PHYSICAL PROPERTIES AND STRUCTURE OF FERROELECTRIC – FERROELASTIC DMAAS CRYSTALS

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INTRODUCTION

Recently it has been found [1] that DMAAS crystals

$$[(CH_3)_2NH_2Al(SO_4)_2 \cdot 6H_2O]$$

possess ferroelectric and ferroelastic properties. Single crystals of good quality have been grown by the evaporation method. At room temperature DMAAS crystals are monoclinic; a = 11.819 Å, b = 6.415 Å, c = 10.768 Å, γ = 68.13°, Sp. gr. P112$_1$/a or a_n = 11.152 Å, b_n = 6.415 Å, c_n = 10.768 Å, γ_n = 100.4°, Sp. gr P1̄12$_1$/n [2].

Nearly tricritical second order phase transition takes place at Tc = 150 K with the symmetry change 2/m – m [1]. The transition can be classified as the proper ferroelectric order-disorder type. It has been found [3] that ferroelectric phase transition observed in DMAAS crystals is due to changes in the orientation mobility of sulphate and dimethylamine sublattices. No soft modes were observed in Raman spectra of both phases down to 7 cm^{-1}. Above Tc DMAAS crystals exhibit ferroelastic properties. The geometry of the domain structure and the orientation of the optical indicatrices of domain correspond to the orthorhombic symmetry of the prototype phase (mmm), but the ferroelastic phase transition does not occur up

to the decomposition temperature (358 K). The mechanical hysteresis (stress-strain) loop at room temperature is of a rectangular shape, spontaneous strain is considerable, about 10^{-1}, the coercive stress is 5.10^5 Pa.

It was found [4] that mecanical properties are substantially anisotropic – the crystals showed almost no plastic deformation along the two-fold axis and were rather brittle, whereas in the plane m they showed anomalous plasticity with the yield limit 2.10^5 Pa, the maximum plastic deformation being 5-7%. There are two mechanisms of plastic deformation, the first one is ferroelastic twinning and the second one is gliding. Twinning is reversible, is accompanied by very weak deformation hardening, irreversible deformation due to gliding is characterized by powerful strengthening and jumpwise deformation.

Here in order to understand the behaviour of DMAAS crystals upon deformation we have analyzed changes of the crystal stucture. We have considered crystallographic aspects of twinning and gliding processes and shown new data on dielectric properties of DMAAS crystals.

EXPERIMENTAL

1. *Electric properties*

Figure 1 shows results of dielectric measurements of DMAAS crystals in polar direction [110] at various biasing electric field strength and temperature dependence of tg δ. The dielectric constant was measured using the E7-8 bridge at 1 kHz, the temperature was stabilized with an accuracy of 5.10^{-3} K. As one can see from the figure, the temperature of maximum tg δ is below Tc and equals 110 K. Above Tc the behaviour of ε obeys the Curie-Weiss law both for E = 0 and E ≠ 0, the Curie constant C = (2.2 − 3) · 10^3 K. The data of spontaneous polarization and coercive field obtained using D − E hysteresis loop at 50 Hz are presented in figure 2. According to our measurements, the behaviour of spontaneous polarization and dielectric constant at dc electric field is typical of second-order ferroelectric phase transition. The maximum of tg δ coincides in temperature with an abrupt increase of coercive field due to less mobility of ferroelectric domains.

