

Note

THERMAL ANALYSIS AND INFRARED SPECTRA OF SOME NATURAL AND SYNTHETIC URANIUM MICAS

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Uranium micas having the general formula $M^{2+}(UO_2)_2(PO_4)_2 \cdot nH_2O$ and $M_2^+(UO_2)_2(PO_4)_2 \cdot nH_2O$ form one of the largest and most widespread groups of secondary uranium minerals. A characteristic feature of these compounds is their layer structure, in which uranium is bound in uranylphosphate layers. Cations and water molecules located in the inter-layer space contribute to the linking together of layers by electrostatic forces and hydrogen bonds. The stepwise dehydration of uranium micas has been observed (e.g., refs. 1 and 2). In this paper, the correlation of thermal decomposition curves with infrared spectra of original and dehydrated phases (the range of structure destruction of anhydrous phases) is given using site and factor group analysis [3,4] and published X-ray crystal structure data. Natural and synthetic metaautunites, metatorbernites and metauranocircites(II) were studied.

The paper is part of the scientific reassessment of secondary uranium minerals from the collections of the National Museum in Prague.

EXPERIMENTAL

Metaautunite, $Ca(UO_2)_2(PO_4)_2 \cdot xH_2O$ (natural $x = 6$, synthetic $x = 9.4$), metatorbernite, $Cu(UO_2)_2(PO_4)_2 \cdot xH_2O$ ($x = 9$ and 8 , respectively), and metauranocircite(II), $Ba(UO_2)_2(PO_4)_2 \cdot 6H_2O$, were studied. Details of syntheses are given in ref. 4. The phases studied were identified by use of a Rigaku Denki X-ray powder diffractometer, with $CuK\alpha$ radiation and Ni

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filter. Water content was calculated from TG curves. Thermal analysis was carried out by use of (1) a Stanton-Redcroft (TG 750) thermobalance (natural phases: $10^{\circ}\text{C min}^{-1}$, sample weight 10 mg, dynamic air atmosphere, 10 ml min^{-1}), (2) a Theta Gravitronic II (synthetic phases: $10^{\circ}\text{C min}^{-1}$, sample weight 90 mg, static air atmosphere), and (3) micro-DTA by Blažek [5] ($10^{\circ}\text{C min}^{-1}$, static air atmosphere, sample weight: 20 mg, natural phases; 30 mg, synthetic phases, reference sample Al_2O_3). In addition, the samples were dehydrated by heating at 600°C for 2 h. Infrared spectra were measured with a Perkin-Elmer 325 spectrophotometer in the range $4000\text{--}200\text{ cm}^{-1}$ in Nujol and with KBr disks. No differences in the IR spectra taken using both techniques were observed.

RESULTS AND DISCUSSION

The course of the dehydration of uranium micas studied running in several steps was inferred from the TG and DTA curves (Figs. 1 and 2) (metaautunite endotherms at: 73, (85), 115, (130), 195°C , natural; 160, 235°C , synthetic; metatorbernite endotherms at: 133, 172, 265°C , natural; 195, 222, 295°C , synthetic; metauranocircite(II) endotherms at: 165, 220, 245°C , synthetic). The infrared spectra of the phases studied are given in Fig. 3. The site symmetries of the UO_2^{2+} group are C_{2v} (metaautunite and

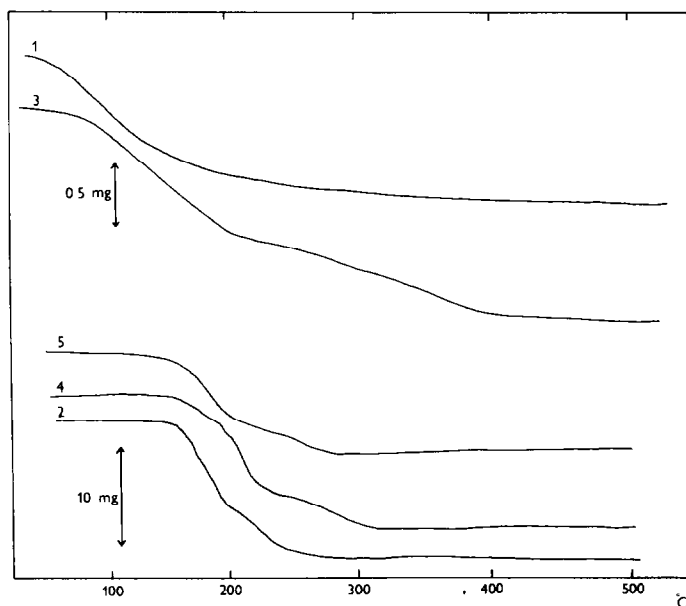


Fig. 1. TG curves of natural and synthetic metaautunite (1,2), metatorbernite (3,4) and synthetic metauranocircite(II) (5).

