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THERMAL AND INFRARED SPECTRUM ANALYSES OF CURITE

Jiří Čejka Jr[+], Institute of Chemical Technology
166 28 Praha 6, ČSSR
Alexander Muck, Institute of Chemical Technology
166 28 Praha 6, ČSSR
Zdeněk Urbanec[x], Nuclear Research Institute,
250 68 Řež, ČSSR
Jiří Čejka, National Museum in Prague,
115 79 Praha 1, ČSSR

ABSTRACT

Thermal decomposition /combined TG and DTA/ of a secondary uranium mineral curite, approx. $3PbO.8UO_3.5H_2O$, was studied. The loss of water /dehydration and dehydroxylation/ was observed followed by a probable volatilization of PbO during the thermal decomposition process. The formation of a lead uranate as the endproduct of the thermal decomposition is supposed. The results were correlated with infrared absorption spectra of curite and its decomposition product and with published data of crystal structure analysis.

INTRODUCTION

On the basis of X-ray structure analysis the chemical formula of curite was proposed as $3PbO.8UO_3.5H_2O$ /ref.1/ or $[Pb_{8-x}/OH/_{4-2x}/H_2O/_{2x}][/UO_3/_8O_8/OH/_6]_2$, /x=1.34-2/ /ref.2/ or $[U_8O_x/OH/_{30-x}]_3Pb_3/OH/_{24-x}/x-21/H_2O$, $/24 \geqslant x > 21/$ /ref.3/. TG curve of natural and synthetic[4] curite, its IR spectrum[5] and infrared spectroscopic study of thermal decomposition of curite[6] were published.

In this paper, which is a part of the scientific reassessment of secondary uranium minerals from the collections of the National Museum in Prague, thermal decomposition of natural curite is studied by use of TG, DTA and X-ray diffraction analyses and infrared spectroscopy. The results are correlated with published X-ray structure analysis of curite[1-3].

EXPERIMENTAL

The curite specimen used for this study was chosen from the

[+] Present address: J.Heyrovský Institute of Physical Chemistry and Electrochemistry, Czechoslovak Academy of Sciences, 121 38 Praha 2 ČSSR

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collections of the National Museum in Prague. It was identified using the X-ray powder diffractometer Rigaku Denki, Cu-Kα radiation, Ni filter. The X-ray diffraction data were compared with JCPDS Selected powder diffraction data for minerals /14-267/; DTA curve was recorded by use of micro-DTA apparatus by Blažek[7] /heating rate 10°C.min^{-1}, static air atmosphere, reference sample Al_2O_3, sample weight 20 mg/. No chenges were observed on the DTA curve. TG analysis was carried out with Stanton Redcroft Thermobalance TG 750 /heating rate 10°C.min^{-1}, dynamic air atmosphere 10 ml.min^{-1}, sample weight 18.208 mg/. 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 325 Spectrophotometer /KBr disks/. TG curve of curite is given in Fig.1 and IR spectra of curite and its decomposition product in Fig.2.

