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Phase Transition in Synthetic Troegerite at Room Temperature

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Abstract

A reversible phase transition from a tetragonal (high temperature) to a low symmetry (low temperature) form has been observed in synthetic troegerite ($H_2(UO_2)_2(AsO_4)_2 \cdot 8\,H_2O$). Observed transition temperature ranges from 18°C to 28°C. Under the influence of a strong electric field the transition temperature decreases.

DTA curves show an endothermic peak in the vicinity of 25°C; no dehydration occurs since TGA curves show no weight loss up to 85°C.

If the tetragonal crystals are slowly cooled past the transition temperature, the low temperature form becomes visible as sets of anisotropic domains and sub-domains in the optically isotropic basal plates.

Domains probably arise as a result of the asymmetric distortion of the lattice accompanying the transformation from the tetragonal to the low symmetry form on cooling. Despite the biaxial optics, precession films of the twinned crystals showed a geometrically tetragonal cell and no evidence of twinning.

Introduction

Troegerite, $H_2(UO_2)_2(AsO_4)_2 \cdot 8\,H_2O$ may be considered a member of the metatorbernite group. Members of this group conform to the formula: $A^z(UO_2XO_4)_z \cdot n\,H_2O$ where A may be almost any monovalent or divalent cation, and X may be P or As; n ranges from 8 to 2.

While the unit cell obtained by X-ray study is tetragonal, there is morphological and optical evidence in the literature that the true symmetry of several minerals in this group is lower than tetragonal; twinning, sectoral crystals, and an anomalous biaxial character are cited (Donnay and Donnay, 1955).

The biaxial character has been reported as being due to strain (as in metatorbernite) or to be dependent on the water content of the crystals (as in meta autunite) (Palache, Berman, and Frondel, 1966, p. 991, 985). Nuffield and Milne (1953) believe that the biaxiality in metauranocircite is due to the distribution of the water molecules within the structure. Referring to twinning, they state that the twinning observed optically is an indication of an irregular arrangement of water molecules and does not represent a true twinning of the structure. Despite the biaxial optics, rotation and Weissenberg films showed a geometrically tetragonal cell. In his detailed studies of several members of the group, Walenta (1963, 1964, 1965) noticed twinning and biaxial character in some natural and synthetic samples and considered the distribution of the water molecules to be responsible for those effects. He found that twinning and the coexistence of uniaxial and biaxial areas was frequent in crystals of metauranocircite.

Palache, Berman, and Frondel (1966, p. 967) report that natural troegerite was considered monoclinic by Schrauf in 1871, but that Goldschmidt in 1899 interpreted it as probably tetragonal, even though the optical properties of the mineral indicate monoclinic symmetry. Weiss *et al* (1957), while studying crystals from Schneeberg, observed that the basal plates showed isotropic areas merging into birefringent ones; the different zones were sometimes arranged in a reticular array. Weiss *et al* considered that the different areas represented troegerite with different water contents, the birefringent zones corresponding to a form rich in water.

All the minerals of the metatorbernite group exhibit isomorphous replacement and a water content dependent on temperature and water vapor pressure; the optical properties may vary therewith, as shown by Beintema (1938) for autunite. Hence, it is difficult to compare the optical properties of natural samples from different localities.

To circumvent this difficulty, Mrose (1953) prepared and studied synthetic uranospinites. She reported the formula $H_2(UO_2)_2(AsO_4)_2 \cdot 8\ H_2O$ for synthetic hydrogen-uranospinite (synthetic troegerite) air dried at room temperature. X-ray rotation and Weissenberg films showed it to be tetragonal, $a = 7.16$ Å, $c = 8.80$ Å, probable space group $P4/nmm$. Walenta reported $a = 7.12$ Å, $c = 17.48$ Å for synthetic troegerite (Strunz, 1970, p. 354).

The present paper describes a reversible phase transformation from a high-temperature tetragonal form to a low-symmetry (pseudo-tetragonal) low-temperature form that occurs at room temperature in synthetic troegerite.

