

EFFECT OF HYDROSTATIC PRESSURE ON THE POLARIZATION SWITCHING PROCESS IN ALUMINIUM-GUANIDINE SULPHATE HEXAHYDRATE SINGLE CRYSTAL (GASH)

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Maximum polarization switching current i_m and polarization switching time t_s were measured at various values (up to 5 kbar) of hydrostatic pressure, applied to GASH single crystal at room temperature. i_m and t_s are found to decrease with growing pressure. The exponential laws $i_m = i_\infty \exp \left[-\frac{\alpha}{E} \right]$ and $t_s = t_\infty \exp \left[\frac{\alpha}{E} \right]$ are obeyed in the entire range of pressures applied. The activation field α grows linearly, $\left[\frac{1}{\alpha} \frac{\partial \alpha}{\partial p} \right]_{p=0} = 9 \cdot 10^{-5} \text{ bar}^{-1}$, with growing pressure. Evaluation of the domain wall energy in GASH single crystal at normal conditions performed with reference to Miller's [11] ferroelectric domain wall model and the work of Merz [10] yielded a result of about 17 erg/cm². Also, the change in domain wall energy under the influence of hydrostatic pressure is calculated.

1. Introduction

The dielectric properties of GASH have been studied by Holden [1, 2], Merz [3, 4], Wieder [6], and Prutton [7, 8]. This strong interest in GASH is due to the fact that its properties differ from those of other ferroelectrics. The behaviour of GASH under high hydrostatic pressure was investigated by Merz [3, 4] and Klimowski [5]. Merz studied the spontaneous polarization P_s as a function of hydrostatic pressure up to 5 kbar at room temperature. Ref. [5] contains results on the changes in P_s and coercive force caused by high hydrostatic pressure at various temperatures. As yet, no results are available concerning the energy of 180°-domain walls in GASH single crystals. The present paper permits the assessment of their energy at normal conditions as well as the change in their energy due to hydrostatic pressure at room temperature.

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2. Experimental

We used samples cut from GASH single crystal in a manner to obtain rectangular hysteresis loops. The samples had a surface area of $S = 0.040 \div 0.055 \text{ cm}^2$ and a thickness of $d = 0.020 \div 0.035 \text{ cm}$. The surface were coated with silver paste electrodes. The sample was then processed thermoelectrically (rejuvenated) by heating for 2 hrs at 70° C in a 50 Hz electric field of intensity higher than the coercive force.

Observation of the current and time of polarization switching was performed with a rectangular pulse generator of maximum voltage amplitude 150 V and frequency about 0.7 kHz. The growth time of the pulse was of the order of 0.5 μs .

The device for producing hydrostatic pressure as proposed by Klimowski [9] consisted of a pressure multiplier with difference piston, conveying high pressure to a cavity filled with paraffin in which the sample was placed. The pressure within was measured by means of a scaled manganine sensor.

3. Results of measurements

The effect of hydrostatic pressure on the maximum polarization switching current i_{max} and polarization switching time t_s in GASH single crystals was measured at room temperature. From our measurements, the polarization switching process in GASH takes place in two steps, similarly to that observed by Merz [3] in BaTiO_3 single crystals.

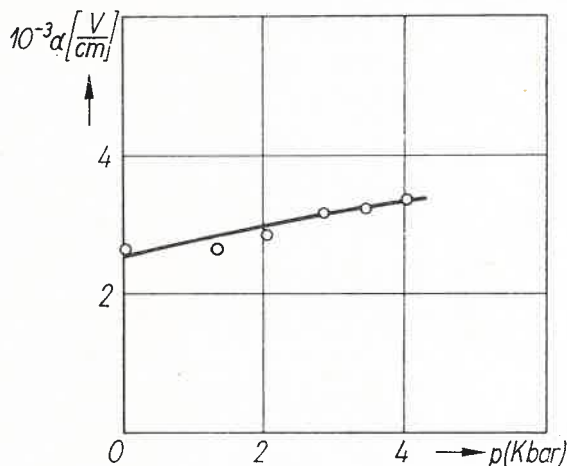


Fig. 1. Activation field α versus the hydrostatic pressure applied to GASH single crystal

The process is described by an exponential dependence of i_{max} on the electric field strength E :

$$i_{\text{max}} = i_{\infty} \exp(-\alpha/E),$$

where: i_{∞} is the maximal polarization switching current in an infinitely strong field;

α is a constant, dependent on temperature, pressure and the thickness of the sample referred to as the activation field.