RESULTS AND DISCUSSION

Curite contains not only molecular water in its structure, but also hydroxyl ions. OH^- ions are mostly bound in layers formed by uranyl polyhedrons, while remaining OH^- ions together with water molecules /their mutual ratio may vary/ and with Pb^{2+} ions are located in the interlayer space and participate in the formation of hydrogen bonds in the layer structure of curite. From the TG curve can be inferred that the release of all water contained in curite passes continuously in the range cca 20-700°C and may consist of two overlapping stages, corresponding to the processes of dehydration and dehydroxylation. An analogous course was observed on the TG curve of synthetic curite[4]. It was, however, determined on the DTG curve of curite[3] that the mass decrease characterized by peaks at 50°C /0.43 %, the removal of loosely bound H_2O molecules at 20-120°C/ and at 350°C /3.46 %, the removal of molecular water and OH^- ions at 120-400°C/ corresponded to the release of all present water, while the peak at 460°C could be due to loss of Pb as PbO. The decrease of Pb content in the endproduct of the thermal decomposition of curite in comparison with the initial sample observed by us agrees with this conclusion. We observed on the TG curve of curite, the character of which was similar to the TG curve of kasolite, a small mass decrease in the range 700-900°C corresponding evidently to the mentioned release of a part of PbO. It was determined that the mass decreases were in the range 20-510°C 4.39 %, up to 700°C 4.55 % and up to 900°C; altogether 4.82 %. It is evident that the whole water content found in natural or synthetic curites may vary[8,9], however, it is always lower than the mass decrease found in our curite in the range 20-900°C. We infer from these results, in agreement with the chemical analyses, that in the course of the thermal decomposition of curite not only all water contained in curite is released, but also a part of PbO chemically not bound to the uranium present volatilizes. From the IR spectrum of curite, the presence of two types of molecular water /δH_2O 1590 and 1625 cm^{-1}/ in the crystal structure of curite is inferred. The presence of two structurally nonequivalent uranyl groups could be supposed if the absorption bands at 909 and 867 cm^{-1} are assigned to the antisymmetric stretching vibration ν_3 UO_2^{2+}. The latter agrees with the crystal structure analysis of curite[1-3]. The X-ray diffraction data, infrared spectrum, the presence of Pb and the reddish brown colour prove that the endproduct of the thermal decomposition of curite is not U_3O_8, but a lead uranate. Because of the lead to uranium ratio in curite /approx. 3:8/, the composition of the lead uranate may probably be PbU_3O_{10}. The surplus PbO continuously volatilized. If uranium is in excess /Pb:U = 1:5 or more/, U_3O_8 is formed, in other cases not yet defined lead uranates result[10]. Péters[11] did not found U_3O_8 in the endproducts on studying the thermal decomposition of $1.15PbO \cdot 2UO_3 \cdot 1.75H_2O$ /1000°C/, $PbO.6UO_3.10H_2O$ /900°C/, $2PbO.5UO_3.3H_2O$ /600°C/.

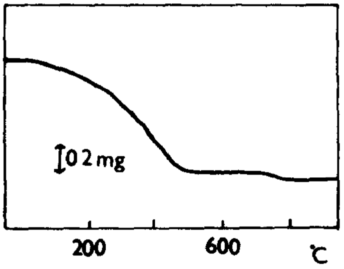

Fig. 1 TG curve of curite /18.208 mg/

The system Pb-U-O is evidently insufficiently defined, the volatilization of PbO may be one of the causes. The system Pb-U-O and the detailed determination of the chemical composition and crystal structure of the endproduct of the thermal decomposition of curite will be subjects of our further investigation.

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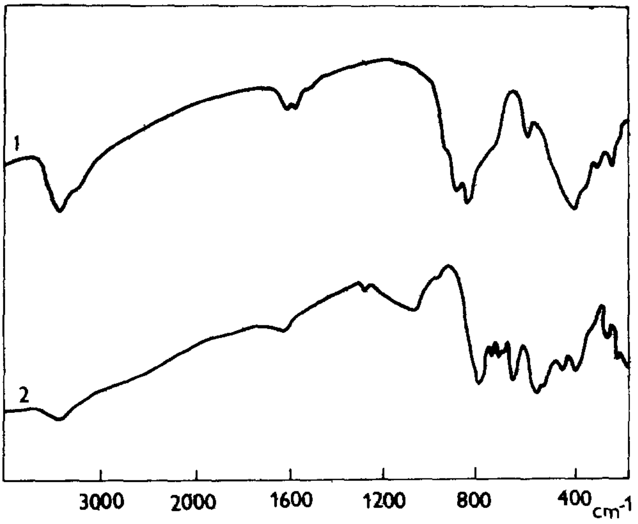

Fig. 2 Infrared spectra of curite /1/ and its decomposition product /2/