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# Damage to TGS crystals caused by hydrostatic pressure

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In this letter we address a particular aspect of the finite size effect on ferroelectric instability: the polarization suppression under high hydrostatic pressure. We have shown that in TGS ($[NH_3^+CH_2COOH)_2(NH_3^+CH_2COO^-)SO_4^{2-}]$) single crystals under high pressure the critical temperature $T_C$ of ferroelectric –paraelectric phase transition grows monotonically up to about 1.8 GPa. Above the critical pressure $p_C \geq 2.4$ GPa, the ferroelectricity disappears and the coefficient $\gamma$ becomes negative for small ferroelectric regions which appear due to crystal break up.

Key words: *TGS crystal; ferroelectric instability; crystal braek-up*

## 1. Introduction

The investigation of finite-size effects on ferroelectricity is an interesting problem from both a scientific viewpoint as well as for practical reasons. The reduction in the physical sizes of ferroelectrics, from the macroscopic regimes down to mesoscopic ones results in a change in the polarization stability [1, 2]. Small ferroelectric particles exhibit dielectric properties different from those of bulk crystals, because the Coulomb long-range force plays a crucial role in them. For ferroelectrics of perovskite structure, it has been shown experimentally [3] that there is a critical crystal dimension $D$ above which finite-size effects disappear. We have also shown that crystal damage under high hydrostatic pressure leads to finite-size dielectric properties.

## 2. Experimental and results

The effect of hydrostatic pressure was measured in a standard three-layer steel vessel [4, 5] up to the pressures of 3 GPa. Our data show that up to $p$ = 1 GPa the critical temperature $T_C$ increases linearly with pressure in accordance with the relation:

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$$T_c(p) = T_c^0(1 + \gamma p) \tag{1}$$

The change in the value of spontaneous polarization is equal to

$$\Delta P_S = P_S^P - P_S^{T_c}$$

where $P_S^P$ and $P_S^{T_c}$ are the values of spontaneous polarization obtained at given $p$ values and resulting from a change in $\Delta T_C$ (Fig. 1).

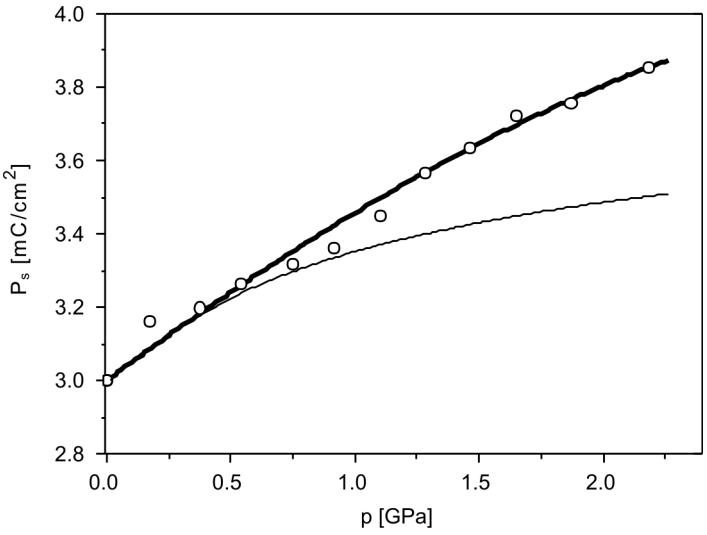


Fig. 1. Pressure dependence of the spontaneous polarization $P_s$ (bold line) and $P_s$ value only from $T_C$ change (thin line)

The $\Delta P_S$ value results from additional tilting of glycine I (GI) from the *ac* crystal plane. This tilt comes from a slowing down of the rotation frequency of the $NH_3$ group in a double-well potential [6, 7].

Ferroelectricity appears when both potential minima are nonequivalent. High hydrostatic pressure leads to a rising potential barrier $\Delta U$ between the two minima. The monotonic growths of $P_S$ and $E_C$ values were recorded up to the pressure of 2.1 GPa. Below this p value all results were reproducible for a good sample quality. Above the pressure of 2.1 GPa, the samples started to be "milk-white" because pressure liquid penetrates and destroys single crystals having nanometric dimensions.. This mechanism explains recent results by Kobayashi et al. [5] for the sign change in the coefficient $\gamma = dT_C/dp$ at high pressure.

