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Tricriticality in Co-doped $BaTiO_3$

L. Benguigui
Solid State Institute, Technion-Israel Institute of Technology, Haifa, Israel

Y. Beaucamps
Laboratoire des Dielectriques, Faculte des Sciences, Dijon, France

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In measurements of the tetragonal distortion of single crystals of $BaTiO_3$ doped with cobalt (Co), we found that for about 2.5 at.% Co the ferroelectric-paraelectric transition is a tricritical point. We relate this tricritical point to the phase-diagram topology. It is likely that the coupling of the polarization with the electrons is responsible for the appearance of this tricritical point.

I. INTRODUCTION

Tricritical points occur relatively frequently in ferroelectrics. They have been observed in $BaTiO_3$,[1] SbSI,[2] KH_2PO_4,[3] in triglycine sulfate (TGS),[4] by application of pressure, and in the solid solutions $(Ba,Sr)TiO_3$,[5] $Pb(Zr,Ti)O_3$,[6] and Te(Sn,Ge).[7] The condition for appearance of tricritical properties is a coupling between the order parameter and another parameter. It is well known that ferroelectrics are characterized by relatively strong coupling between the polarization and the other properties of the crystal. In the above-mentioned cases several tricritical points appear because of the coupling between the polarization and the strain. For the solid solutions Te(Sn,Ge) other couplings are possible, as suggested by Clarke.[7]

In this paper, we report another case of tricritical point in $BaTiO_3$ crystals doped with cobalt.[8] It is not clear what coupling is involved in these crystals. We shall discuss this point in connection with the shape of phase diagram (T,x) where x is the atomic percentage of the cobalt atoms.

II. EXPERIMENTAL RESULTS

The crystals were grown at the Laboratoire des Dielectriques of the University of Dijon. We performed measurements of the tetragonal distortion c/a for crystals with 0, 0.5, 1.0, 1.5, and 2 at.% Co. Details of the crystals growth and the compensation mechanism are given in Ref. 16. We believe that the Co ions are located at Ti sites. We used as-grown samples which are multidomain. This fact was used to perform x-ray diffractometry with the Cu-$K\beta$ line in order to avoid the use of a monochromator. We performed a θ-2θ scan of the (400) lines in the tetragonal phase and always found two lines of unequal height. For $x > 2$ at.% Co, the intensity of one of the lines was so low that we were not able to measure the tetragonal distortion. Using the lines (400), we detected a variation of the $(c/a)-1$ of the order of 10^{-4}. The samples were heated with a special furnace with berylium windows, and cooled by solid CO_2. Temperature stability was better than 0.1 °C.

Figure 1 shows the variation of $(c/a)-1$ as a function of T for the five crystals. The discontinuity of $(c/a)-1$ at the transition temperature T_t decreases with the amount of cobalt. Drawing this jump as a function of x (Fig. 2), one sees that for $x \simeq 2.5\%$, the jump becomes null; i.e., the transition is continuous. This transition is a tricritical point. From the curve giving the variation of the transition temperature T_t as a function of x (not indicated here), we conclude that the transition temperature of the tricritical point is $T_t \simeq 12\,°C$.

In all the samples studied we observed a coexistence region near the transition temperature, as expected in a first-order transition. A third line appears which is identified with the parts of the crystal that have cubic structure. For the pure sample the temperature extension of the coexistence region is about 10 °C. This is in agreement with the value of $T_t - T_0 = 12\,°C$ (T_0, the Curie-Weiss temperature) deduced from dielectric measurements. For $x = 2$ at.% the temperature extension decreases to about 1 °C. This temperature interval is analogous to thermal hysteresis, and is consistent with a change in the order of the transition.

