



Vibrational spectroscopy of synthetic analogues of ankoleite, chernikovite and intermediate solid solution



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ABSTRACT

Ankoleite ($K(UO_2)PO_4 \cdot nH_2O$), chernikovite ($H_3O(UO_2)PO_4 \cdot nH_2O$) and intermediate solid solutions are frequently encountered in the uranium ores that result from the alteration of uranium primary minerals. This paper reports a thorough FTIR and Raman study related to synthetic analogues for these minerals. First, the vibration bands associated to the UO_2^{2+} uranyl ion were used to calculate the $U=O$ bond length which appeared in good agreement with the data coming from PXRD. Then, the examination of the phosphate vibration modes in both sets of spectra confirmed the general formulation of the samples and ruled out the presence of hydrogenphosphate groups. Finally, the presence of H_2O as well as protonated H_3O^+ and/or $H_5O_2^+$ species was also pointed out, and could be used to clearly differentiate the various phases prepared. Vibrational spectroscopy then appeared as an efficient method for the investigation of such analogues of natural samples. It should be particularly relevant when identifying these phases in mineral ores or assemblies.

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1. Introduction

Uranium(VI) phosphates constitute an important part of the so-called secondary minerals, that result from the alteration of the primary pitchblende [1]. Among them, the more generally encountered are probably autunite, $Ca(UO_2)_2(PO_4)_2 \cdot nH_2O$, as well as torbernite, $Cu(UO_2)_2(PO_4)_2 \cdot nH_2O$, [2] that constitute parent compounds of a large family of minerals adopting comparable crystal structures. If both compounds are commonly described as 2D layered structure with sheets composed by UO_2^{2+} ions and phosphate polyhedrons, they mainly differ through the size and the coordination of the cation hosted in the interlayer space, and through the subsequent number of water molecules also located between the layers [3,4]. Consequently, a wide variety of less abundant phosphate compounds containing sodium, iron, magnesium or barium frequently occur in uranium ores of economic interest [5]. Several of these phases remain hardly identifiable, due to their poor occurrence, but also to structural and textural characteristics close to that of the parent compounds [2]. In these conditions, the progresses made during the last years in portable Raman spectrometers could allow this technique to be used on the field in order to supply important help in the identification of rare minerals [6], that appears mandatory to characterize extensively the mining sites to be exploited.

In the same time, numerous compounds belonging to the general uranyl-based mineral group with the general formula $M(UO_2)XO_4 \cdot nH_2O$ (where $X = P, V$ or As and M is a monovalent cation), were extensively investigated in the framework of their application as cationic exchangers or as solid electrolytes for proton conductivity [7–9]. Among this family, $K(UO_2)PO_4 \cdot nH_2O$ and $H_3O(UO_2)PO_4 \cdot nH_2O$ were particularly studied and appear to constitute synthetic analogues of the natural minerals ankoleite and chernikovite, respectively. Although numerous data were reported concerning the crystal structure of these compounds (tetragonal, space group $P4/ncc$) [10] and their phase transitions occurring both at low [11] or high temperatures [12], vibrational spectra remain poorly documented [13], especially concerning Raman spectroscopy.

In the present study, the preparation then the characterization of synthetic analogues of ankoleite and chernikovite, as well as that of an intermediate solid solution, was then undertaken through vibrational spectroscopy, namely Raman and FTIR. Particularly, the relevant aspects dealing with the spectral features of uranyl molecular ion, phosphate polyhedrons, and H_2O -derived species will be discussed in link with the crystal structure of the samples.

2. Experimental

2.1. Preparation and characterization of the samples

All the chemicals used during the preparation of the powdered samples, except U(VI) solution, were supplied by Sigma-Aldrich and were of

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analytical grade. Uranyl nitrate solution was obtained by the dissolution of the corresponding salt in 0.05 M HNO_3 in order to reach uranium concentrations ranging between 0.5–1.5 M.

$\text{H}_3\text{O}(\text{UO}_2)\text{PO}_4 \cdot n\text{H}_2\text{O}$, also frequently called HUP, was prepared as a synthetic analogue of the natural chernikovite through the protocol reported by Vochten and Deliens [14]. Concentrated phosphoric acid (2 M) and uranyl nitrate were mixed in an open vessel, considering a ratio P/U = 1.1 in order to ensure the quantitative precipitation of the cations. The mixture of solutions was further stirred during 1 h at room temperature then aged during 3 days. The precipitate formed was separated from the supernatant by centrifugation (4500 rpm, 3 min), washed several times with deionized water and ethanol and finally dried at 40 °C in an oven.

Similar procedure based on wet chemistry method was applied for the preparation of $\text{K}(\text{UO}_2)\text{PO}_4 \cdot n\text{H}_2\text{O}$ (KUP), standing as synthetic analogue for ankoleite. Uranyl nitrate, potassium nitrate and phosphoric acid were thus mixed in stoichiometric proportions in a sealed PTFE reactor, then placed in an oven at 60 °C for four days. Nevertheless, the yellow crystals obtained thereafter were always composed by a mixture of ankoleite and chernikovite. Such incomplete reaction was already observed during attempts to perform the direct synthesis of autunite by Vochten et al. [15]. Pure ankoleite was then further obtained through cationic exchange reaction, by immersing the powdered sample in concentrated KNO_3 solution (1 M, pH = 2) for 7 days, considering a molar ratio of U/K = 1/2. Moreover, intermediate $(\text{K},\text{H}_3\text{O})(\text{UO}_2)\text{PO}_4 \cdot n\text{H}_2\text{O}$ solid solution (thereafter noted as (K,H)UP) was obtained through the reverse cationic exchange, i.e. by placing ankoleite in 1 M HNO_3 for about 1 month. In these conditions, potassium was partly substituted by hydronium ions.