The dependence of $T_C$ on pressure for a non-distorted crystal structure is shown in Fig. 2 and the shift of $T_C$ can be described by linear and quadratic pressure dependences up to about 1.8 GPa ($T_C$ in K, $p$ in GPa)

$$T_C(p) = 322 + 22.5p - 1.73p^2 \tag{2}$$

The $\gamma(p)$ value in the range from 0 to 1 GPa is constant. For $p \geq 1$ GPa, $T_C(p)$ shows a nonlinear behaviour. Above 1.5 GPa, the observed plateau in the $T_C(p)$ profile is a signature of the damage process in TGS crystal due to the penetration of liquid into the crystal structure: for pressures up to 2.1 GPa this process is reversible.

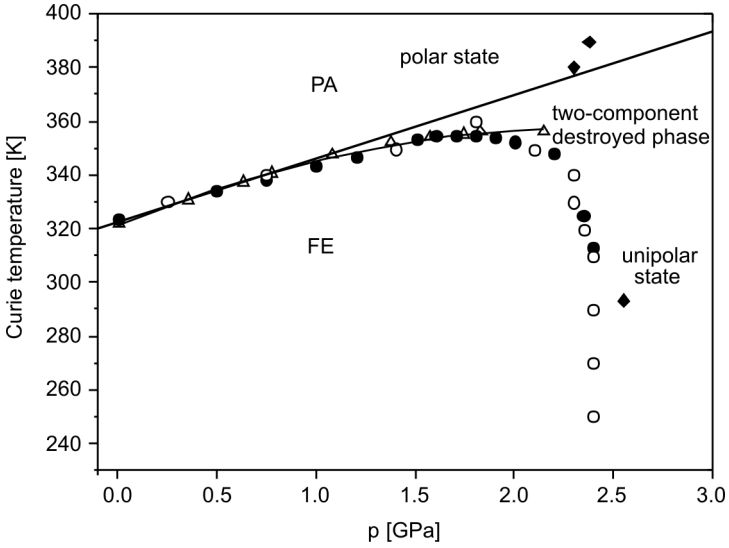


Fig. 2. The ferroelectric phase transition temperature $T_C$ obtained under various pressure–temperature conditions: filled circles – $p$ = const [5], open circles – $T$ = const [5], triangles – $T$ = const [4], diamonds – $T$ = const > $T_c^0$ [5]

Upon approaching the critical pressure $p_C = 2.4$ GPa, the crystal damage process becomes of the avalanche type. Samples form a two component system, and dimension of the crystalline regions decreases with time. This confirms the data of Kobayashi et al. [5], namely that above some pressure, $T_c^{\max}(p)$, the $\gamma$ coefficient changes its sign from $\gamma > 0$ at ferroelectric phase to $\gamma < 0$.

The destruction of the sample above the $p_C$ value, where pressure liquid penetrating inside the crystal diminishes dipole–dipole interaction between GI molecules, is responsible for spontaneous polarization. The value of the Curie–Weiss constant $C = \mu^2 N/3$ is diminished. A similar effect in a distorted crystal has been observed for irradiated TGS crystals [8]. X-irradiation leads to disintegration of ferroelectric crystals into regions of the order of 100 Å and a decrease of $T_C$. In our experiments [4, 5] crystal disintegration on small regions of the order of nanometers leads to a decrease in $T_C$. The transition under $p_C \geq 2.4$ GPa does not depend on dielectric dipole ordering but reveals a transition to an amorphic mixture of pressure liquid and nanosized TGS particles.

