence of critical lines in the two dimensional representations such as the temperature-misfit strain phase diagram, which correspond to the critical temperature points along the temperature axis.

Despite the potential interest of these lines, they have never been presented in the temperature-misfit strain phase diagrams⁶ available in the literature.

The main goal of this work is to determine the critical lines and show their impact on the properties of BTO thin films from the viewpoint of information storage. Since there are many models producing significantly different diagrams, we have selected several that we believe are the most representative among those presented in the literature. Depending on the model, we highlight the appearance of coexistence regions of two or three phases in the temperature-misfit strain diagram.

The history of electronic information storage is based on the existence of two electrically distinguishable stable states. Lots of efforts motivated by the improvement of storage capacity have focused on the search for more than two logic levels. Recently, Lee *et al.*⁷ reported the electrical switching among three stable out-of-plane polarizations in bismuth ferrite thin films. We also demonstrated the possibility to build logic units with three or four levels of symmetry protected in Lead Titanate thin films.⁸ In this article, we show the existence of three, four, five, and six stable states in BTO thin films that constitute the first step for investigating the possibility to build multivalued logic units based on this lead free compound.

II. FERROELECTRIC THIN FILMS DESCRIPTIONS

Due to its historical importance in the context of bulk ferroelectrics, the Landau–Devonshire theory of phase transitions served naturally as the theoretical foundation for ferroelectric thin films and nanostructures description. The loss of symmetry during the paraelectric–ferroelectric transition in the case of first and second order transitions was initially described with even polynomials, respectively, up to the sixth and fourth powers of the polarization. Originally, only the coefficient of the squared polarization term depended on the temperature. Of course, this approach based on the Taylor development had a range of validity limited in the vicinity of the phase transition temperature. Later, in order to describe also the transitions between the different ferroelectric phases, dependencies with the temperature of the coefficients of the power terms greater than two were introduced. This led to extending the validity of this approach to a wider range of temperatures in the case of the bulk material. Let us remember that it is the confrontation with the experimental results that contributed to this evolution. Nevertheless, it should be kept in mind that the further away from the transition temperatures one goes, the more the theory is likely to diverge from the experiment.

The bulk material thermodynamic potential G depends on the polarization $P(P_1, P_2, P_3)$ and the temperature T . The pioneering work concerning the ferroelectric thin films³ used the modified thermodynamic potential \tilde{G} [Eq. (1)], which also depended on the misfit strain u_m and the elastic compliance coefficients s_{ij} ,

$$\begin{aligned} \tilde{G}(P, T, u_m) &= a_1^*(P_1^2 + P_2^2) + a_3^*P_3^2 + a_{11}^*(P_1^4 + P_2^4) + a_{33}^*P_3^4 \\ &+ a_{13}^*(P_1^2 + P_2^2)P_3^2 + a_{12}^*P_1^2P_2^2 + a_{111}(P_1^6 + P_2^6 + P_3^6) \\ &+ a_{112}[P_1^4(P_2^2 + P_3^2) + P_2^4(P_3^2 + P_1^2) + P_3^4(P_1^2 + P_2^2)] \\ &+ a_{123}P_1^2P_2^2P_3^2 + a_{1111}(P_1^8 + P_2^8 + P_3^8) + a_{1112}[P_1^6(P_2^2 + P_3^2) \\ &+ P_2^6(P_3^2 + P_1^2) + P_3^6(P_1^2 + P_2^2)] + a_{1122}(P_1^4P_2^4 + P_1^4P_3^4 + P_2^4P_3^4) \\ &+ a_{1123}(P_1^4P_2^2P_3^2 + P_1^2P_2^4P_3^2 + P_1^2P_2^2P_3^4) + \frac{u_m^2}{s_{11} + s_{12}}. \end{aligned} \quad (1)$$

The method used to built \tilde{G} from G and the dependences of a_i^* , a_{ij}^* , a_{ijk}^* , and a_{ijkl}^* with the physical parameters of the problem are reported in Sec. 3 of the [supplementary material](#). The properties of \tilde{G} allowed to determine the physical properties of single-domain thin film with a mechanically free upper surface.

When one moves away from the transition temperatures in the case of bulk material, it is expected that the deviations between the properties predicted by the T – u_m diagram and the experiment increase with the misfit strain. Due to the limited experimental data, it is not possible at this time to modify the dependencies of the coefficients of \tilde{G} with the mechanical parameters like that has been made in the past for the coefficients of G concerning the temperature dependencies.