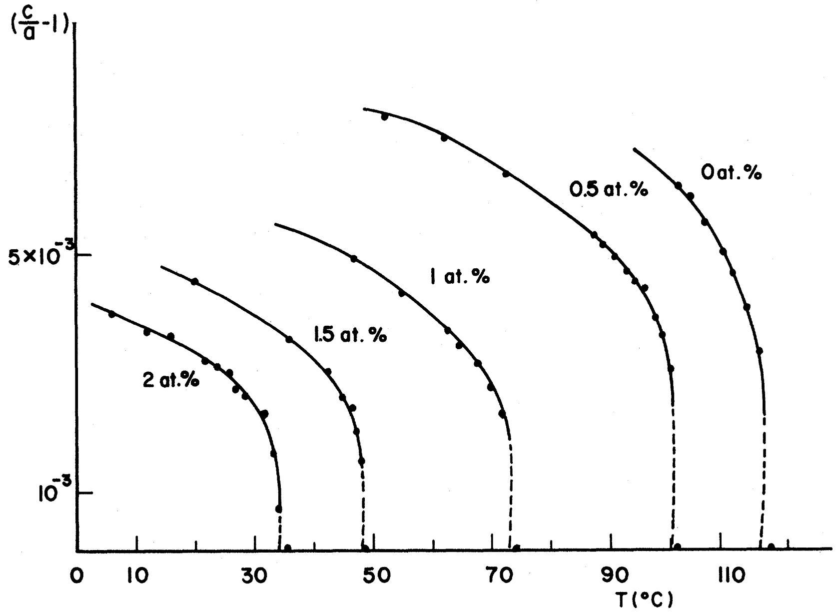

FIG. 1. Variation of the tetragonal distortion $(c/a)-1$, as a function of the temperature for different values of x (cobalt concentration).

III. DISCUSSION

A. Free-energy expansion

In ferroelectrics, the Landau theory gives a very good description of the phenomena. Thus we write the free energy (in the tetragonal phase)

$$F=F_0+\alpha P^2+\tfrac{1}{2}\beta_1P^4+\tfrac{1}{3}\gamma_1P^6\ , \tag{1}$$

with $\alpha=\alpha'(T-T_0)$. P is the polarization. Minimizing F with respect to P, we obtain the equation giving P in the tetragonal phase as

$$\alpha'(T-T_0)+\beta_1P^2+\gamma_1P^4=0\ . \tag{2}$$

Writing $(c/a-1)=\Delta=P^2/k$ (electrostrictive coupling), Eq. (2) becomes

$$\alpha'(T-T_0)+\beta_1k\Delta+\gamma_1k^2\Delta^2=0 \tag{3}$$

or

$$\frac{\beta_1}{\alpha'}k+\frac{\gamma_1}{\alpha'}k^2\Delta=\frac{T_0-T}{\Delta}\ . \tag{4}$$

From a plot of $(T_0-T)/\Delta$ as function of Δ, it is possible to obtain values of β_1k/α' and γ_1k^2/α' (see Ref. 7). In Fig. 3, we plot Eq. (4) for different values of x. We have assumed that the difference (T_t-T_0) decreases linearly from 10 °C for $x=0$ at.% to 1 °C for $x=2$ at.%. One sees from Fig. 3 that γ_1k^2/α' is approximately constant. We find that β_1k/α' is negative, as expected for a first-order transition, but increases if x increases [Fig. 3(b)] β_1k/α' becomes null for $x\approx2.2$ at.%, in agreement with the results of Fig. 2. This quantitative analysis shows that the decrease of the discontinuity in c/a at T_t is related to a decrease of β_1, and not to an increase of γ_1. This confirms the tricritical properties of the Co-doped samples of BaTiO$_3$.

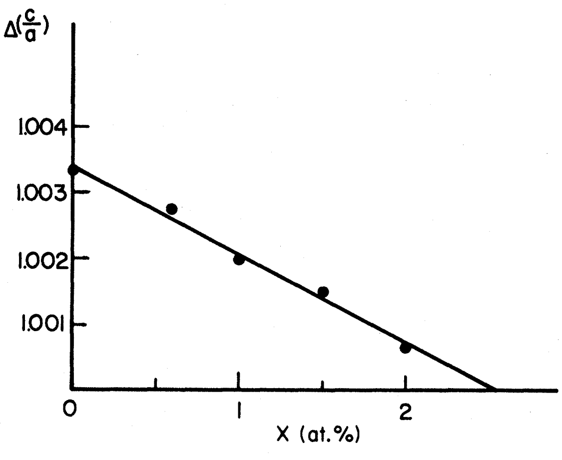

FIG. 2. Variation of the $(c/a)-1$ discontinuity at the transition temperature $T_t(x)$, with x.

