

A NEW FERROELECTRIC: GUANIDINIUM URANYL SULFATE TRIHYDRATE

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(Received January 17, 1977)

Dielectric behaviour studies have been carried out on $(\text{C}(\text{NH}_2)_3)_2 \cdot \text{UO}_2 \cdot (\text{SO}_4)_2 \cdot 3\text{H}_2\text{O}$, a member of the family of guanidinium sulfate hydrates. The uranyl compound, which is not isomorphous with G.A.S.H., is ferroelectric from about 100°C (decomposition temperature) down to -30°C , the lowest we have employed. Domain structure and etch-pit configuration are quite similar to those observed in G.A.S.H.

INTRODUCTION

Holden *et al.*^{1,2} discovered that guanidinium aluminium sulfate hexahydrate (G.A.S.H.) is a ferroelectric material, prepared and investigated a series of isomorphous compounds (G.Cr.S.H.; G.Ga.S.H.; G.A.Se.H. and G.Cr.Se.H.) and established that all those compounds show essentially the same properties.

The present paper describes experimental results on the dielectric behaviour and domain structure of guanidinium uranyl sulfate hydrate, obtained as part of a study on the relationship between crystal structure and physical properties of uranyl compounds.

Finally a comparison with the results of G.A.S.H. is given.

EXPERIMENTAL RESULTS

Crystals of guanidinium uranyl sulfate trihydrate, $(\text{C}(\text{NH}_2)_3)_2 \cdot \text{UO}_2 \cdot (\text{SO}_4)_2 \cdot 3\text{H}_2\text{O}$ (G.U.S.H.), were prepared from an aqueous solution of guanidinium sulfate and uranyl sulfate hydrate in the stoichiometric ratio, following the method described by G. Canneri.³ Well-formed crystals were obtained by slow evaporation at room temperature. The transparent, yellow, optically biaxial crystals show two typical habits: prisms elongated along the *b*-axis and thick six-sided plates, tabular on (001), with (101) and (110) present; (111), (100) and (103) are either minor or absent. Cleavage is perfect on (001). Frequently multiple crystals are obtained, with slim, wedge-like included individuals, their tips usually protruding slightly from the host crystal (crystals C, C'

Figure 1). Under crossed polarizers the wedges appear as bright sections when the host crystal is in the extinction position.

Etch pits produced by water were observed on as-grown and cleaved crystals; on (001) and (00 $\bar{1}$) faces the cocked, triangular, irregular pyramids, appear as if related by a centre of symmetry (Figure 2a, b), like the etch figures observed in G.A.S.H. by Holden *et al.*² These etch pits correspond most probably to grown-in dislocations with dislocation lines making an angle with the cleavage face, like the etch pits observed in G.A.S.H. by Nakamura.⁵

Electron micrographs of shadowed replicas of etched crystals (etchant: 1/3 saturated aqueous G.U.S.H. solution, 2/3 water) show the pyramid bases to be scalene triangles, most of them with one curved side

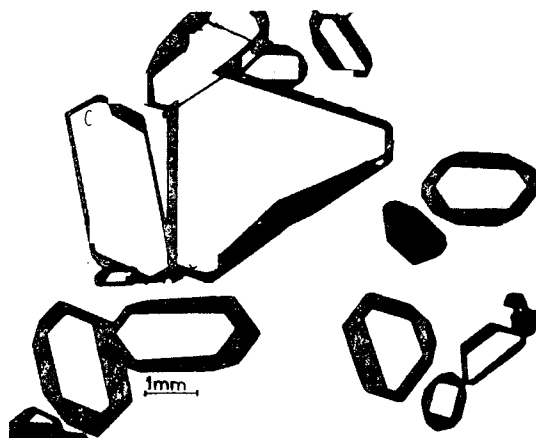


FIGURE 1 Optical micrograph of G.U.S.H. crystals.