The formation of ferroelastic domains in thin films⁹ can also cause some important changes on the phase stability condition. Theoretical models of dense domain structures¹⁰ and phase-field simulations¹¹ lead to substantial differences with respect to the single domain phase diagrams. In addition (and especially for ultrathin films), the effect of the surface on the polarization becomes significant, and the depolarizing-field effect must be introduced in the theory.¹² In the first temperature misfit-strain diagrams,^{3,4} the attention was focused on the boundary between the stable phases. This was fully coherent since the properties that had motivated these works, such as electric susceptibility or binary logic, concerned the stable phases. In this context, it was legitimate not to study the properties of metastable phases. It is, therefore, wrong to consider that the initial model of description of thin films has revealed all of the information that appears useful today. Because we focused on one up until now ignored aspect of the properties of thin films, we naturally thought that the popular single domain diagram would be the most appropriate choice for the first step to investigate metastable properties. Trivially and in other words, it might seem simply logical to use it as a toy model to study new aspects of the phase diagram like coexistence regions. Despite many more recent, more sophisticated approaches that are better adapted to other contexts, the description of a single domain has not revealed all its potential interest and should not be considered only as a toy model. Indeed, from a much more important point of view, it was experimentally demonstrated that the monodomain configuration could be stabilized even in ultrathin films and maintained preserved during the switching process by an electric field.¹³ This fundamental experimental result proved that the homogeneous polarization reversal from a monodomain state to another one was possible under certain conditions. Another argument in favor of the interest of this model comes from our theoretical work concerning Lead Titanate, where the temperature-misfit strain phase diagram is not a subject

of controversy. We demonstrated that (I) metastable phases coexisted with stable phases in large regions of the diagram delimited by a critical line quite far away from the thermodynamic transition line and (II) the corresponding metastable states could be reached by applying the electric field, thus creating additional logic states. The classical use of the original approach³ consists in finding the global minimum of the potential landscape $\tilde{G}(P, T, u_m)$, for each pair of values of T and u_m . The position of the global minimum (P_1, P_2, P_3) allows us to determine the phase. Then, it is possible to build a two dimensional phase diagram with temperature as the ordinate axis and misfit strain as the abscissa axis. The maximum number of phases found in the temperature-misfit strain diagrams for barium titanate when growth is realized on cubic substrate is equal to six; it depends upon the model used: the paraelectric phase (P) with $P = (0, 0, 0)$, and five ferroelectric phases called: c with $P = (0, 0, P)$, a with $P = (P, 0, 0)$, aa with $P = (P, P, 0)$, ac with $P = (P, 0, P')$, and r with $P = (P, P, P')$. In other words, at each point (T, u_m) , one can affect a phase symbol P , c , a , aa , ac , and r , which corresponds to the stable state from strictly speaking the thermodynamic point of view. The areas of the existence of the different phases correspond to regions of the plan $T-u_m$. As an example of the notation used in the following of this article to refer to the different regions, $\{c\}$ corresponds to a region inside which only the c phase is stable.

The phase boundaries are the lines that separate two adjacent phase regions. At this stage, it is not possible to distinguish between first and second order phase transitions. The analysis of polarization variation components across the phase boundary and application of the continuity criteria allows us to determine the order of transition. Usually, a temperature-misfit strain phase diagram is made up of solid lines (second order) and dashed lines (first order). These lines of the plan $T-u_m$ correspond to the extension in one dimension of the temperature point T_{it} encountered in the bulk material case. This kind of graphic representation has been very successful, as evidenced by a large number of studies it has inspired.

It is somewhat surprising to note that it never been any results reported of critical lines and coexistence regions in temperature-misfit strain phases diagrams. This gap is filled in the following of this article. To do that, in the case of one order phase transition lines, we determined the limit of stability of each adjacent phase. The points with coordinates (T, u_m) that zero the determinant of the Hessian matrix of the potential $\tilde{G}(P_1, P_2, P_3)$ give lines located in the adjacent phase, and they extend in one dimension the critical temperature points properties (see the [supplementary material](#), Sec. 1, for an overview of the main concepts and Sec. 2 for an illustration of the notations and representation tools we have adopted for this paper, in the well-known case of the paraelectric-ferroelectric transition in bulk material). We enrich the basic $T-u_m$ diagram by adding for each phase, when they exist two limits of stability lines and highlight coexistence phase regions.

III. THE FULL TEMPERATURE-MISFIT STRAIN DIAGRAMS OF BARIUM TITANATE THIN FILMS: POSITION OF THE CRITICAL LINES AND LOCATION OF THE COEXISTENCE REGIONS

The determination of the thermodynamic equilibrium phase gives all of the valuable information in the case of a second order

phase transition. On the contrary, when the transition is of the first order, the knowledge of the coexistence condition is of fundamental importance and requires the determination of the metastable phase boundaries.