Our measurements show that the shape of $i_{\max}(E)$ remains unaffected by external hydrostatic pressure, whereas the current decreases with growing pressure.

From the experimental results, we determined the activation field as a function of the pressure (Fig. 1). The activation field was found to increase with growing pressure as

$$\left[\frac{1}{\alpha} \frac{\partial \alpha}{\partial p} \right]_{p=0} = 9 \cdot 10^{-5} \text{ bar}^{-1}.$$

4. Evaluation of the 180°-domain wall energy

Hydrostatic pressure, when applied to crystals in the ferroelectric phase, can cause changes in nucleation and in motion of domain walls. The shape of the polarization switching current remains unchanged by pressure. This points to stability of the nucleation, and domain wall mobility alone is presumably affected.

Let us confront our experimental results with the Miller-Weinreich [11] model of 180°-domain wall. The MW theory assumes domain wall motion to be related with nucleation and growth of new domains on the edge of a wall. According to their theory, the activation field α at varying wall energy σ_w per cm^2 behaves as:

$$\alpha \sim \sigma_w^{3/2}. \quad (1)$$

The energy of a 180°-domain wall in GASH single crystal per unit surface area, σ_w , can be expressed as a function of the spontaneous polarization as follows:

$$\sigma_w = \sum_{i=1}^{\infty} a_i [P_s^m]^i, \quad (2)$$

where m is a constant.

On restricting ourselves, in a first approximation, to the first term of the expansion, we have:

$$\sigma_w \sim P_s^m. \quad (3)$$

By Eqs (1) and (3) and on assuming that the hydrostatic pressure p affects the preceding quantities, we obtain:

$$\frac{1}{\alpha} \frac{\partial \alpha}{\partial p} = \frac{3}{2} m \frac{1}{P_s} \frac{\partial P_s}{\partial p}. \quad (4)$$

On inserting into (4) the experimental values:

$$\left[\frac{1}{\alpha} \frac{\partial \alpha}{\partial p} \right]_{p=0} = 9 \cdot 10^{-11} \text{ cm}^2/\text{dyne} \text{ (our present results),}$$

$$\left[\frac{1}{P_s} \frac{\partial P_s}{\partial p} \right]_{p=0} = 16.9 \cdot 10^{-11} \text{ cm}^2/\text{dyne} \text{ (result of Ref. [5]),}$$

we obtain a value of $m = 0.35$.

With regard to (3), and on taking the derivative with respect to pressure, we obtain the following equation:

$$\frac{1}{\sigma_w} \frac{\partial \sigma_w}{\partial p} = m \frac{1}{P_s} \frac{\partial P_s}{\partial p}, \quad (5)$$

which can be re-written as follows:

$$\frac{\partial \sigma_w}{\partial p} = m \gamma \sigma_{w0} \quad (6)$$

with σ_{w0} denoting the domain wall energy per unit area unacted on by pressure; $\gamma = \frac{1}{P_{0s}} \frac{\partial P_s}{\partial p}$; P_{0s} is the polarization at normal conditions.

A solution of (6) is provided by the following expression:

$$\sigma_w = \sigma_{w0} + m \gamma \sigma_{w0} p, \quad (7)$$

which holds in the entire range of pressures applied.

A relevant model of the domain wall of a ferroelectric has been proposed for Rochelle Salt by Mitsui and Furuichi [12]. They assume that the polarization value varies within the wall. Merz [10], on the model adapted to barium titanate, made an assessment of the energy density of a "c" domain wall (*i.e.* one between domains of antiparallel polarization). According to the above authors, the change in polarization is related with distortions due to electrostriction, which one has to take into account when calculating the energy and thickness of a wall. The energy density of the wall can be expressed as follows:

$$\sigma_w = \sigma_{\text{dip}} + \sigma_{\text{dis}}, \quad (8)$$

with: σ_{dip} the energy of a wall per unit area due to dipole interaction; σ_{dis} the energy of a wall per unit area due to distortion.

The interaction energy σ_{dip} of the dipoles forming the wall is, after Merz [10]:

$$\sigma_{\text{dip}} = \frac{10^{-14}}{Na^2} \left[\frac{\text{erg}}{\text{cm}^2} \right], \quad (9)$$

where N is the wall thickness in units of the lattice constant a .