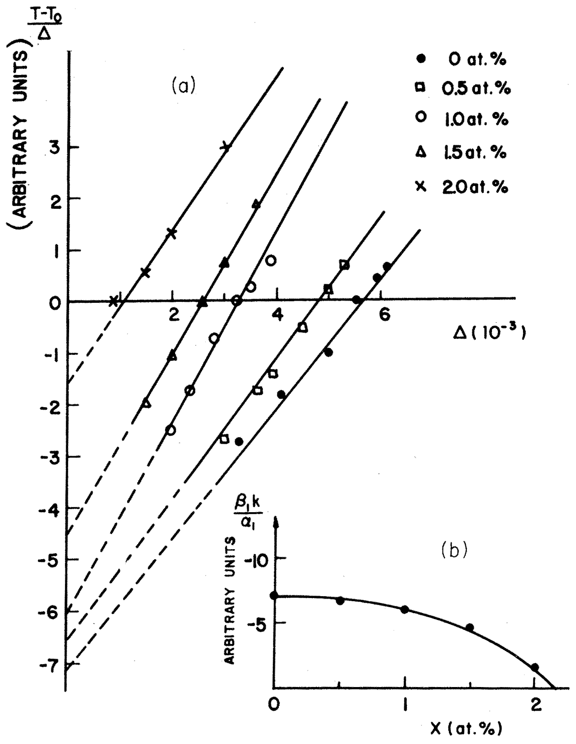

FIG. 3. (a)$(T_0-T)/\Delta$ as a function of Δ, showing a linear relation as predicted by Eq. (4). (b) Variation of $\beta_1 k/\alpha'$ as function of the Co concentration. $\beta_1 k/\alpha'$ is given by the intercept of the lines of (a) with the vertical axis.

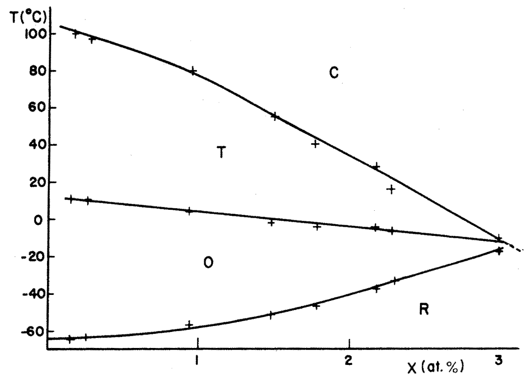

FIG. 4. Phase diagram of the Co-doped $BaTiO_3$ crystals. C = cubic, T = tetragonal, O = orthorhombic, R = trigonal.

B. Phase diagram

In Fig. 4, we show the phase diagram (T_t,x). It is taken from Ref. 9, and the transition temperatures have been determined by pyroelectric measurements. On this diagram, the tricritical point is not indicated because it is not detected by the pyroelectric measurements. It should be indicated on the upper line at the point $T=12\,^{\circ}\mathrm{C}$, $x=2.5$ at.%. The lines which divide the different regions of the phase diagram converge to the same point for $x\approx 3$ at.%. The special topology of the phase diagram is not particular to these crystals. There are other systems in which the three transition lines converge to the same point, such as the solid solutions $Ba(Ti,Sn)O_3$,[10] and $BaTiO_3+Ba(Fe_{1/2}Ta_{1/2})O_3$.[11] We want to show that the topology of the phase diagram is related to the occurrence of the tricritical point.

If we write the free-energy expansion as a function of the polarization components P_x,P_y,P_z, we have:

$$F=F_0+\alpha P^2+\tfrac{1}{2}\beta_1(P_x^4+P_y^4+P_z^4)$$
$$+\beta_2(P_x^2P_y^2+P_y^2P_z^2+P_z^2P_x^2)$$
$$+\tfrac{1}{3}\gamma_1(P_x^6+P_y^6+P_z^6)\ . \tag{5}$$

Devonshire[12] has shown that for pure $BaTiO_3$, $\beta_1<0$ and $\beta_2>0$ at fixed pressure. In each phase the free energy can be written as follows:

tetragonal $\qquad \phi_T=F-F_0=\alpha P^2+\tfrac{1}{2}\beta_1P^4+\tfrac{1}{3}\gamma_1P^6\ ,\qquad$ (6a)