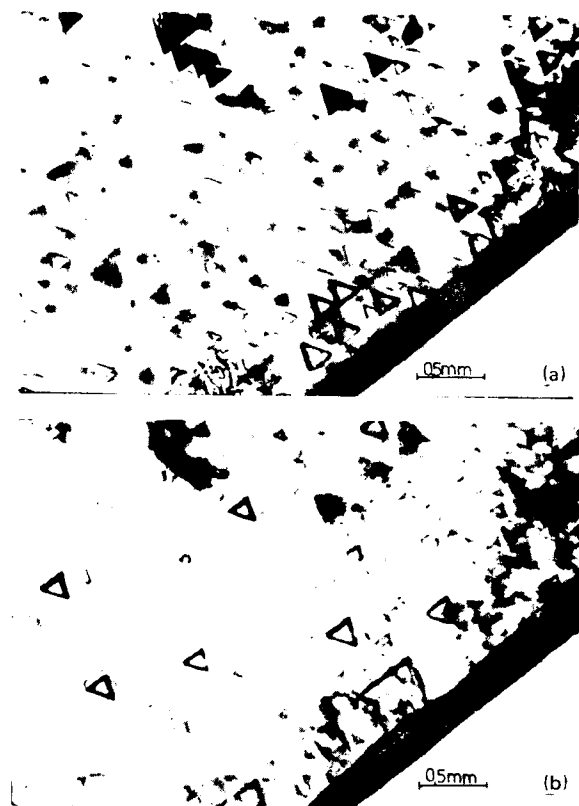


FIGURE 2 Etch pits on the (a) upper and (b) lower cleavage faces of a G.U.S.H. crystal.

and apparently not consistent with monoclinic m or $2/m$ symmetry (Figure 3).

Although Canneri states that guanidinium sulfate hydrate crystallizes with four water molecules, a thermogravimetric analysis performed, under an atmosphere of dry air, shows that it loses 8.3% of its weight between 60 and 100°C (Figure 4). This weight change is in agreement with the theoretical value corresponding to the complete dehydration of the trihydrate. Besides, the structure determination of G.U.S.H. carried out by Baggio *et al.*⁴ also shows the presence of three water molecules.

FERROELECTRIC PROPERTIES

Ferroelectric properties were measured on (001) crystal plates, with an area of about 6 mm² and 2 mm thick. To avoid the possible dehydration of the sample, the crystals were electroded with a gold film, as already described in Benyacar *et al.*⁵ The crystal surfaces were previously corroded with a non-saturated aqueous

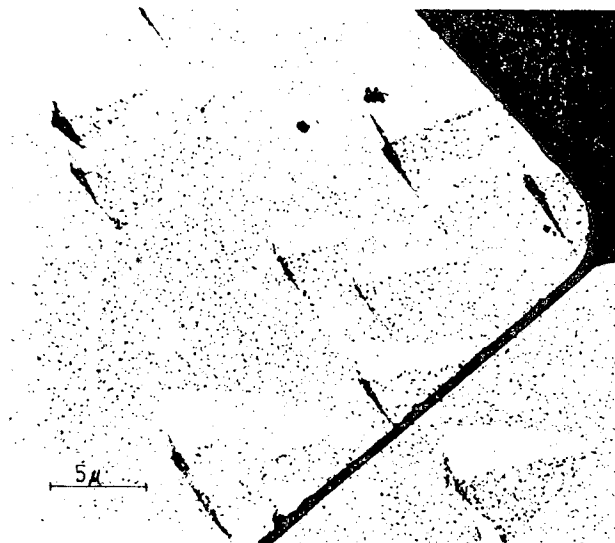


FIGURE 3 Electron micrograph of etch-pits.

solution. The 50 Hz sine wave hysteresis loops were measured using a Sawyer-Tower⁶ circuit.

Well-defined saturated hysteresis loops were obtained when fields higher than 25 kV/cm were applied in a direction perpendicular to the (001) surface. With lower fields it behaves like a dielectric with losses.

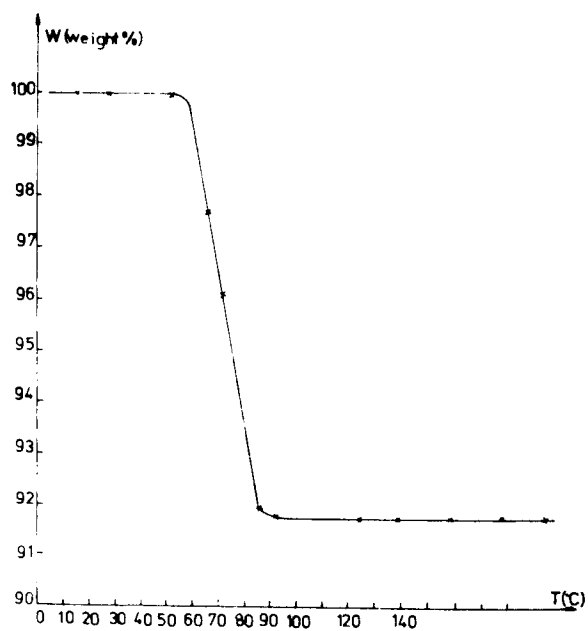


FIGURE 4 Thermogravimetric curve.

At room temperature P_r is about 6×10^{-2} micro-coulombs per sq. cm, an order of magnitude lower than the corresponding value for G.A.S.H. The saturation polarization is slightly higher than P_r .

The ferroelectric properties were observed between -30°C and 100°C . As crystals are easily damaged when kept under such high voltages for more than a few minutes, a careful study of the dependence of P_r on temperature could not be carried out, but no appreciable changes of P_r with temperature were observed. The material presents no ferroelectric-paraelectric transition up to its decomposition temperature.