The main objective of this article is to investigate these properties in the context of BTO thin film. The misfit strain phase diagram of BTO thin films does not seem to be clearly and definitely established. Our purpose is not to discuss the validity or interest of the published diagrams but to fully describe, when first-order transitions have been reported, the coexistence properties, which, as we will point out, can potentially be observed experimentally and used for applications in the field of non-binary logic.

A. Sixth order potential models

With regard to its historical importance, the first diagram published by Pertsev *et al.*³ that is regularly used in studies¹⁴ deserves to be investigated in this work. Pertsev *et al.*,³ have found five phases different from those observed in bulk crystals. Later, by keeping the same P^6 thermodynamic potential and by using another set of coefficients, the same authors proposed a qualitatively different phase diagram.⁴ The sets of parameters given in Ref. 3 and in Ref. 4 are presented in a single table for easy comparison in the [supplementary material](#).

We first investigated the coexistence properties by using the set of parameters used by Pertsev *et al.*³ in their original approach (model I). The black lines of the phases diagram in Fig. 1(a) with coordinates (T_{it}, u_{it}) indicate the limit of the global stability of each phase (thermodynamic transition lines). In addition, we observe the presence of a triple point (a point where three phases coexist), at this stage of the description, we only recalled the results obtained by Pertsev *et al.*³

We determined the limit of metastability for each phase and reported the resulting lines on the diagram by using solid colored lines. On either side of a coexistence line (dashed black line), one observes a colored solid line. These lines show the extension of one phase as metastable in a region where another phase is stable. As a consequence, there exist coexistence regions indicated in the diagram by the presence of dots in some regions of the diagram.

This behavior is illustrated by the ac - aa boundary and observed in a large region of the diagram reported in Fig. 1(a), from about 40 °C to the bottom of the diagram (−200 °C). Along a straight line of the $T-u_m$ plan parallel to the abscissa axis, which cut the line of thermodynamic ac - aa transition (dashed black line) and the two critical lines (colored line), we observe the following corresponding sequence: $[ac]$, $[ac, aa]$, $[ac, aa]$, $[ac, aa]$, $[ac, aa]$, $[ac, aa]$, and $[aa]$. It is analog to the well known first order paraelectric-ferroelectric transition along the temperature axis (see Sec. 2 in the [supplementary material](#)).

In order to extend the sequential one dimensional notation used along the misfit strain axis, we introduced hugging characters as symbols of delimitation of two dimensional regions of the temperature-misfit strain plan. We used italic underlined character and italic character to, respectively, refer to critical and metastable situations of the different phases (for example, \underline{c} and c).

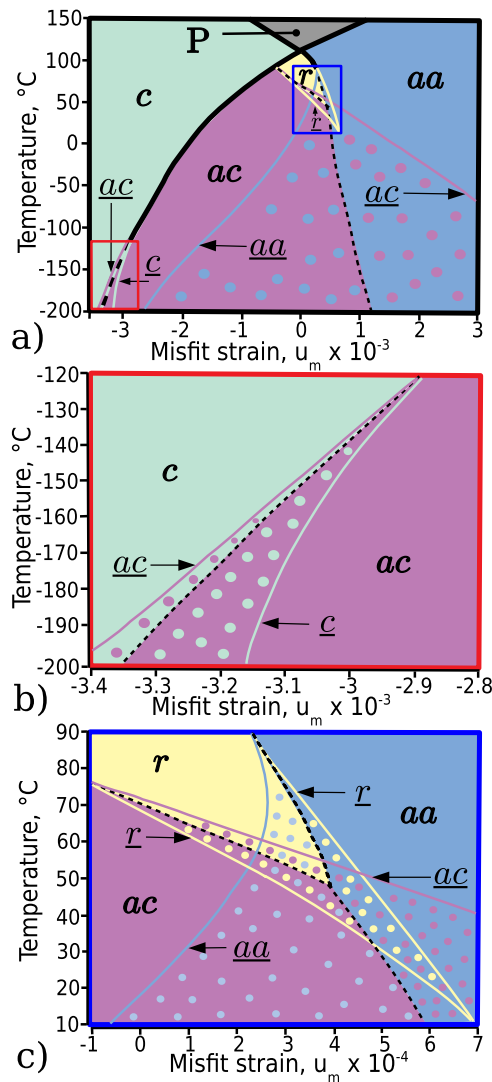


FIG. 1. Temperature-misfit-strain phases diagram of BTO thin film (model I). The thermodynamical phase boundaries are indicated by black lines, first order transitions with dashed lines, and second order transitions with solid lines. The name of the stable phase is indicated with bold black characters and is associated with the background color. Colored dots report the presence of metastable phase(s). The colored solid lines are the critical lines and indicate the limit of metastability of different phases (named with black underlined characters). (a): overview diagram, some information are absent of the rectangular blue and red zones, they are detailed in (b) and (c), (b): enlargement of the red zone in (a), and (c): enlargement of the blue zone in (a).