Experimental

Crystals of synthetic troegerite averaging 2 × 2 × 0.5 mm were prepared according to the method given by Mrose (1953). The phase obtained was identified as synthetic troegerite from its powder pattern. (ASTM card No. 8-326). Crystals chosen for study were stored in the mother liquor at room temperature, dried with a filter paper, quickly washed with water, and air dried. During optical observation they were kept under silicon oil to prevent any change in water content.

As *00l* reflections are particularly sensitive to changes in water content and the micaceous character of the sample allows easy orientation on (001), diffractometer records of oriented samples were taken at different temperatures to detect any change in the degree of hydration.

When non-oriented samples were X rayed, the necessary reduction in size was accomplished by fine chopping of the crystals with a razor blade.

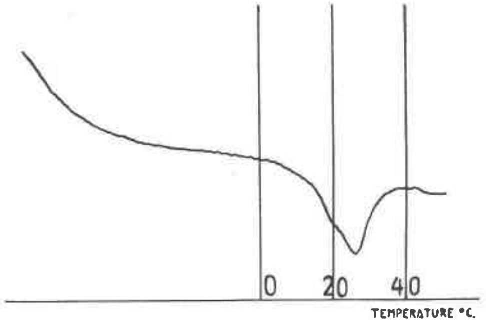

FIG. 1. Typical differential thermal analysis curve for synthetic troegerite.

Morphology

Synthetic troegerite is obtained as thin {001} square plates. The larger crystals are eight-sided in outline, the edges of the plates being commonly modified by dipyramidal forms whose presence is apparent only under the petrographic microscope. Except for the faces of the pinacoid {001}, which give excellent reflections, the crystals are of poor quality for optical goniometry. The forms observed are: {001} dominant; {110}, {011}, {112}, {100}, common; {123} uncertain. The axial ratio derived from goniometer measurements is $a{:}c = 1{:}2.44$, which agrees with the ratio calculated from the unit cell parameters given in the literature for synthetic troegerite. Mrose's X-ray diffraction data give, after doubling c, $a{:}c = 1{:}2.48$; Walenta's results, (Strunz, 1970, p. 354) lead to $a{:}c = 1{:}2.45$.

On the other hand, neither the axial ratio nor the forms reported for natural troegerite (Palache, Berman, and Frondel, 1966, p. 966) are in good agreement with those reported for synthetic material.

Thermal Study

Differential thermal analyses of synthetic troegerite were made from −30°C to about 50°C with a heating rate of 15°C per minute. The DTA curve (Fig. 1) is characterized by the presence of an endothermic peak at about 25°C; this peak was not observed when the sample was loosely packed or the heating rate was high.

A TGA curve shows that dehydration occurs above 85°C; no weight loss was recorded in the 10°–85°C range.

Phase Transition

A reversible phase transition from a tetragonal (Phase I) to a low symmetry (low temperature) form (Phase II) has been observed in the synthetic troegerite. The transition temperature varies for different batches of crystals, but is constant for crystals of the same batch. Observed transition temperatures ranged from 18°C to 28°C.

The behavior observed under the polarizing microscope was the same for all crystals examined. Above the transition temperature thin basal plates of troegerite are homogeneous, isotropic, uniaxial, and negative; no twinning, sectoral crystals, or anomalous biaxial character was observed. If the plates, slowly cooled past the transition temperature, are observed between crossed polarizing prisms with parallel light and perpendicular incidence, anisotropic domains become visible in the isotropic, tetragonal matrix. These domains disappear when the sample is heated above the transition temperature, only to reappear in related but distinctly altered configurations when the crystal is cooled again through the transition temperature. If the temperature is kept constant after the transition has started, the relative proportion of the two phases does not change with time. The anisotropic domains resemble long, slender "pencils" with tapered ends, which grow in the forward direction until stopped by another domain oriented at 90°. On further cooling there is a slight increment in their width and new domains suddenly appear in the tetragonal matrix until practically all the crystal is transformed into two groups of low symmetry domains, of equal volumes, oriented at 90° to each other (Fig. 2a); the crossing of the domains produces a checkerboard pattern. The length of the domains is essentially parallel to ⟨110⟩ tetragonal. The extinction looks homogeneous, at 45° from the length of the domains, and parallel to ⟨100⟩ tetragonal. Observation with a gypsum plate shows that parallel domains alternate their vibration directions and could be interpreted as twin-related lamellar individuals with composition planes parallel to {110} tetragonal. In plain unpolarized light the domain walls are visible as fine striae because of the differences in refractive indices in neighboring domains. If pressure is applied with a needle, domains move and change their orientations. Thermal shock gives rise to a fine grid type array of many small domains.