2. *Polarization microscope observation*

Figure 3 shows changes that occur in the sample upon compression as the load increases. One can see the changes in the specimen shape during
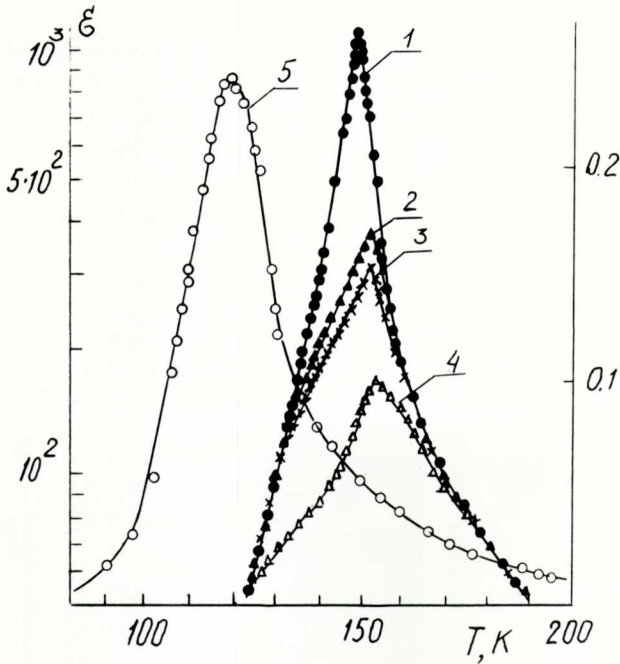
Fig. 1. Temperature dependence of dielectric constant ε at various biasing electric field strength: 1 – 0, 2 – 5, 3 – 15, 4 – 27 kVcm^{-1} and 5 – tg δ of DMAAS crystals.
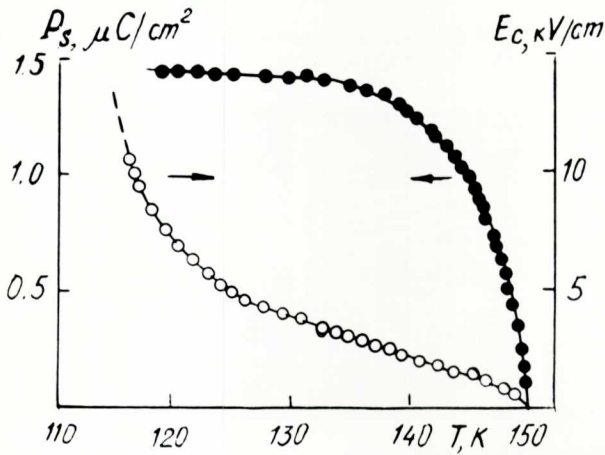

Fig. 2. Temperature dependence of spontaneous polarization and coercive field of DMAAS crystals (50 Hz).

reconstruction of ferroelastic domains under the action of compressive stress. When we stop the compression force the domain picture remains the same and specimen shape is not changed. The observations were made in polarizing microscope on the specimen perpendicular to the two-fold axis.

Feroelastic domain being the reflection twins with the $(\bar{1}10)$ twinning plane, appear and disappear easily under shear strain, that in practice substitutes the compression press strain. The spontaneous deformation tensor U_{ij} should contain two components $-U_{12}$ and U_{21} upon hypothetic phase transition mmm – 2/m. The twinning occurs under the action of shear deformation which can be realized by means of compression or tension along $[\bar{1}30]$ (Sp. gr. $P112_1/a$) or $[\bar{2}10]$ (Sp. gr. $P112_1/n$). Figure 4 shows changes that occur in the sample upon compression as the load increases
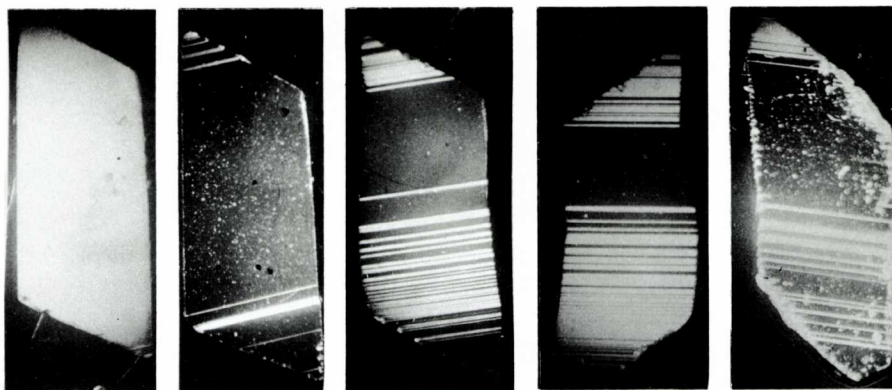

Fig. 3. The change of the ferroelectric domain structure and specimen shape under external mechanical stress (0.2 – 0.6 MPa) at 300 K.
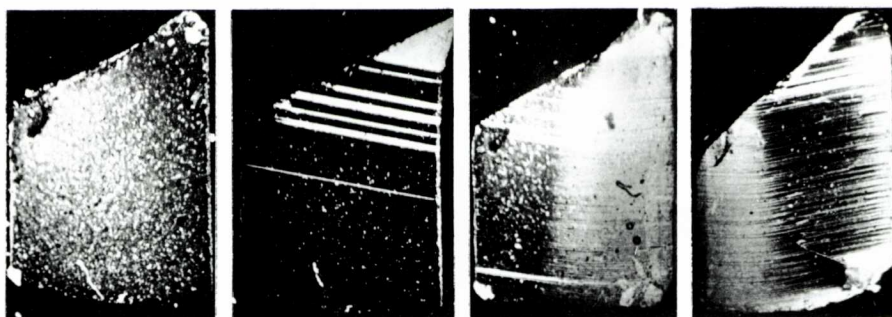