With the present model studied (I), the coexistence regions of the ac and aa phases are both wide and correspond to the following adjacent regions: $\{ac\}$, $\{ac, aa\}$, $\{ac, aa\}$, $\{ac, aa\}$, $\{ac, aa\}$, $\{ac, aa\}$, and $\{aa\}$.

In the region of strong compressive strain and low temperature [Fig. 1(b)], below about -120°C and -0.0029 misfit strain (coordinates of the tricritical point), the transition between the c and ac

phases ceases to be of second order and becomes of first order. The lines that correspond to the limit of metastability of these phases emerge from this tricritical point. A sequence, analog to that previously described but involving the c and ac phases, is observed: $\{c\}$, $\{c, ac\}$, $\{c, ac\}$, $\{c, ac\}$, $\{c, ac\}$, $\{c, ac\}$, and $\{ac\}$. Like for the ac - aa coexistence, the areas of the coexistence regions $\{c, ac\}$ and $\{c, ac\}$ are not symmetrical.

The situation is more complex close to the triple point where the r , ac , and aa phases coexist. The enlargement of the region in the vicinity of this point [Fig. 1(c)] allows a detailed description. The critical lines of the phases emerge, as previously described, from the second order transition line. The critical line of the r phase exhibits two branches. One of them starts at one r and aa tricritical point, while the other one starts at one r and ac tricritical point, both branches meet each other in the aa stable region. Near the appearance of critical lines and on both sides of the thermodynamic transition line, we observe three pairs of regions where two phases coexist: $\{ac, r\}$, $\{ac, r\}$, $\{aa, r\}$, $\{aa, r\}$, $\{aa, ac\}$, and $\{aa, ac\}$.

In addition to these six coexistence regions of two phases, there exist three regions where the r , ac , and aa phases coexist. These regions are induced by several crossings of critical lines between them. Within these regions, one phase is stable and the other two are metastable: $\{ac, r, aa\}$, $\{ac, r, aa\}$, and $\{ac, r, aa\}$, which are adjacent and surround the triple point.

The next model we have investigated corresponds to the one that was proposed later by Pertsev *et al.*⁴ (model II), in which a different temperature-misfit strain phase diagram for BTO is obtained based on another set of coefficients for the sixth order Landau-Devonshire polynomial. Significant differences were observed with respect to the original version on the general appearance of the phase diagram, and this evolution is not commented on in the literature. As can be seen in Sec. 4 of the [supplementary material](#), the use of Bell's parameters¹⁵ rather than those of Jona's¹ is at the origin of these differences. These two sources are still regularly used in the literature, particularly in temperature-misfit strain diagrams. We have chosen to consider these two sources carefully in this work as in a previous article,¹⁶ and we have used them both (see also, for example, the main text and the [supplementary material](#) of this last reference). Except for the low temperatures and large tensile or compressive strain, the whole shape of the phase diagram (model II) has similarities with that obtained by using *ab initio* simulations.¹⁷

The enlargement of the right bottom corner of a diagram in Fig. 2(a) is represented in Fig. 2(b). The r - aa transition is of first order only for temperatures lower than about 25°C . On the contrary to what has been previously shown for the ac and aa phases in Fig. 1(a), the lines that represent the limits of stability of the r and aa phases are close to that of thermodynamic transition. As a consequence, the coexistence regions $\{r, aa\}$ and $\{r, aa\}$ are confined near the line of thermodynamic transition.

In the left side of the temperature-misfit strain phase diagram [Fig. 2(a)], the ac phase separates the c and r phases. The corresponding phase transitions c - ac and ac - r are both of first order. As shown in Fig. 2(c), the four critical lines and the two coexistence lines are very close. In the top part of this inset, two classical behaviors are observed for the c - ac and ac - r first order phase transitions. For each transition, the two coexistence regions $\{c, ac\}$ and $\{c, ac\}$, $\{ac, r\}$, and $\{ac, r\}$ are observed. We can notice that the one $\{ac\}$ region

