Suppression of ferroelectricity in TMA-$ZnCl_4$ crystals by a low stress

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It has been observed that a slight uniaxial compressional stress causes the spontaneous polarization to disappear in tetrachlorozincate-tetramethylammonium crystals. The effect is reversible and is associated with the proximity of the state of the crystal to the critical point on the stress-temperature phase diagram.

We know that the piezoelectric effect allows stresses to actively influence the state and physical properties of ferroelectrics: By selecting a component of the stress tensor which is related in a linear fashion to the polarization one can switch a crystal from a nonpolar state to a polar state, from a polydomain state to a single-domain state, and back. In the process, one can achieve a maximum change in dielectric properties.[1]

In this letter we are reporting the results of an observation of a giant change in the dielectric properties upon the application of a uniaxial stress. The ultimate result of this effect is a reversible disappearance of ferroelectricity in the crystal, in contrast with the situation concerning the ordinary piezoelectric effect.

The test sample was a crystal of tetrachlorozincate-tetramethylammonium, $\{N(CH_3)_4\}ZnCl_4(\text{TMA-}ZnCl_4)$, which has five structural phase transitions: $Pmcn$ $(D^{16}_{2h})\rightarrow$incommensurate phase)$\rightarrow P2_1cn(C^9_{2v})\rightarrow P112_1/n(C^5_{2h})\rightarrow P12_1/c1(C^5_{2h})$ $\rightarrow P2_12_12_1(D^4_2)$ at $+20°$, $+6.6°$, $+3.3°$, $-92°$, and $-112\,°C$, respectively. In the one ferroelectric phase, $C^9{}_{2v}$, the spontaneous polarization is directed along the $a(X)$ axis. The cell parameter along the $c(Z)$ axis is five times that in the original high-temperature phase,[2] D^{16}_{2h}. Hydrostatic compression at $p\geqslant 1000$ bar erases the polar phase.[2]

The experiments were carried out on a single crystal growth from solution. The samples were rectangular bars with dimensions of $2.5\times 2.8\times 5$ mm. The edges of the samples were oriented along the X, Y, and Z crystallographic axes of the orthorhombic cell of the high-temperature phase. Electrodes were deposited from a silver paste on the faces of the samples oriented perpendicular to the $a(X)$ polar axis. The dielectric constant ε_a was measured at a frequency of 1.6 kHz with the help of a standard capacitance bridge; the spontaneous polarization P_s was determined from the dielectric hysteresis loops on a plot of the polarization P_a versus the electric field E_a at a frequency of 50 Hz (Ref. 1).

A stress σ_{zz}, compression or tension, along the Z axis has an anomalous effect on the dielectric properties and structural transitions to the polar phase (this direction is that of the quintupling of the cell in the polar phase or of a modulation of the structure

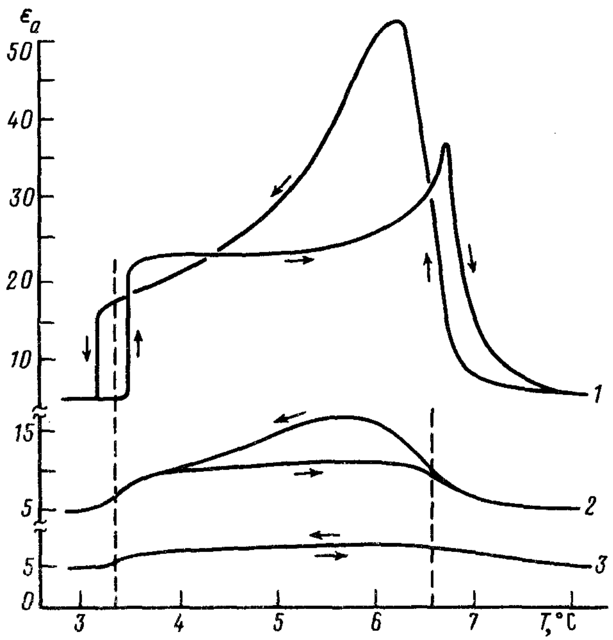

FIG. 1. Temperature dependence of the dielectric constant ϵ_a of a TMA-$ZnCl_4$ crystal at various compressional stresses σ_{zz}. 1—$\sigma_{zz} = 0$; 2—20; 3—40 kgf/cm^2.