Fig. 4. Photograph in polarized light of a DMAAS crystal deformed by compression along $[\bar{1}30]$ with an increase in load; a, b – deformation by twinning (0.2 – 0.6 MPa), c, d – deformation by gliding (2 – 6 MPa).

from 0.2 to 6 MPa at 300 K. One can readily see that first twins appear (figure 4a, b). If we increase the compression force from 2 to 6 MPa slip bands appear (figure 4c, d). The slip plane is $(\bar{1}11)$, slip direction is [110].

In order to determine twinning elements such as shear plane S, twin shear direction η_1 and crystallographic shear s computations were made according to the program for the determination of twinning elements from structural data. Taking into account lattice constants and the twinning plane orientation found from the experiment it was found by means of special transformation that the shear plane indices S = (001). Twin shear direction was found as a transection line of shear and twinning plane: $\eta_1 = [110]$, crystallographic shear was estimated to be s = 0.27. To illustrate the result of the computation figure 5 presents the arrangement of glide and twin elements in a DMAAS unit cell. The modulus of the Burgers vector [110] was estimated from lattice constants, B = 13.236 A.
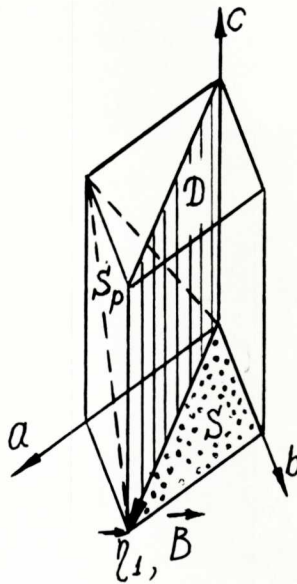

Fig. 5. Arrangement of slip elements (slip plane Sp and Burgers vector B) and twinning elements (twinning plane d, shear plane S and twinning shear direction η_1 in a DMAAS unit cell).

3. Structure investigations

The DMAAS structure is of the ionic type [5], its basis being a framework of hydrogen bonds. The SO_4^{2-} complex anions form almost regular

tetrahedra, six H_2O molecules surround the Al^{3+} ion thus building up $[Al \cdot 6H_2O]^{3+}$ octahedral anionic complexes that are linked with the SO_4^{2-} anionic complex by strong hydrogen bonds $R(O–H \ldots O) = 2.5 – 2.7$ Å. The $[(CH_3)_2NH_2]^+$ cations are located at void channels of this three-dimensional framework.

Figure 6 shows a projection of the shear plane (001) of the DMAAS twin. Solid lines denote the structure before twinning, dotted lines after twinning. Under deformation structural elements are displaced along the $(\bar{1}10)$ twinning plane. A trace of this plane is indicated by a D – D line in figure 6. Besides all almost regular SO_4^{2-} tetrahedra, $[Al \cdot 6H_2O]^{3+}$ octahedra and $[(CH_3)_2NH_2]^+$ linked to them are rotated about [001]. The hydrogen bonding system in this case is hardly distorted, the structure permits the existence of two stable positions.