For each synthesis, the resulting powder was analysed by Powder X-Ray Diffraction (PXRD) using the Bruker D8 advance diffractometer equipped a lynxeye detector and having copper radiation ($\lambda_{\text{K}\alpha_{1,2}} = 1.54184 \text{ \AA}$). The collected PXRD patterns (Fig. 1a) showed the formation of single and pure phases of HUP, (K,H)UP, and KUP, all adopting the same structural type. Indeed, chernikovite and ankoleite compounds are isostructural and both crystallize in the P4/ncc space group of the tetragonal system [10].

Each uranyl group is coordinated equatorially to four oxygen atoms to form distorted octahedrons. Each of those is connected to the phosphate groups through the share of oxygen corners to form 2D layers perpendicular to the c axis. These layers are separated by water molecules and randomly disordered H_3O^+ (HUP) and/or K^+ (KUP) [7]. A

general view of the structure is presented down the a axis in Fig. 1b, drawn from the crystal data reported by Fitch and Cole [10].

SEM micrographs were then recorded by the means of a FEI Quanta 200 electronic microscope (Fig. 2) to evidence the morphology of the samples prepared. Ankoleite was found to crystallize as large platelet-type crystals up to 50 μm in length. Such morphology is in good agreement with its 2D-layered structure, and was also reported for other uranyl phosphates belonging to the same family, such as autunite [16] or meta-torbernite [17]. Intermediate (K,H)UP sample exhibited a comparable morphology. However, due to its preparation route, the edges of the particles appeared to be more rounded, probably as a result of the alteration of the initial ankoleite in 1 M HNO_3 . Chernikovite formed smaller square-shaped platelets with a size close to 5 μm . Such morphology is probably inherited from the conditions of synthesis since they provide very rapid precipitation of the sample, generally associated with a small size of crystal.

Finally, in order to check the stoichiometry of the solids prepared, the complete dissolution of 2–6 mg of powder was undertaken in 4 M HNO_3 . The concentration of the various elements of interest in the resulting leachate was further determined by the means of ICP-AES (Spectro Arcos EOP). Prior to the analyses, the apparatus was calibrated with SPEX standard solutions diluted to concentrations ranging from 0.1 to 15 $\text{mg}\cdot\text{L}^{-1}$. The results reported in Table 1 confirmed that the U/P ratio was found systematically close to 1, in good agreement with the general formulae of the minerals belonging to the torbernite family. Chemical analysis also allowed the determination of the precise composition of the intermediate solid solution which was characterized by a K/U mole ratio of about 0.4. Moreover, it is to note that for the KUP sample, a small depletion in potassium was evidenced, probably coming from an incomplete cationic exchange in the experimental conditions described above. Nevertheless, the potassium content appears largely higher than in the (K,H)UP sample, and KUP still can be considered as a convenient analogue of ankoleite.

The water content of the various compounds prepared was also evaluated through TG analyses performed on a Mettler-Toledo STAR^e system apparatus. Powdered samples were heated up to 1000 °C ($5 \text{ }^\circ\text{C}\cdot\text{min}^{-1}$) under air atmosphere. The relative weight loss observed between room temperature and 500 °C (see supplementary material, Fig. S1) was assigned to the full dehydration of $\text{M}(\text{UO}_2)\text{PO}_4 \cdot n\text{H}_2\text{O}$, and led to n values ranging from 2.5 to 4.5 (Table 1). The water content appeared to increase when going from ankoleite to chernikovite

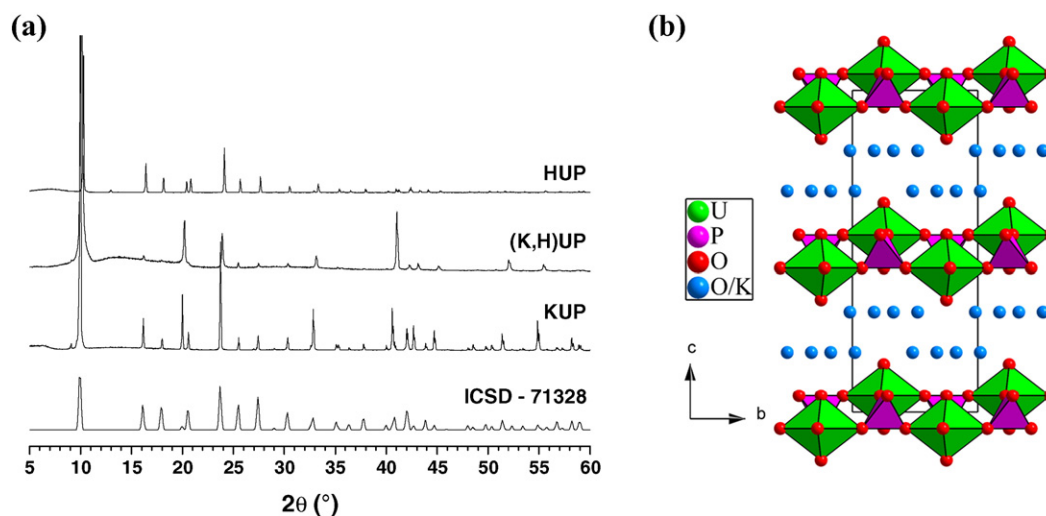


Fig. 1. (a) PXRD patterns recorded for synthetic analogues for ankoleite (KUP), chernikovite (HUP), intermediate solid solution (K,H)UP and comparison with ICSD file #71328 ($\text{K}(\text{UO}_2)\text{PO}_4 \cdot 3\text{D}_2\text{O}$) [10]. (b) General view of the chernikovite/ankoleite structure down the a axis, drawn from the crystal data reported by Fitch and Cole [10].

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