in the incommensurate phase). Figure 1 shows the temperature dependence of ε_a near both transitions to the ferroelectric phase for various values of the compressional stress σ_{zz}. An increase in σ_{zz} causes the following changes: The value of ε_a decreases sharply over the entire ferroelectric temperature interval, as do the values of the thermal hysteresis and the jumps in ε_a at the transition points (the first-order phase transitions become continuous). The anomalies in ε_a at the transition points do not disappear, however, and inflection points appear in place of the jumps on the temperature dependence of ε_a. These inflection points move slightly toward each other along the temperature scale as σ_{zz} is increased further. The dielectric-hysteresis loop also undergoes a substantial transformation with increasing σ_{zz} (Fig. 2a): Its amplitude and width decrease gradually, and at $\sigma_{zz} > 20$ kgf/cm^2 the loop essentially degenerates into a straight line; i.e., the spontaneous polarization disappears (Fig. 2, a and b).

The changes in the dielectric properties are reversible: When the stress σ_{zz} is removed, all the dielectric characteristics recover their previous values essentially completely (within 10%). The time scale of this relaxation to the equilibrium values does not exceed 1 s.

The temperature region in which P_s exists (the ferroelectric phase) shrinks more rapidly than the interval between the anomalies in ε_a as the crystal is compressed (Figs. 1 and 2c). The part of the σ_{zz}, T phase diagram constructed from the data on the temperature anomalies in ε_a and the temperature points at which P_s vanishes thus