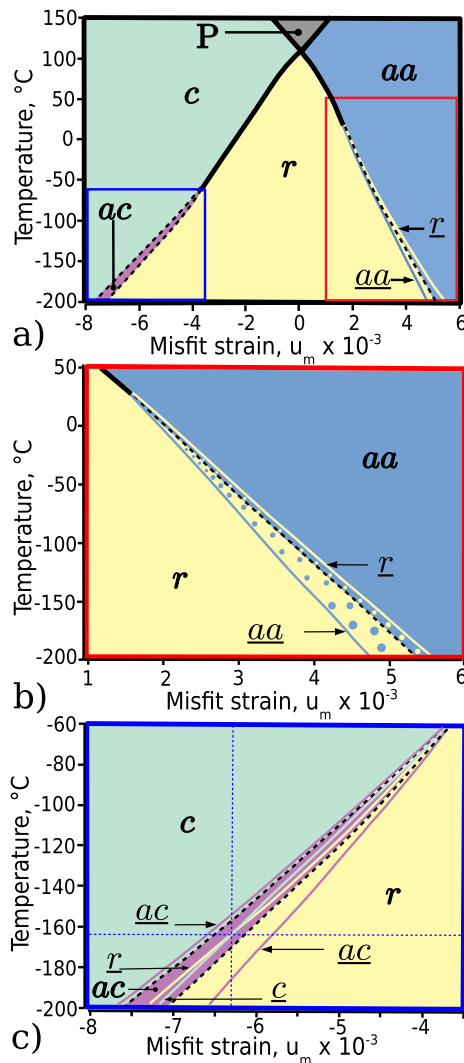


FIG. 2. Temperature-misfit-strain phase diagrams of BTO thin film. The set of parameters used for the calculation is given by Pertsev *et al.*⁴ (model II). The thermodynamical phase boundaries are indicated by black lines, first order transitions are indicated with dashed lines, and second order transitions are indicated with solid lines. The name of the stable phase is indicated with bold black characters and is associated with the background color. Colored dots report the presence of metastable(s) phase(s). The colored solid lines are the critical lines and indicate the limit of metastability of different phases (named with black underlined characters). (a) Overview diagram; some information are absent from the rectangular blue and red zones, which are detailed in (b) and (c), (b) enlargement of the red zone in (a), and (c) enlargement of the blue zone in (a). Due to the fact that all the lines are very close to each other, we have not represented in (c) the dots that indicate the metastable phases. The intersection of dashed blue lines indicates the crossing point of the green and yellow critical lines.

separates the $\{c, ac\}$ and $\{ac, r\}$ regions as long as the temperature is greater than about -60°C . At this temperature and approximately $u_m = -0.0037$, the critical lines of the c and r phases cross each other. The regions $\{c, ac\}$ and $\{ac, r\}$ overlap partially. In these conditions,

the region $\{ac\}$ disappears and is replaced by a very thin region where three phases c , ac , and r coexist, the c and r phases being metastables: $\{c, ac, r\}$. The coexistence of six different states c^- , c^+ , ac^- , ac^+ , r^- , and r^+ with symmetry protected polarization vector⁸ suggests that it is possible to build memory cells based on six logic levels.

The highlighting of this property is facilitated by examining the situation at the temperature -200°C (Fig. 3). We observe that at this temperature the coexistence of the c , ac , and r phases occurs in the range of misfit-strain -0.0074 – -0.0073 . The variation of the polarization as a function of the misfit strain is discontinuous, which corresponds to the property of first order phase transition. One can remark that the magnitude of discontinuity is very weak for the out of plane component P_3 . The polarization jump is mainly observed in the variation of the in plane components P_1 and P_2 . In this region of the phase diagram, the component P_3 of the polarization in the different phases c , ac , and r is so close together that the translation of the polarization value into a logical state could

