

Vibrational spectroscopic study of hydrated uranyl oxide: Curite

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Abstract

Raman and infrared spectra of the uranyl oxyhydroxide hydrate: curite is reported. Observed bands are attributed to the $(\text{UO}_2)^{2+}$ stretching and bending vibrations, U–OH bending vibrations, H_2O and $(\text{OH})^-$ stretching, bending and librational modes. U–O bond lengths in uranyles and O–H...O bond lengths are calculated from the wavenumbers assigned to the stretching vibrations. These bond lengths are close to the values inferred and/or predicted from the X-ray single crystal structure. The complex hydrogen-bonding network arrangement was proved in the structures of the curite minerals. This hydrogen bonding contributes to the stability of these uranyl minerals.

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1. Introduction

The lead uranyl oxide hydrate minerals, *PbUOHs*, are a group of natural uranyl oxide hydrates that are formed and therefore are also present in oxidized zones of geologically old uranium deposits, owing to the buildup of radiogenic divalent Pb^{2+} [1–3]. Crystal structures of eight PbUOH mineral species are known, however, some new natural PbUOHs are yet insufficiently described. The name masuyite probably may be related to more than one natural phase. Some new PbUOHs were also synthesized [4]. According to Burns [5–7], the protasite anion topology is represented by richetite (molar ratio Pb:U 1:4.15), $\text{M}_x\text{Pb}_{8.57}[(\text{UO}_2)_{18}\text{O}_{18}(\text{OH})_{12}]_2(\text{H}_2\text{O})_{41}$ (refined by Li [3]) as $\text{M}_x\text{Pb}_{9.33}[(\text{UO}_2)_{18}\text{O}_{17}(\text{OH})_{13}]_2(\text{H}_2\text{O})_{40}$, (Pb:U 3.86, $\text{M}_x = \text{Ni}$, Co and Mg), and the yet known structure of masuyite (Pb:U 1:3.00), $\text{Pb}[(\text{UO}_2)_3(\text{O}_3(\text{OH})_2)(\text{H}_2\text{O})_3]$,

and fourmarierite anion topology by fourmarierite (Pb:U 1:4), $\text{Pb}[(\text{UO}_2)_4\text{O}_3(\text{OH})_4](\text{H}_2\text{O})_4$, and vandendriescheite (Pb:U 1:6.36), $\text{Pb}_{1.57}[(\text{UO}_2)_{10}\text{O}_6(\text{OH})_{11}](\text{H}_2\text{O})_{11}$. All these structures are characterized by sheets based upon topologies containing triangles and pentagons [5]. Structures containing sheets based upon anion topologies with triangles, squares and pentagons are related to spriggite (Pb:U 1:2; $\beta\text{-U}_3\text{O}_8$ anion topology), $\text{Pb}_3[(\text{UO}_2)_6\text{O}_8(\text{OH})_2](\text{H}_2\text{O})_3$, sayrite (Pb:U 1:2.50; sayrite anion topology), $\text{Pb}_2[(\text{UO}_2)_5\text{O}_6(\text{OH})_2](\text{H}_2\text{O})_4$ sayrite anion topology), curite (Pb:U 1:2.67; curite anion topology), $\text{Pb}_3[(\text{UO}_2)_8\text{O}_8(\text{OH})_6](\text{H}_2\text{O})_3$, and wölsendorfite (Pb:U 1:2.15; wölsendorfite anion topology) $\text{Pb}_{6.16}\text{Ba}_{0.36}[(\text{UO}_2)_{14}\text{O}_{19}(\text{OH})_4](\text{H}_2\text{O})_{12}$ [5,8].

Curite was originally described at Shinkolobwe, Shaba Province (now Republic Democratic of Congo) by Schoep [9] as a product of uraninite alteration-weathering which involved oxidizing processes and hydration. Crystal structure of curite was first studied by Protas [10], by Courtois [11] in his unpublished thesis, by Sobry [12], Piret [13] and Čejka et al. [14], Taylor et al. [15], Li [3], Li and Burns

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[16,17], Burns and Hill [18] and Mereiter [19]. Mereiter [19] studied the crystal structure of natural and synthetic curite. Dissolution experiments on crystals of synthetic curite were recently described by Schindler et al. [20]. Infrared spectrum of curite was described without any details by Gevork'yan et al. (together with curite thermal decomposition) [21,22]. Thermal analysis and infrared spectra of curite were published by Čejka et al. [23] and reviewed in detail by Čejka [24]. Kubatko et al. [25,26] recently described the thermodynamics of curite formation.