If crystals, just picked from the mother liquor, are slowly cooled and observed while the transition is taking place for the first time, each crystal shows only a few broad domains. Observation in a universal stage with oblique illumination, between crossed polarizing prisms, shows that each domain is a composite of several subdomains (Fig. 2b). These subdomains have an irregular shape and are usually bounded by planes nearly parallel to the {100} and {110} planes of the tetragonal matrix. Their boundary walls cannot be observed with perpendicular incidence as there is only a very slight difference in refractive indices of neighboring subdomains. The subdomains in each domain can be grouped into two sets, according to the orientation of the optical indicatrix. One of the principal axes of the ellipsoids, lying on the plane of the plates, is common to both sets and is parallel to the direction of maximum refractive index; a second axis makes an angle of approximately 7° with the plane of the plates, pointing alternately downwards or upwards in neighboring subdomains (Fig. 3).

The observable optical properties are limited by the small size of the subdomains. In convergent light a flash figure is obtained; the acute bisectrix is probably nearly perpendicular to (001) tetragonal and the optical character is negative, but the possibility of an obtuse bisectrix figure is not absolutely ruled out.

The lamellar domains and the irregularly shaped subdomains appear simultaneously at the transition

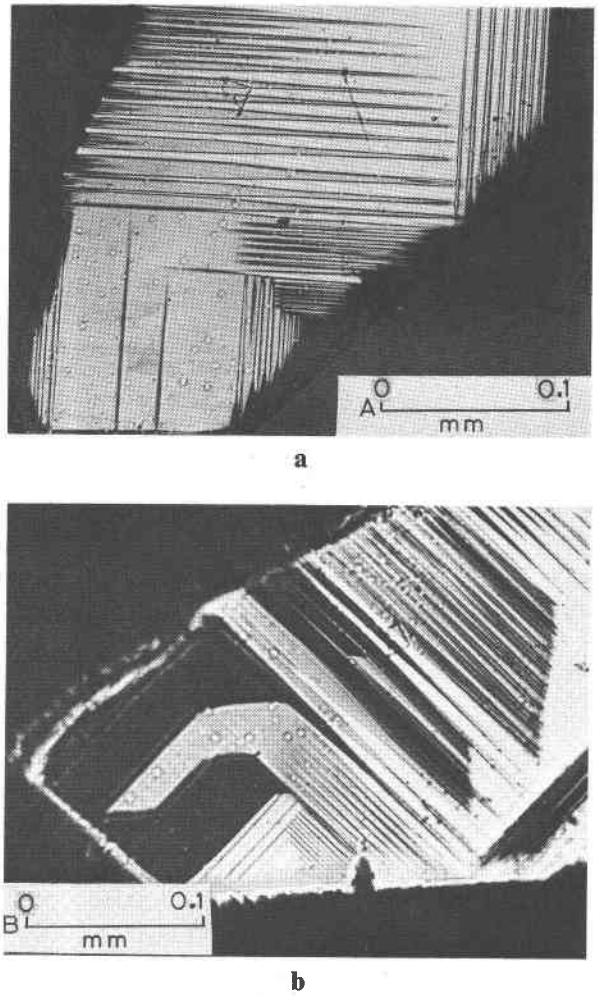

FIG. 2. Domain structure in a crystal of synthetic troegerite: (a) Perpendicular incidence. Picture printed from black and white film made from a color plate. Blue domains appear here a little darker than yellow ones. (b) Composite structure of domains. The universal stage was rotated so that all four types of subdomains occurring in a twinned crystal are visible.

temperature. When the low-temperature form is heated, the difference in optical orientation between subdomains slowly disappears; domains multiply and thin domains appear inside those already present; sometimes a twisted structure is observed (Fig. 4). On further heating the crystals reverse to the tetragonal phase. Now the extinction in the basal plates is not always homogeneous, an inhomogeneous extinction due to residual tensions being sometimes observed. Domains and subdomains reappear in altered configurations after the sample is cooled again through the transition. As the crystal repeatedly undergoes the phase change, the domains appear as thinner and thinner lamellae; no subdomains were visible in the very thin lamellae and broad domains never reappear in such crystals.