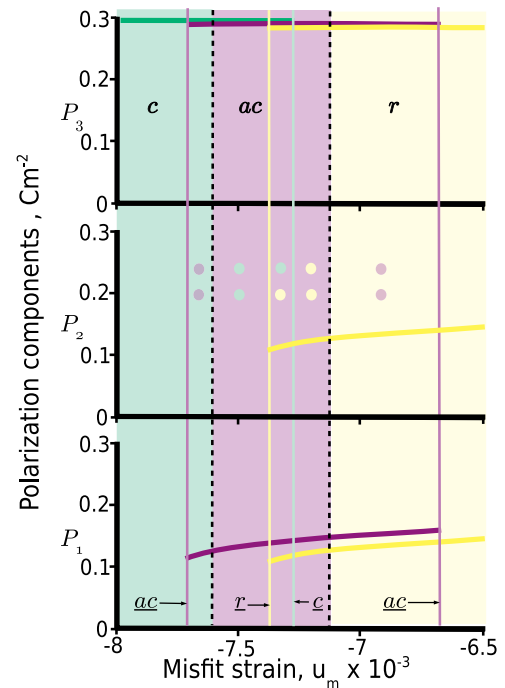


FIG. 3. Evolution of the polarization components as a function of the misfit-strain u_m at -200°C . The abscissa axis corresponds to a line segment located at the bottom of Fig. 2(c). Black dashed lines indicate the misfit strain value at which two adjacent phases coexist with the same energy. The name of the thermodynamically stable phase is indicated on the top graph in bold black font, which corresponds to the background color. The limits of metastability of the different phases (whose name is specified in an underlined font in the bottom graph) are indicated with colored lines. The colored dots represented on the middle graph indicate the metastable(s) phase(s) and allow for localizing the coexistence regions. The in-plane components P_1 and P_2 are, respectively, represented in the bottom and the middle graph, whereas the out of plane component P_3 is represented in the top graph, by using colored curves. The colors that correspond to those used for the background of the stable phase region are slightly darker.

be confusing. Indeed, assuming that it is possible to switch from a stable to a metastable state using the electric field,⁸ the reading operation that is equivalent to measuring surface charges should be much more accurate than usual due to the almost equal charges density in each phase. It seems unlikely that this property will be possible to use straightly to create memories with six logical states corresponding to the positive and negative states of phases *c*, *ac*, and *r*. In such a situation, the distinction of the different phases could be possible by measuring other quantities such as permittivity or specific heat. These alternative strategies could be the subject of future work.

Partsev *et al.*'s⁴ study has been completed by Shirokov *et al.*'s.¹⁸ work to evaluate the impact of the value of the electrostrictive coefficients Q_{ij} on thin film properties. Results with the same six-order potential and with two sets of parameters published by Bell *et al.*^{15,19} have been compared. Shirokov *et al.*¹⁸ found the same general shape for the temperature-misfit strain phase diagram, with the same phases, and minor changes consisting of little parts of some first order thermodynamic transition lines being transformed into second order lines.

B. Eighth order potential models

Under compressive strain larger than 0.4% and for a certain temperature range, there is no equilibrium solution for the polarization when using the sixth-order polynomial thermodynamic potential previously investigated⁴ (the coefficient a_{111} becomes negative). To overcome this problem, Li *et al.*²⁰ constructed a Landau-Devonshire potential based on an eight-order polynomial expansion, and they gave a set of temperature-independent an-harmonic coefficients.

It has been shown that the values of elastic compliances and electrostrictive coefficients could affect the temperature-misfit strain phase diagram. Haeni *et al.*²¹ reported a potential strong shift of the paraelectric-ferroelectric transition temperature in strontium titanate films. This study revealed a continuous deformation of the diagram's shape but no change in its general aspect.

Following this, Shirokov *et al.*¹⁸ have investigated the influence of the electrostrictive coefficient Q_{12} on the phase diagram with the Li *et al.*²⁰ eight order potential. Two values published by Bell *et al.* $Q_{12} = -0.034$,¹⁵ $Q_{12} = -0.045$ ¹⁹ have been used for comparison, the major change in the second diagram with respect to the first is the suppression of the *ac* phase and the replacement of some first order transitions by second order transitions. In these conditions, one can conclude that the influence of the electrostrictive coefficients on the coexistence regions is only quantitative and limited in interest in the context of this study concerned with coexistence properties. Shirokov *et al.*²² have also adopted Li *et al.*'s potential²⁰ to investigate the influence of the elastic compliances s_{ij} on the BTO thin films phases diagram. They showed, by considering two sets of parameters, published by Berlincourt²³ (model III) and Bond²⁴ (model IV), that these parameters played an important role in the number of phases found in the BTO thin film diagram.

Figure 4(a) established by using the model III shows two transitions of second order: *p*-*aa* and *c*-*r* and three transitions of the