$(P_z\neq 0,\quad P_x=P_y=0)$

orthorhombic $\qquad \phi_O=F-F_0=\alpha P^2+\tfrac{1}{4}(\beta_1+\beta_2)P^4+\tfrac{1}{12}\gamma_1P^6\ ,\qquad$ (6b)

$(P_z=P_y\neq 0,\quad P_x=0)$

trigonal $\qquad \phi_R=F-F_0=\alpha P^6+\tfrac{1}{6}(\beta_1+2\beta_2)P^4+\tfrac{1}{27}\gamma_1P^6\ .\qquad$ (6c)

$(P_x=P_y=P_z\neq 0)$

In Eq. (5) we assume that only α is temperature dependent, although in principle, all the coefficients may be concentration dependent.

It is more convenient to work with reduced variables, and we divide the three equations (6a), (6b), and (6c) by $\alpha_{t0}P_{t0}^2$, where $\alpha_{t0}(P_{t0})$ is the value of $\alpha(P)$ at the transition temperature T_t for the pure sample $(x=0)$. With

$$a=\frac{\alpha}{\alpha_{t0}}\ ,\quad p=\frac{P}{P_{t0}}\ ,\quad \varphi=\frac{\phi}{\alpha_{t0}P_{t0}^2}\ ,$$

Eqs. (6) become

$$\varphi_T = ap^2 + 2\frac{\beta_1}{|\beta_{10}|}p^4 + \frac{\gamma_1}{\gamma_{10}}p^6\ , \tag{7a}$$

$$\varphi_O = ap^2 + \frac{\beta_1+\beta_2}{|\beta_{10}|}p^4 + \frac{1}{4}\frac{\gamma_1}{\gamma_{10}}p^6\ , \tag{7b}$$

$$\varphi_R = ap^2 + \frac{2}{3}\frac{\beta_1+2\beta_2}{|\beta_{10}|}p^4 + \frac{1}{9}\frac{\gamma_1}{\gamma_{10}}p^6\ . \tag{7c}$$

In Eq. (7) β_{10} is the value of β_1 for $x=0$. We now calculate the phase diagram under the assumption that only two parameters are variable: $a(T,x)$ and $\beta_1(x)$. We fix the ratio $\beta_2/|\beta_{10}|=q$ and suppose that $\gamma_1=\gamma_{10}$. Equations (7) become

$$\varphi_T = ap^2 + 2bp^4 + p^6\ , \tag{8a}$$

$$\varphi_O = ap^2 + (b+q)p^4 + \tfrac{1}{4}p^6\ , \tag{8b}$$

$$\varphi_R = ap^2 + \tfrac{2}{3}(b+2q) + \tfrac{1}{9}p^6\ , \tag{8c}$$

where

$$b(x) = \beta_1(x)/|\beta_{10}|\ .$$

Devonshire[12] has calculated the ratio $\beta_2/|\beta_{10}|$ for pure $BaTiO_3$. We adopt his value of $q=1.2$, assuming that it is independent of x. Varying a and b, we can calculate which of the three phases has the lowest free energy. The free energy is determined by introducing into Eq. (8) the value of p given by $(\partial\phi/\partial p)=0$. This gives the phase diagram in the plane (a,b). For getting it in the plane (x,T) we have to choose the functions $a(T,x)$ and $b(x)$, but the topology will not be changed. In Fig. 5, we show the results. The important points are that for $b=0$, the cubic-tetragonal transition is a tricritical point, and that the three transition lines converge. With numerical computation we cannot determine this convergence exactly, but even if it is not exact the intersection points of the three lines must be very close to each other. The topology of the calculated diagram is the same as that determined experimentally (see Fig. 5). This convergence point is a little surprising since it contradicts the Gibbs rule which states that in a system with two parameters more than three phases cannot be in equilibrium. We repeated the calculation with another value of the ratio $q=\beta_2/|\beta_{10}|$, with $q=0.7$. We found essentially the same results [Fig. 5(b)]. It is possible that the Gibbs rule is not applicable because one of the transitions (cubic-ferroelectric, either tetragonal or trigonal) is of second order around the convergence point.