DOMAIN STRUCTURE

From x-ray diffraction work⁴ G.U.S.H. can be considered to belong to space group $C2/c$, but this space group is incompatible with the observed ferroelectric properties. The non-centrosymmetry associated with ferroelectricity can be ascribed to the hydrogen atoms not resolved by x-ray diffraction methods, as stated by Baggio *et al.*,⁴ but the possible existence of a domain structure should not be overlooked. Were this the case, there should not be appreciable differences in the position of heavy atoms in both domain orientations as suggested by x-ray diffraction work.

Domains were not observed under transmitted polarized light, so that if domain structure is present polarization reversal does not bring about any rotation of optic planes and the existence of 180° domain walls should be investigated.

Domain structure was studied using the electron microscope decoration method recently employed by Hilczer *et al.*⁷ to study domain structure of G.A.S.H. Crystals grown from water solution were cleaved parallel to (001), in air. A quantity of silver chloride which would give a mean thickness of 200 Å if spread uniformly over the surface was deposited with perpen-

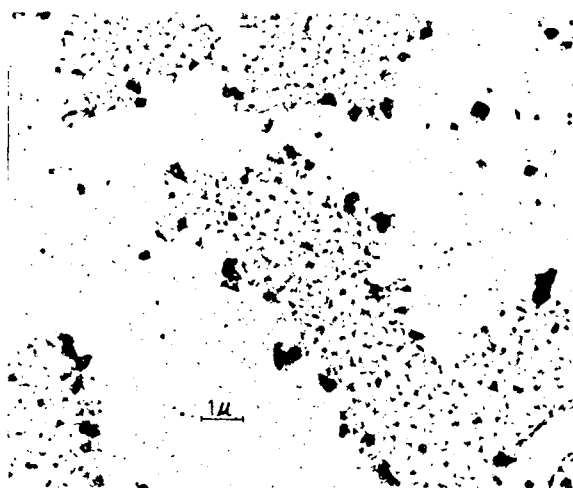


FIGURE 5 Electron micrograph of domain structure in G.U.S.H.

dicular incidence in a vacuum of 5×10^{-5} Torr; the crystal was held at room temperature. After the silver chloride evaporation, a backing film of amorphous carbon was evaporated. The composite film was stripped from the substrate by immersion in distilled water and mounted on electron microscope grids; it was examined by conventional transmission electron microscopy. Typical pictures of irregularly shaped domains of $4-6 \mu^2$ are shown in Figure 5, where positive and negative domains show different nucleation density. These are quite similar to the domains observed in G.A.S.H. single crystals by Hilczer *et al.*⁷

DISCUSSION

Holden *et al.*² reported that a material isomorphous with G.A.S.H. is not formed on replacing SO_4 by CrO_4 nor replacing Al by Tl, Sc or the rare earths and that the stability of the trigonal hexahydrated structure

| | G.U.S.H. | G.A.S.H. | References for G.A.S.H. |
|--------------------------------------|--|---|--|
| Symmetry | Monoclinic (Baggio <i>et al.</i> ⁴) | Trigonal | Schein <i>et al.</i> ⁹ |
| Cleavage | Perfect on (001) | Perfect on (0001) | Holden <i>et al.</i> ² |
| Etch pits | On (001): cocked triangular irreg. pyramids | On (0001): perpendicular and cocked triangular pyramids | Holden <i>et al.</i> ² Nakamura ⁸ |
| Dielectric behaviour | Ferroelectric from -30°C up to decomposition temperature | Ferroelectric from -175°C up to decomposition temperature | Holden <i>et al.</i> ² |
| Polarization direction | Perpendicular to (001) or nearly so | Perpendicular to (0001) | Holden <i>et al.</i> ² |
| Saturation polarization (room temp.) | Order of magnitude: $6 \times 10^{-2} \mu\text{coul}/\text{cm}^2$ | $35 \times 10^{-2} \mu\text{coul}/\text{cm}^2$ | Holden <i>et al.</i> ² |
| Domain structure | 180° domain walls | 180° domain walls | Hilczer <i>et al.</i> ⁷ |

appears to be due to the peculiarities of the guanidine ion. As far as we know no ferroelectric properties have been previously detected outside the family of compounds isomorphous with G.A.S.H.

Although G.U.S.H. is not isomorphous with G.A.S.H., most of the physical properties of both materials are quite similar, as listed on p. 489.

The crystal structure of both compounds have a layered structure with sheets built of SO_4^- and UO_2^{++} (or Al^{+++}) ions; the sheets being connected by guanidinium and water molecules.

ACKNOWLEDGEMENT

The authors thank Dra. Alicia Gladchtein, who kindly performed the thermogravimetric analysis.

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