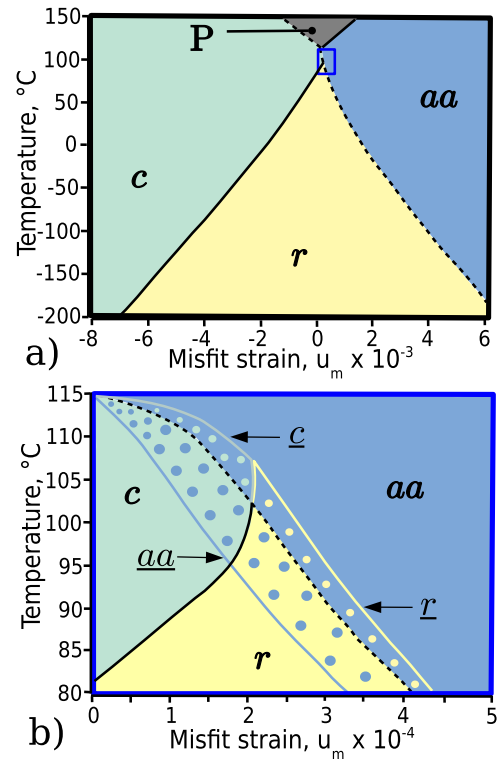


FIG. 4. Temperature-misfit-strain phase diagrams of BTO thin film. The set of parameters used for the calculation is given by Shirokov *et al.*²² (model III). The thermodynamical phase boundaries are indicated by black lines, first order transitions are indicated with dashed lines, and second order transitions are indicated with solid lines. The name of the stable phase is indicated with bold black characters and is associated with the background color. Colored dots report the presence of metastable(s) phase(s). The colored solid lines are the critical lines that indicate the limit of metastability of different phases (named with black underlined characters). (a) Overview diagram, some information are absent from the rectangular blue zone and are detailed in (b), and (b) enlargement of the blue zone in (a).

first order: *p*-*c*, *c*-*aa*, and *r*-*aa*. As compared to the phases diagrams obtained with the sixth order potential,^{3,4} all the first order phase transitions are initiated close to the point with coordinates corresponding to the bulk transition temperature and the zero misfit strain. The corresponding coexistence regions of ferroelectric phases are shown in the enlarged figure [Fig. 4(b)]: {*c*, *aa*} and {*c*, *aa*}, {*aa*, *r*} and {*r*, *aa*}. The critical lines of the *c* and *r* phases located in the *aa* phase region emerge from the point ending the *c*-*r* second order phase transition line at the limit of the *aa* region.

The second set of parameters for the eight order potential (model IV) gives the phase diagram presented in Fig. 5(a), we can notice the presence of two intermediate *a* and *ac* phases missing in the diagram obtained with the first used eight order potential.

Let us remark that the overall look of this phase diagram is very close to that published by Li *et al.*,²⁵ who have examined the stability of multi-domain structures. Both diagrams are almost stackable.

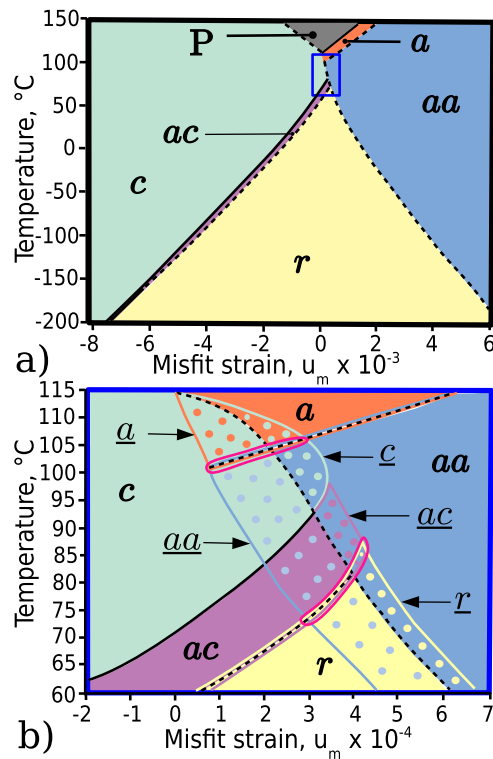


FIG. 5. Temperature-misfit-strain phase diagrams of BTO thin film. The set of parameters used for the calculation is given by Shirokov *et al.*²² (model IV). The thermodynamical phase boundaries are indicated by black lines, first order transitions are indicated with dashed lines, and second order transitions are indicated with solid lines. The name of the stable phase is indicated with bold black characters and is associated with the background color. Colored dots report the presence of metastable phase(s). The colored solid lines are the critical lines that indicate the limit of metastability of different phases (named with black underlined characters). (a) Overview diagram, some information are absent from the rectangular blue zone and detailed in (b), and (b) enlargement of the blue zone in (a), three phases coexist within the region delimited with the magenta closed line. Due to the fact that all the lines are very close to each other in this region, the dots that indicate the metastable phases are not represented inside this region.

This suggests that the second phase of a domain structure consisting of two phases described by Li and Chen²⁵ could emerge from a metastable phase.

Among all the transitions shown in Fig. 5(a), only two of them are of second order: c - ac and p - a . We found [Fig. 5(b)] the two pairs of double coexistence regions already displayed in Fig. 4(b). Due to the presence of the a and ac phases, the four c - a , a - aa , ac - aa , and ac - r first order phase transitions lead to the existence of four pairs of coexistence regions $\{c, a\}$ and $\{c, a\}$, $\{a, aa\}$ and $\{a, aa\}$, $\{ac, aa\}$ and $\{ac, aa\}$, and $\{ac, r\}$ and $\{ac, r\}$.