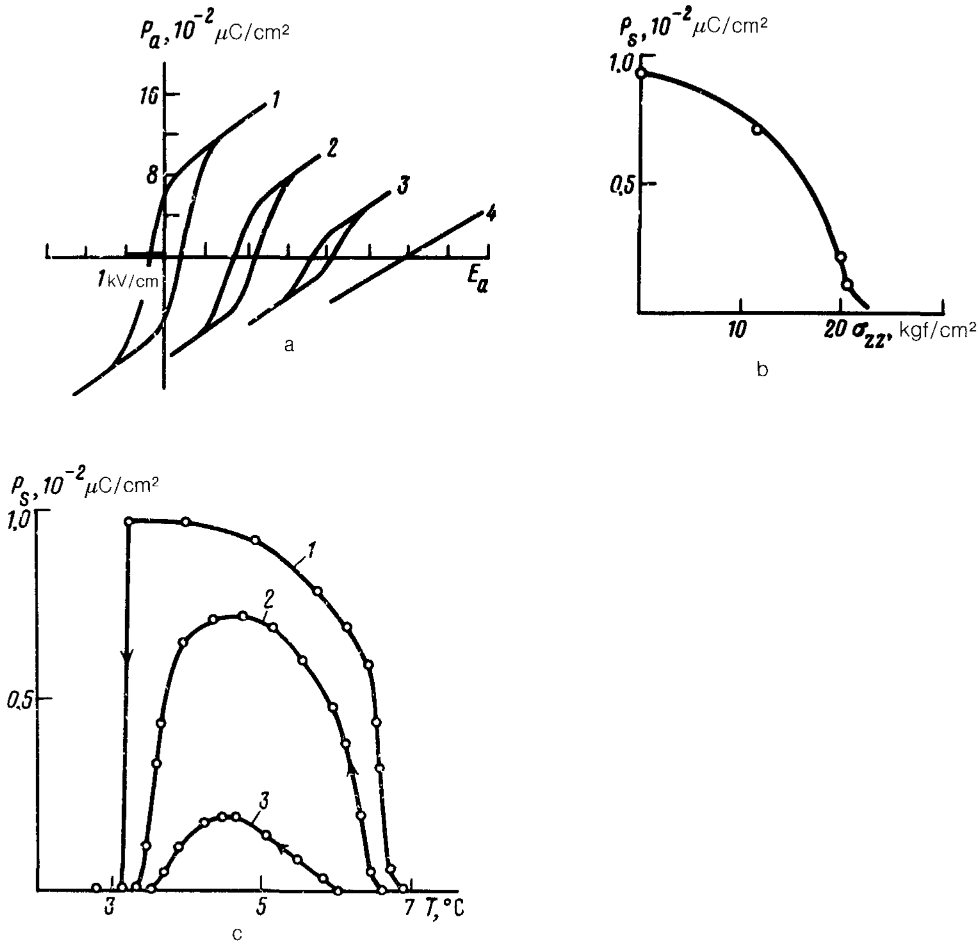

FIG. 2. Several properties of TMA-$ZnCl_4$ crystals at various compressional stresses σ_{zz}. a: Dieletric-hysteresis loop on the plot of the polarization P_a versus the electric field E_a. b: Spontaneous polarization P_s at + 5 °C. Temperature dependence of P_s. 1—$\sigma_{zz} = 0$; 2—10; 3—20; 4—30 kgf/cm^2. The measurements were taken after the crystal was cooled to the given temperature.

has some additional branches, which tend to join as σ_{zz} is increased, roughly at the center of the temperature interval which we studied (Fig. 3). A point which remains unclear is just which passes are realized in the crystal between the two anomalies in ε_a (which are extremely faint) after the polar phase has been suppressed by the stress σ_{zz}.

During hydrostatic compression of the crystal, one branch of the p, T phase diagram, bordering the polar phase, appears only at a pressure $p \neq 0$ (Ref. 2), as in our case in Fig. 3. In each case, the first step is evidently the splitting of a phase into two or three phases, respectively, at nonzero values $p \neq 0$ and $\sigma_{zz} \neq 0$; later, at higher values of p and σ_{zz}, the polar phase disappears completely.

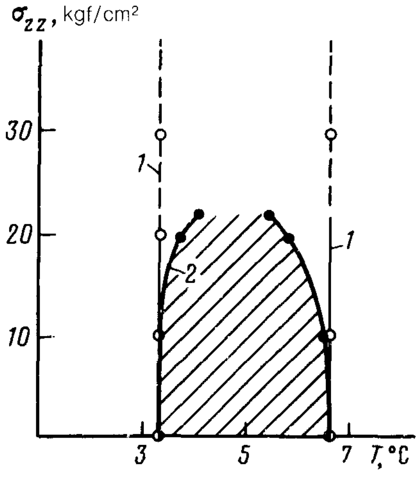

FIG. 3. Phase diagram of the stress σ_{zz} versus the temperature T of a TMA-$ZnCl_4$ crystal according to measurements of (1) the dielectric constant ε_a and (2) the spontaneous polarization P_s. The hatching shows the region of the polar phase. The measurements at each temperature point were carried out after the crystal was cooled.

A stress σ_{zz} and a hydrostatic pressure p do not change the symmetry of the crystal in either its original *Pmcn* high-temperature phase or its $P2_1cn$ polar phase. These are invariant quantities. Consequently, in accordance with the group-theory analysis of Ref. 3, the coefficients of the invariant combinations of the various quantities in the thermodynamic potential which describes the entire sequence of phase transitions in the crystal may depend on σ_{zz}. The fact that the polar phase is unstable with respect to small values of σ_{zz} is evidence that the state of the crystal is close to the critical point on the σ_{zz}, T phase diagram. The lines of three different phases meet at this point.

Note the extremely large changes in the dielectric characteristics of the crystal over the entire interval in which the polar phase exists during compression by a comparatively low stress. For example, a stress $\sigma_{zz} = 20$ kgf/cm^2 reduces ε_a by a factor of ten (Fig. 1) and causes P_s to change from 0.01 μC/cm^2 to essentially zero (Fig. 2b). The coefficients which determine the (average) sensitivity to the stress are $K_\epsilon = (\Delta\epsilon/\epsilon)/\sigma_{zz} \approx 0.5$ cm^2/kgr and $D = \Delta P_s/\sigma_{zz} = 5\times10^{-4}$ μC/kgf $= 2\times10^{-6}$ esu. The coefficient D is approximately equal in magnitude to the piezoelectric coefficient d of many ferroelectrics.[1]

It would be interesting to attempt to observe a corresponding effect in other crystals which exhibit a sequence of several phase transitions. The number of such crystals, whose lattices easily lose stability with respect to various distortions, is now fairly large.

We wish to thank Sh. Savada for furnishing the crystals used in this study.

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Translated by Dave Parsons