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THERMAL AND INFRARED SPECTRUM ANALYSES OF SOME URANYL SILICATE MINERALS

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ABSTRACT

Thermal decomposition /combined TG and DTA/ of some secondary uranium minerals of the uranyl silicate group /uranophane, β-uranophane, sklodowskite, cuprosklodowskite, kasolite and soddyite/ was studied with special regard to the water content in the minerals. The obtained results were correlated with the infrared absorption spectra and published crystal structure data of the minerals studied.

INTRODUCTION

The uranyl silicate minerals are divided into three groups on the basis of their uranium to silicate ratios /1:1, <1:1, >1:1/ /ref.1/. A characteristic feature of most of them is their layer structure. The role of the amount and arrangement of molecular water and the presence of OH^- or H_3O^+ ions remain still open. Different formulas are given, therefore, to these compounds. In this paper, which is a part of the scientific reassessment of secondary uranium minerals from the collections of the National Museum in Prague, the following minerals /uranophane and β-uranophane, $CaO.2UO_3.2SiO_2.nH_2O$, sklodowskite, $MgO.2UO_3.2SiO_2.nH_2O$, cuprosklodowskite, $CuO.2UO_3.2SiO_2.7H_2O$, kasolite, $PbO.UO_3.SiO_2.H_2O$ and soddyite, $2UO_3.SiO_2.2H_2O$/ were studied by use of DTA, TG, X-ray diffraction analyses and infrared spectroscopy.

EXPERIMENTAL

All minerals studied were chosen from the collections of the National Museum in Prague. They were identified by use of the X-ray powder diffractometer Rigaku Denki and Mikrometa Chirana, camera Ø 114.6 mm, Cu-Kα radiation, Ni filter. The X-ray diffraction data were compared with JCPDS Selected powder diffraction data for minerals. Thermal analysis was carried out by

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use of Stanton Redcroft Thermobalance TG 750 /10°C.min^{-1}, dynamic air atmosphere 10 ml.min^{-1}/ and micro-DTA by Blažek[2] /10°C.min^{-1}, static air atmosphere/. The help of Dr. J. Ederova, Prague Institute of Chemical Technology, in recording the thermal analysis curves, is acknowledged. Infrared spectra were measured with Perkin-Elmer 225 Spectrophotometer /KBr micropellets/ and Perkin-Elmer 325 Spectrophotometer /KBr disks/. TG curves of the minerals studied are given in Fig.1, DTA curves in Fig.2 and IR spectra in Fig.3. The lack of samples did not allow the recording of TG and DTA curves of β-uranophane and DTA curve of cuprosklodowskite. The available published data[3,4] were used, therefore, in the two cases.

RESULTS AND DISCUSSION

Uranophane and β-uranophane dehydrate in three steps /uranophane: endotherms at 160°C - 1H_2O and at 215°C - 2H_2O; β-uranophane: endotherms at 150-180°C - 2H_2O and 190-200°C - 1H_2O; the remaining part of water - OH^- or $H_3O^{+?}$ - escapes continuously up to 785 and 670°C resp./. The character of the absorption bands in the range of bending vibrations δH_2O and stretching vibrations ν OH confirms the presence of two different types of molecular water. Two different hydrogen bonds are supposed to be present, however, without assignment to OH^- ions or molecular water. The absorption band observed in the IR spectrum of β-uranophane at ~ 1750 cm^{-1} could be probably assigned to ν_4 H_3O^+, however, it may be caused by the preparation of KBr micropellets[5]. No absorption bands were observed in the range 1470-1400 cm^{-1} which could be assigned to OH groups located in the apexes of SiO_4 tetrahedrons[6]. The water content in the two minerals determined by TG / 5H_2O/ agrees with the X-ray structure data[1], however, it is not possible to define explicitely the arrangement of the "constitutional water" escaping at the temperature higher than 200°C. The crystal structure of uranophane should be more stable than of β-uranophane[7,8]. A characteristic intensive endotherm at 218°C and small endotherms at 350 and 650°C for sklodowskite and endotherms at 140, 160, /220/ and 640°C for cuprosklodowskite were observed. They are in agreement with dehydration in the sequence 2.5, 2.5 and 0.5 H_2O /sklodowskite/ and 4, 1, 2 H_2O + 0.5 O_2 /cuprosklodowskite/. The observed water content in sklodowskite / 5H_2O/ agrees with the X-ray crystal structure analysis published by Mokeeva[1] and is in disagreement with that by Ryan and Rosenzweig /$7H_2O$/[1], the water content in cuprosklodowskite / $7H_2O$/ accords with that found by these authors. The IR spectra of both minerals are similar to that of uranophane with exception of the absorption band at ~ 1170 cm^{-1} observed in sklodowskite. For kasolite, a large endotherm in the range 100-360°C was observed. Water is released continuously up to 900°C and corresponds to $1H_2O$. IR spectrum confirms the presence of molecular water in kasolite, coordinated by lead atom[1]. Soddyite is characterized by an asymmetric endotherm at 400°C and a small endotherm at 724°C corresponding to the continuous release of $2H_2O$ in the range 320-720°C /after the escape of a small amount of "zeolitic water"/ and the destruction of the anhydrous molecule connected with the formation of U_3O_8. The IR spectrum confirms the presence of molecular water in soddyite which is bound in uranium coordination polyhedrons[1] and its feature indicates the similarity with the structure of β-$UO_2/OH/_2$.