Because of the meeting or crossing of first order transition lines, there also exist six regions where three phases coexist: $\{c, a, aa\}$, $\{c, a, aa\}$, $\{c, a, aa\}$, $\{ac, r, aa\}$, $\{ac, r, aa\}$, and $\{ac, r, aa\}$. All these six regions located inside a magenta colored closed line in

Fig. 5(b) are small and surround the crossing point of two first order thermodynamic transition lines.

IV. CONCLUSIONS

Over the years, BTO has been used in a wide variety of applications in various forms of crystals, ceramics, and thin films. The interest in improving the theoretical description of its bulk crystal form is permanent since the discovery of the ferroelectric property of this compound. For about twenty years, thin films are the subject of the same attention. In this work, we enriched the most popular tool used to describe phase transitions in thin films; more precisely, we highlight the characteristic properties of first order phase transitions: critical lines and coexistence regions. Because of the diversity in choosing among the set of parameters available in the literature, we have chosen for the present investigation four of them that seemed to us representative of the published studies. The location of the critical lines in the temperature-misfit strain phase diagram, their shape, and the phase coexistence regions are found to be strongly dependent on the set of parameters introduced in the model. The observation of metastable phases can be fortuitous or random, and it can depend strongly on the history of the sample. In such situations, the system occupies a polarization state with a Gibbs free energy \tilde{G} that corresponds to a local minimum in the energy landscape. In the absence of external perturbations, the system does not evolve toward a stable state (global minimum). The existence of an energy barrier between the two types of minimum preserves the metastable situation in the absence of an electric field; this is related to the concept of symmetry protected memory introduced in a previous study.⁸ Moreover, it is natural to look for metastable phases in regions of the phases diagram far enough from the critical lines where they spontaneously disappear. Under experimental conditions, with T and u_m fixed, it is more likely that the stable phase is observed first. The crucial question is, therefore: how to reach the metastable phase starting from the stable phase? This could be done by applying an electric field whose direction, intensity, and duration can be controlled. It is possible, after stopping the application of this field, that the system reaches a metastable state. The probability of this happening is thus not related to the height of the energy barrier between two phases in the absence of an electric field, this scenario is conditioned to the possibility, with the help of the electric field, to deform the energetic landscape in order to open a path from the stable phase toward the metastable phase. In other words, it is a question of exchanging between two phases, the local and global minima of \tilde{G} during the application of the electric field. The polarization could then be pinned in the metastable phase after the suppression of the electric field. As shown previously,⁸ the study of these mechanisms is complex. Depending on the values of T and u_m , the transition from the stable toward the metastable phase by the previously described method is not always possible (see cases I and II in Fig. 4 of one previous article⁸). Further theoretical investigations, concerning the properties in the presence of an electric field, would, therefore, be very useful to guide experimentalists studying BTO films. The coexistence of two or three phases is possible, as a consequence, by including the in-plane phase with $P_z = 0$ (a and aa phases) and the out of plane phases with $P_z \neq 0$ (c , ac , and r phases), we found regions of the temperature-misfit strain diagram where 1, 2, 3, 4, 5, or 6 different algebraic values are possible for the out of

plane polarization P_z . Thus, one can expect that this property, which results from the existence of metastable phases and states, would be useful to design multi-valued memories based on BTO ferroelectric thin films.

As discussed before, the existence of metastable states is required to break the free binary logic of traditional ferroelectric memories. One must also point out that it is not a sufficient condition: the different states must be distinguishable from electrical measurement viewpoint. In addition, the existence of polarization switching mechanisms able to go through the different logic levels is also required. This latter condition goes beyond the scope of this work. In a previous article,⁸ we investigated this point and highlight the existence of a large variety of hysteresis loops topologies in the case of lead titanate thin films for ternary and quaternary logics. One can expect possible additional exotic loops in BTO thin films with 5 or 6 polarization levels. This last point suggests the great interest to develop both theoretical and experimental studies of the polarization–electric field response in BTO thin films within the ranges of temperatures and misfit strains concerned with the phase coexistence that we revealed in this article.

SUPPLEMENTARY MATERIAL

See the [supplementary material](#) for some basic information about phases, potential landscape, stability and criticality concepts, thin film thermodynamical description, and the different set of model parameters for barium titanate.

AUTHOR DECLARATIONS

Conflict of Interest

The authors have no conflicts to disclose.

DATA AVAILABILITY

The data that support the findings of this study are available within the article and its [supplementary material](#).

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