metauranocircite(II)) and C_4 (metatorbernite). The site symmetry C_{4v} inferred from the X-ray structure analysis of metaautunite [6] does not agree with the analysis of the IR spectra. A doubling of the number of absorption bands of the UO_2^{2+} vibrations in metatorbernite was observed. This doubling agrees with the factor symmetry (G_F), however, the presence of two couples of symmetrically nonequivalent and geometrically different uranyl groups in the elementary cell of metatorbernite can rather be assumed. The site symmetries of the PO_4^{3-} groups are D_{2d} (metaautunite) and S_4 (metatorbernite and metauranocircite(II)). Absorption bands of water molecule vibrations are manifested in the IR spectra of uranium micas in three regions: δH_2O bending vibrations in the range $1630\text{--}1650\text{ cm}^{-1}$, νOH stretching vibrations in the range $3350\text{--}3480\text{ cm}^{-1}$, weak and not very sharp absorption bands in the range $580\text{--}700\text{ cm}^{-1}$ in the IR spectrum of metatorbernite assigned to libration modes of water molecules. The dehydration of metaautunite and metatorbernite caused a change or a lowering of elementary cell symmetry. The release of water molecules coordinated by cations in the interlayer space also contributes to the destruction of the coordination polyhedrons of these cations. Changes of electrostatic forces and hydrogen bonds in the interlayer space also probably cause the destruction of uranyl polyhedrons in layers. This fact was inferred from the IR spectra of samples heated at 600°C where a splitting of all doubly and triply degenerate vibrations of UO_2^{2+} and PO_4^{3-} groups and an activation of the

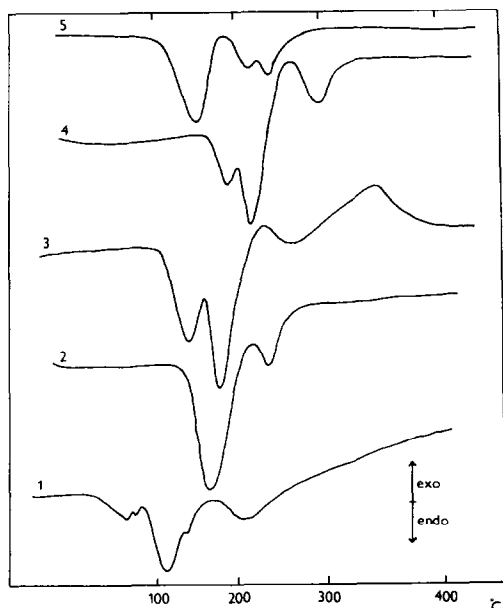


Fig. 2. DTA curves of natural and synthetic metaautunite (1,2), metatorbernite (3,4) and synthetic metauranocircite(II) (5).

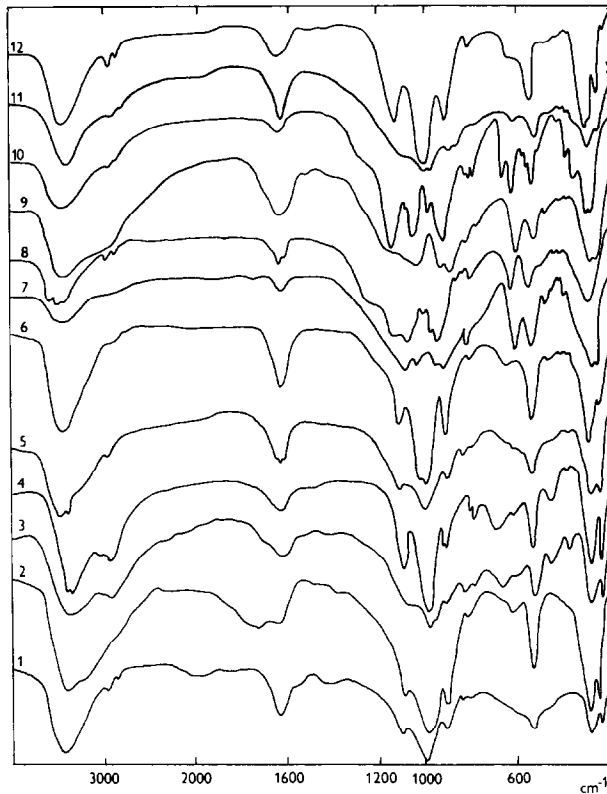


Fig. 3. IR spectra of natural and synthetic metaautunite (1,2), metatorbernite (3,4), metauranocircite(II) (5,6) and of these phases dehydrated at 600°C (7-12), respectively.

$\nu_1\text{PO}_4^{3-}$ symmetrical stretching vibration can be suggested according to the number of absorption bands. From the IR spectra of metaautunite and metatorbernite dehydrated at 600°C, owing to the splitting of these vibrations, the destruction of the crystal structure of these minerals was supposed. On the other hand, the IR spectrum of metauranocircite(II), after dehydration, did not change substantially, hence, a relatively stable crystal structure of this mineral was inferred.

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