Kobayashi et al. data [5] show that, starting from the ferroelectric phase ($T < T_C$), high pressure can transfer ferrolectric order to higher temperatures. Conversely, for

$T > T_C$ high pressure leads to nonferroelectric phase transition at $p_C$ (Fig. 2). In accordance with the theoretical data of Shaoping et al. [10], the limitation of critical size is strongly correlated with the dimension along the spontaneous polarization direction. Relatively stronger dipole–dipole interaction leads to the formation of long dipole chains. In TGS crystals with lamelar structure at RT [6], it is strongly expected that, above a critical pressure, the TGS system changes its dimensionality.

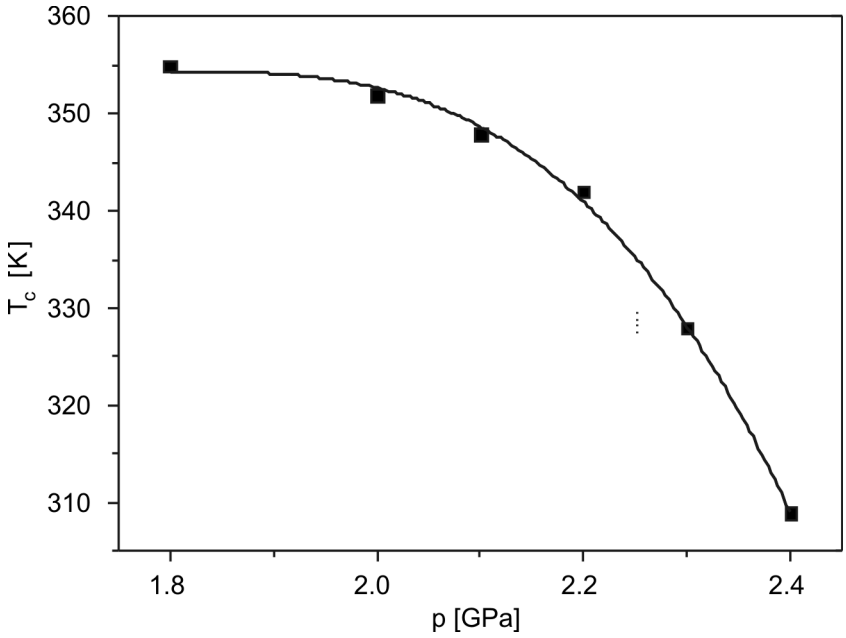


Fig. 3. $T_C(p)$ dependence above critical pressure of 1.8 GPa:
squares – experimental values, solid line –fitting curve in accord with Eq. (3)

In Figure 3, the behaviour of $T_C(p)$ for $T_C^{\max}(p) = 355$ K and $p_C = 1.8$ GPa is described by the equation:

$$T_C(p) = T_C^{\max}\left(1 - A\left(\frac{p - p_C}{p_C}\right)^{1/n}\right) \tag{3}$$

The best fit is found for $n = 0.33$ which may suggest the occurrence of a 3D–2D transition.

## 3. Discussion

Based on the high pressure results of Stankowski et al. [4] and Kobayashi et al. [5] it is evident that at $p_C \approx 2.4$ GPa ionic TGS crystal, with molecular dynamics driven

by $NH_3$ rotation groups and flipping of GI molecules, experiences a structural phase transition which consists in breaking up of ordered ferroelectric phase in amorphous pressure liquid with the unit size volume to be proportional to $p - p_C$. Because of the γ-coefficient anisotropy $\left(\gamma_{\|} \approx 1.9\ \mathrm{K{\cdot}GPa^{-1}}, \nu_{\perp} = 0.8\ \mathrm{K{\cdot}GPa^{-1}}\right)$ with an axial symmetry: $1 - \cos^2 Q$ ($Q$ is the tilt angle of GI) the unit cell catastrophe may be reached by two ways:

- ferroelectric units preserve their own anisotropy and the $T_C$ temperature depends linearly on pressure up to critical value $p_C$,
- ordered areas under high-pressure lose their own anisotropy, and above $p = 2.1$ GPa the $T_C$ value is suppressed monotonically versus $p$, and dimensional effects are dominant: $T_C \propto d^{-1}$[9].

Destruction of the crystal structure essentially depends on ferroelectric dipole –dipole interactions near a "structural catastrophe" of the TGS structure and an anisotropy of unit cell compressibility.

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