For the uranyl silicates studied /with exception of soddyite/ a layer structure with uranyl silicate sheets of composition $|/UO_2/_2/SiO_4/_2|_n^{-4n}$ is characteristic. The activation of the IR forbidden vibrations of SiO_4^{4-} /ν_1, ν_2/ and UO_2^{2+} /ν_1/ groups and the splitting of degenerate ν_2, ν_3, ν_4 vibrations of SiO_4^{4-} group confirm the lowering of the site symmetry of these groups and the distortion of silicate and uranyl polyhedrons in the crystal

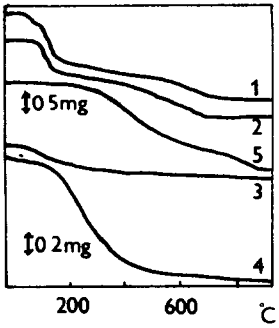

Fig. 1 TG curves of uranophane /15.467 mg/-1, sklodowskite /13.878 mg/-2, cuprosklodowskite /1.731 mg/ -3, kasolite /26.522 mg/-4, soddyite /26.115 mg/-5.

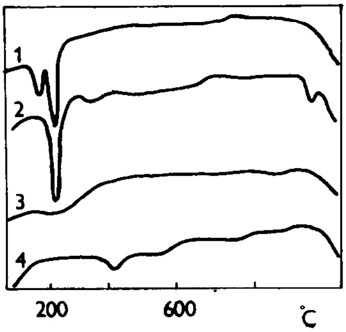

Fig. 2 DTA curves of uranophane /30 mg/-1, sklodowskite /40 mg/-2, kasolite /60 mg/-3, soddyite /40 mg/-4.

structure of the minerals studied. The presence of different types of water molecules can be inferred from thermal analysis data. However, the more detailed assignment on the basis of IR spectra needs the study of deuteroanalogues which is in progress and will be published later.

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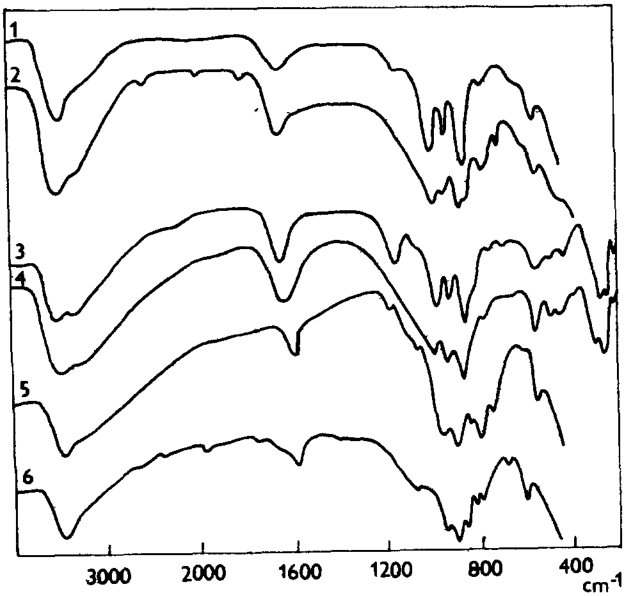

Fig. 3 Infrared spectra of uranophane /1/, β-uranophane /2/, sklodowskite /3/, cuprosklodowskite /4/, kasolite /5/, soddyite /6/.