The elastic energy of the wall on distortion of the elementary cell is:

$$\sigma_{\text{dis}} = \frac{1}{2} c_{33} \varepsilon_c^2 Na, \quad (10)$$

with: c_{33} the elastic coefficient, and ε_c the total strain due to electrostrictive distortion and hydrostatic pressure-induced distortion.

The total strain can be expressed by writing:

$$\varepsilon_c = z + \varepsilon_3, \quad (11)$$

where z and ε_3 are, respectively, the strain due to electrostriction and pressure.

In Eq. (10), only the coefficient c_{33} is taken into account since, from the results of Ezhkova [13] and Haussühl [14], GASH single crystals exhibit maximal distortion in the direction of this component.

With regard to Hooke's law, the distortion is of the form:

$$\varepsilon_i = s_{ij}\sigma_j, \quad (12)$$

where $\{s_{ij}\}$ and $\{\sigma_j\}$ are the tensors of elasticity and stress. By (12), and assuming the applied hydrostatic pressure p as the stresses σ_j , we can re-write the total distortion of Eq. (11) as follows:

$$\varepsilon_c = z + sp. \quad (13)$$

On insertion of (9) and (10) into (8), the total energy density of the wall takes the form:

$$\sigma_w = \frac{10^{-14}}{Na^2} + \frac{1}{2} c_{33} \varepsilon_c^2 Na. \quad (14)$$

At thermodynamical equilibrium, the energy σ_w becomes minimum; the necessary condition for this to occur is:

$$\frac{\partial \sigma_w}{\partial N} = \frac{-10^{-14}}{N^2 a^2} + \frac{1}{2} c_{33} \varepsilon_c^2 a = 0. \quad (15)$$

By solving Eq. (15) taking account of (13), we obtain for the thickness of the wall the expression:

$$N = \left\{ \frac{2 \cdot 10^{-14}}{c_{33} a^3} \right\}^{1/2} \frac{1}{z + sp}. \quad (16)$$

On inserting (16) into (14), one obtains the following energy of the wall per unit area, at thermodynamical equilibrium and at a given value of the pressure:

$$\sigma_w = \left\{ \frac{2 \cdot 10^{-14}}{a} c_{33} \right\}^{1/2} z + \left\{ \frac{2 \cdot 10^{-14}}{a} c_{33} \right\}^{1/2} sp. \quad (17)$$

We thus have two formulas, (7) and (17), defining the energy of the wall per unit area whence we determine σ_{w0} and z as follows:

$$\sigma_{w0} = \left\{ \frac{2 \cdot 10^{-14}}{a} c_{33} \right\}^{1/2} \frac{s}{m\gamma}, \quad z = \frac{s}{m\gamma}. \quad (18)$$

Eq. (18), with the following numerical data: $c_{33} = 1.438 \cdot 10^{11}$ dyne/cm², $a = 1.17 \cdot 10^{-7}$ cm, $s = 6.702 \cdot 10^{-12}$ cm²/dyne, $m = 0.35$ and $\gamma = 16.9 \cdot 10^{-11}$ cm²/dyne, yields for the energy of a 180°-wall per unit area in GASH single crystal at normal conditions the value:

$$\sigma_{w0} = 17 \left[\frac{\text{erg}}{\text{cm}^2} \right].$$

The preceding result and Eq. (17) lead to the following expression permitting the calculation of the change in energy of the wall per unit area under the influence of hydrostatic pressure:

$$\sigma_w = 17 + 10^{-9} p \left[\frac{\text{erg}}{\text{cm}^2} \right],$$

where

$$[p] = \left[\frac{\text{dyne}}{\text{cm}^2} \right].$$

5. Summary and conclusions

Our results can be summarized as follows:

a) The process of change in polarization direction in GASH single crystals under the influence of hydrostatic pressure resembles that assumed for and experimentally confirmed in other ferroelectrics. It runs in two steps: 1) formation of new nuclei and their growth, and 2) lateral motion of the domain walls.

b) The hydrostatic pressure dependence of domain wall energy derived by us is linear.

c) The surface density of domain wall energy of GASH single crystal at normal conditions is of the same order as that of 180°-domain walls of BaTiO₃ and TGS single crystals.

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