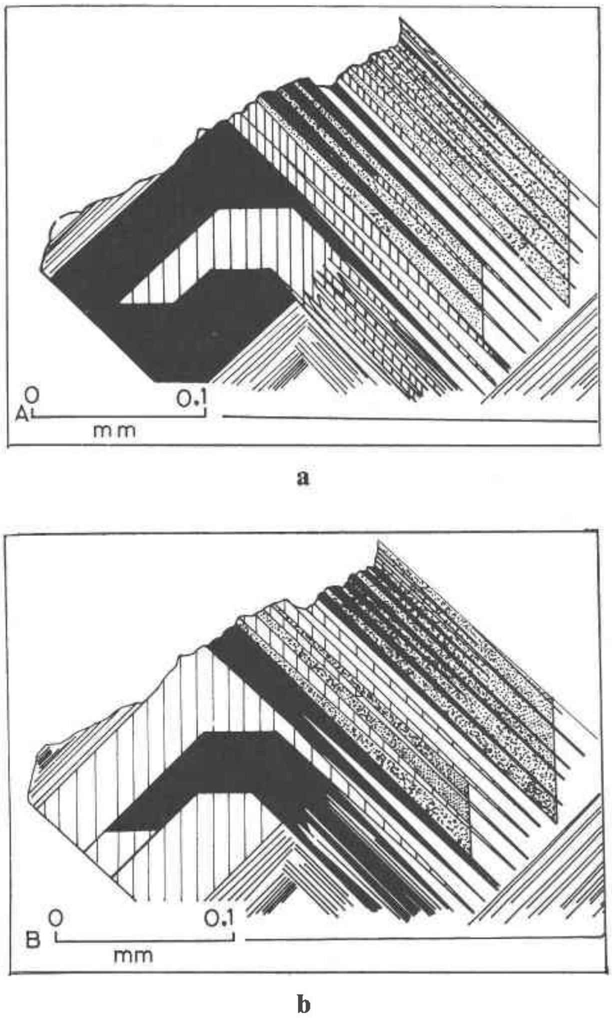

FIG. 3. Reversal of subdomains: (a) Line drawing from Figure 2b, showing subdomain structure. Notice subdomain walls at approximately 45° from domain walls. (b) Line drawing showing half of subdomains reversed by rotation through an extinction position (black and striped areas). Rotation axis E–W. These subdomains belong to domains appearing dark in Figure 2. There is no change in contrast of subdomains belonging to the second set of domains (white and stippled areas).

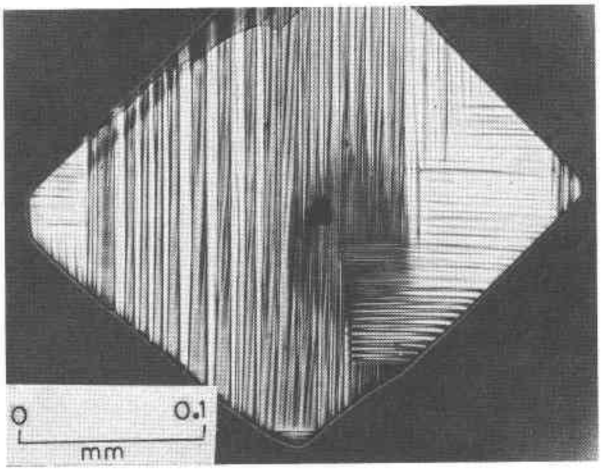

FIG. 4. Synthetic troegerite. Twisted structure appearing gradually as the sample is heated.

In several crystals a superposition of two slightly rotated arrays of anisotropic domains has been observed.

No single crystal diffraction study of the low temperature form could be performed, since such crystals are invariably twinned; (*hk*0) precession photographs of the twinned crystals failed to show any departure from tetragonal symmetry.