In case of gliding deformation the displacement of crystal layers relative to one another along the $(\bar{1}11)$ slip plane (its trace is denoted by the S – S line in figure 6) requires larger stresses, because such displacement is accompanied by hydrogen bond rupture and defect formation. This is
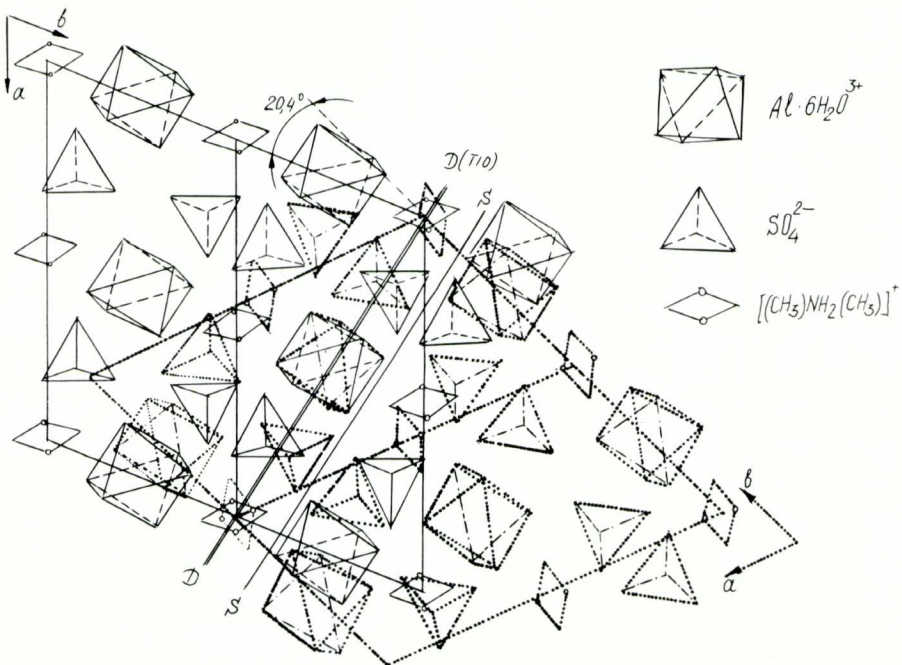

Fig. 6. Projection of DMAAS crystal structure on shear plane (001), D – D – trace of twinning plane $(\bar{1}10)$, S – S – trace of the slip plane $(\bar{1}11)$. Solid lines denote stuctural elements of the original lattice, dashed line – twinning lattice.

seen in figure 7 presenting a projection of the structure onto the (010) plane, where traces of slip S – S and twinning D – D are shown.

A specific feature of the DMAAS structure in the paraelectric phase is complete disorder with respect to the centre of inversion of $[(CH_3)_2NH_2]^+$ group. The ferroelectric phase transition is, apparently, due to order these groups, their drawing near SO_4^{2-} tetrahedra, which results in the formation of noncompensated dipoles and appearance of Ps.
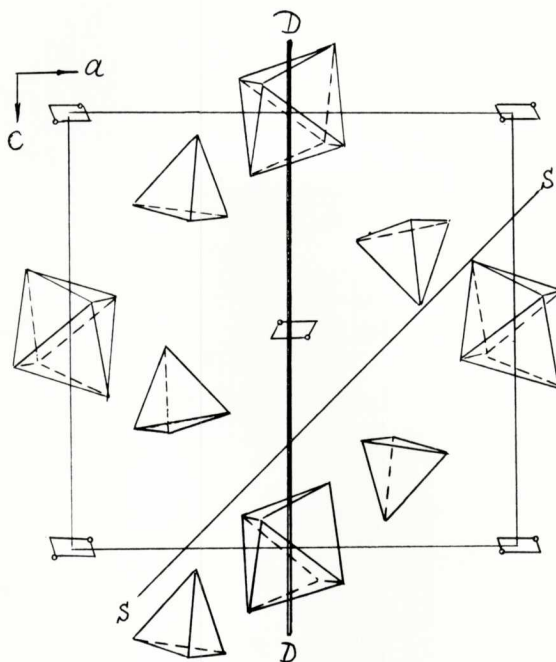

Fig. 7. Projection of DMAAS structure on (010) plane. The traces of the twinning plane – D – D and slip plane S – S are shown.

CONCLUSIONS

1. Upon ferroelectric twinning of DMAAS crystals the twinning plane is ($\bar{1}10$), shear plane S = (001), shear direction η_1 = [110], crystallographic shear s = 0.27.

2. Upon twinning under uniaxial compression perpendicular to the two-fold symmetry axis there occur rotations of almost regular SO_4^{2-} tetrahedra and other structural elements about [001] as well as their displacement along the twinning plane without rupture of the hydrogen bonds.

3. Gliding along the $(\bar{1}11)/[110]$ system is associated with rupture of hydrogen bonds and defect formation which results in a higher flow stress upon gliding as compared to the twinning flow.

4. Ferroelectricity appears due to polar common ordering of $[(CH_3)NH_2]^+$ cations leading to the rotations of SO_4^{2-} tetrahedra and dipole formation.

ABSTRACT

Ferroelectric and ferroelastic properties of new DMAAS crystals are considered. Structural changes upon gliding and twinning as well as the causes of easy processes of twinning and difficulties of gliding are found.

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