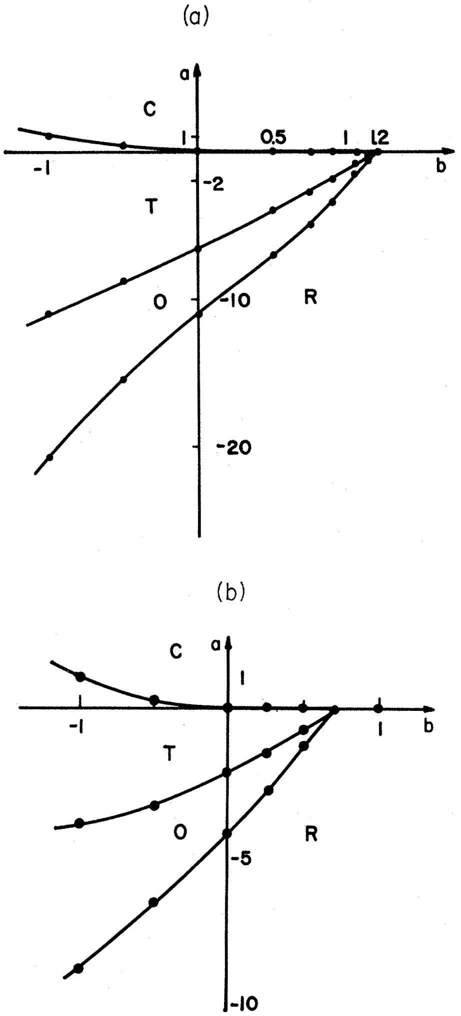

FIG. 5. Calculated phase diagram, from Eq. (8) for (a) $\beta_2/|\beta_{10}|=1.2$, (b) $\beta_2/|\beta_{10}|=0.7$.

C. Speculations

A question of interest is what coupling gives rise to the tricritical point. In $BaTiO_3$, as mentioned in the Introduction, two other cases of tricritical points are known; one was found by application of pressure[1] and another in solid solutions of $Ba_{1-x}Sr_xTiO_3$.[5] In both cases the volume decreases (if p or x increases) and the phase diagrams are similar. One can think that by decreasing the distance between the ions the elastic and/or the electrostrictive constants are modified in such a way that a change in the order of the transition appears.[13] However, in the actual case, we have verified that the cell volume increases with x. This means that addition of Co increases the distance between the ions. Thus we think that we have a new situation which cannot be explained by modification of the elastic (and/or electrostrictive) constants arising from a decreasing cell volume.

It has been suggested[14] that the phonon instability which drives the ferroelectric transition of $BaTiO_3$ has its origin in the coupling with the valence-band electrons. Recently Hidaka[15] used this argument in order to explain the decrease of the transition temperature with increasing percentage Co and Fe. It is well known that the electronic properties are strongly affected in Co- and Fe-doped $BaTiO_3$ crystals.[16] It was shown that the photoconductivity can be explained by the introduction of two levels in the band gap, and that Co-doped $BaTiO_3$ is an n-type semiconductor with a large gap. Thus it is possible that by increasing the amount of Co, one can modify the interaction strength of the electron-phonon coupling, resulting in a change in the order of the transition. This type of explanation has been already given by Clarke[7] for the solid solution Te(Sn,Ge).

In $BaTiO_3$, theoretical models give a second-order transition at constant volume. This was also noted a long time ago by Devonshire[12] on the basis of experimental evidence. Thus, the first-order transition in $BaTiO_3$ has been explained by a coupling of the polarization with the strain. It may be that the situation is more complex and we have to introduce both electron-phonon and acoustic-optical-phonon coupling.

IV. CONCLUSION

Although we have not directly observed the tricritical point in Co-doped $BaTiO_3$, we think that the experimental evidence supporting its existence is very strong. The calculation of the fourth-order coefficient β_1 in the free-energy expansion shows that this coefficient goes to zero for $x \approx 2.2$ at.%. We also showed that the topology of the phase diagram is easily explained, taking this coefficient β_1 increasing from a negative value ($x = 0$ at.%) to a positive value. All these facts offer strong support for the existence of the tricritical point. The explanation likely involves a coupling with the valence-band electrons rather than the strain.

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