Crystals of synthetic troegerite dehydrate when kept in a vacuum at room temperature for several minutes. A low temperature form is no longer visible in the dehydrated sample, even if cooled to −20°C. This behavior precluded the study of the transition in the electron microscope.

A depression of the transition temperature caused by an applied electric field parallel to $\langle 100 \rangle$ or $\langle 110 \rangle$ tetragonal has been observed. A detailed study of the influence of an electric field on the physical properties of synthetic troegerite will be published elsewhere.

Discussion

Significant aspects of this study may be summarized as follows: (1) Synthetic troegerite has a high-low inversion near room temperature. (2) The transition is reversible and non-quenchable. A first order phase transition is inferred from the presence of a peak in the DTA curve. As shown by TGA curves, no dehydration is involved. (3) The character of the domain and subdomain pattern observed in the low temperature form implies that the low-symmetry phase must be a derivative structure of the distortion type (Buerger, 1947). It results from the basic tetragonal structure by the suppression of several sets of operations in its point group; the only symmetry elements preserved are possibly a twofold axis or a symmetry plane.

The presence of domains and their mutual orientation must be the result of a mechanism opposing the development of large strains. These strains may be avoided if the direction of asymmetric distortion is different in alternate small regions so as to produce a macroscopically undistorted crystal. In those alternate small regions the lattice deformation occurs in crystallographically equivalent directions of the parent tetragonal phase.

Transitions similar to the one just described for synthetic troegerite may be anticipated to occur in other members of the metatorbernite group.

We believe the transition temperature to be composition sensitive. The variable composition due to isomorphous replacements so common in minerals of the group might result in the occurrence of both the high and low symmetry forms at ambient temperature. This possibility could account for the optical anomalies frequently reported and would explain the discrepancies found in the literature concerning the crystallography of some members of the metatorbernite group.

References

BEINTEMA, J. (1938) On the composition and the crystallography of autunite and the meta-autunites. *Rec. Travaux Chim. Pays-Bas*, **57**, 155–175.

BUERGER, MARTIN J. (1947) Derivative crystal structures. *J. Chem. Phys.* **15**, 1–16.

DONNAY, GABRIELLE, AND J. D. H. DONNAY (1955) Contribution to the crystallography of uranium minerals. *U. S. Geol. Surv. Rep. TEI*—**507.**

MROSE, MARY E. (1953) Studies of uranium minerals XIII: Synthetic uranospinites. *Am. Mineral.* **38,** 1159–1168.

NUFFIELD, E. W., AND I. H. MILNE (1953) Studies of radioactive compounds: VI- Meta-uranocircite. *Am. Mineral.* **38,** 476–488.

PALACHE, CHARLES, H. BERMAN, AND C. FRONDEL (1966) *System of Mineralogy of Dana.* Vol. 2, 7th ed. John Wiley and Sons, New York.

STRUNZ, HUGO (1970) *Mineralogische Tabellen 5.* Auflage, Akademische Verlagsgesellschaft Geest und Portig K.-G., Leipzig.

WALENTA, KURT (1963) Uber die Barium-Uranylphosphatmineralien Uranocircit I, Uranocircit II, Meta-Uranocircit I und Meta-Uranocircit II von Menzenschwand im südlichen Schwarzwald. *Jh. Geol. Landesamt Baden-Württemberg,* **6,** 113–136.

——— (1964) Beiträge zur Kenntnis seltener Arsenatmineralien unter besonderer Berücksichtigung von Vorkommen des Schwarzwaldes. *Tschermaks Mineral. Petrogr. Mitt. Bd.* **9,** 111–174.

——— (1965) Beiträge zur Kenntnis seltener Arsenatmineralien unter besonderer Berücksichtigung von Vorkommen des Schwarzwaldes. *Tschermaks Mineral. Petrogr. Mitt. Bd.* **9,** 252–282.

WEISS, A., F. TABORSZKY, K. HARTL, AND E. TRÖGER (1957) Zur Kenntnis des Uranminerals Trögerit. *Z. Naturforshg.* **12b,** 356–358.

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