The sheet structure of curite crystals has orthorhombic symmetry, space group $Pnam$, and unit-cell parameters: a , 12.53–12.58; b , 13.01–13.03; c , 8.39–8.40 Å, $Z = 2$ [3,16,17]. Compositional variability has been observed in curite [14,16,17]. The structure of curite contains three symmetrically unique uranium atoms in form of the $(\text{UO}_2)^{2+}$ units, forming $\text{UO}_2\Phi_4$ and $\text{UO}_2\Phi_5$ polyhedra ($\Phi = \text{O}^{2-}$ or OH^-). One uranium cation $\text{U}^{6+}(1)$ is coordinated by three atoms of O^{2-} and one OH^- units at the equatorial position of a tetragonal bipyramid, while the other two uranium cations $\text{U}^{6+}(2)$ and $\text{U}^{6+}(3)$ are both coordinated by three O^{2-} and two OH^- units thus forming uranyl pentagonal bipyramids. There are two structurally distinct Pb^{2+} in the curite structure, both coordinated by six uranyl oxygens, one equatorial O^{2-} of uranyl polyhedra and two water molecules. One symmetrically distinct H_2O site is present [3,16,17].

According to Li and Burns, the geometries of the Pb polyhedra are distorted owing to the electron lone pair stereo activity of Pb^{2+} [16,17]. Because of Pb content variability in the interlayer (some Pb sites are not fully occupied), the charge-balancing mechanism $\text{O}^{2-} \rightleftharpoons \text{OH}^-$ was assumed in the uranyl anion sheets in the crystal structure of curite. Li and Burns studied 14 crystals of natural curite and one crystal of synthetic curite and concluded that the structural formula of curite may be written as $\text{Pb}_{3+x}(\text{H}_2\text{O})[(\text{UO}_2)_4\text{O}_{4+x}(\text{OH})_{3-x}]_2$. From the bond-valence parameters point of view, some O^{2-} ions may be under bonded. The structure of curite contains water molecules and hydroxyl ions. An appropriate arrangement of hydrogen-bonding network present in the curite structure is therefore expected.

Raman spectroscopy has proven very useful for the study of minerals [27–34]. Indeed Raman spectroscopy has proven most suitable for the study of diagenetically related minerals as often occurs with uranyl minerals [29–31,33,35]. Some previous studies have been undertaken by the authors using Raman spectroscopy to study complex secondary minerals formed by crystallisation from concentrated sulphate solutions [36]. The significance of this work rests with the use of Raman spectroscopy to analyse complex mixtures of diagenetically related minerals. Often when studying secondary minerals of uranium, complex mixtures occur. Raman spectroscopy can focus on individual crystals and analyse these individual crystals. This paper forms a part of our Raman and infrared spectroscopy research of secondary minerals including uranyl minerals.

2. Experiments

2.1. Minerals

The curite samples used in this work were obtained from the Mineralogical Research Company and originated from Shinkolobwe Mine and The Ranger Uranium Mine, Northern Territory, Australia. The minerals were analysed by X-ray diffraction for phase purity and for chemical composition by energy dispersive X-ray analysis (EDX).

2.2. Raman spectroscopy

Crystals of curite were placed on the stage of an Olympus BHSM microscope, equipped with 10× and 50× objectives and part of a Renishaw 1000 Raman microscope system, which also includes a monochromator, a filter system and a charge coupled device (CCD). Raman spectra were excited by a HeNe laser (633 nm) at a resolution of 2 cm^{-1} in the range between 100 and 4000 cm^{-1} . Repeated acquisition using the highest magnification was accumulated to improve the signal to noise ratio. Spectra were calibrated using the 520.5 cm^{-1} line of a silicon wafer. In

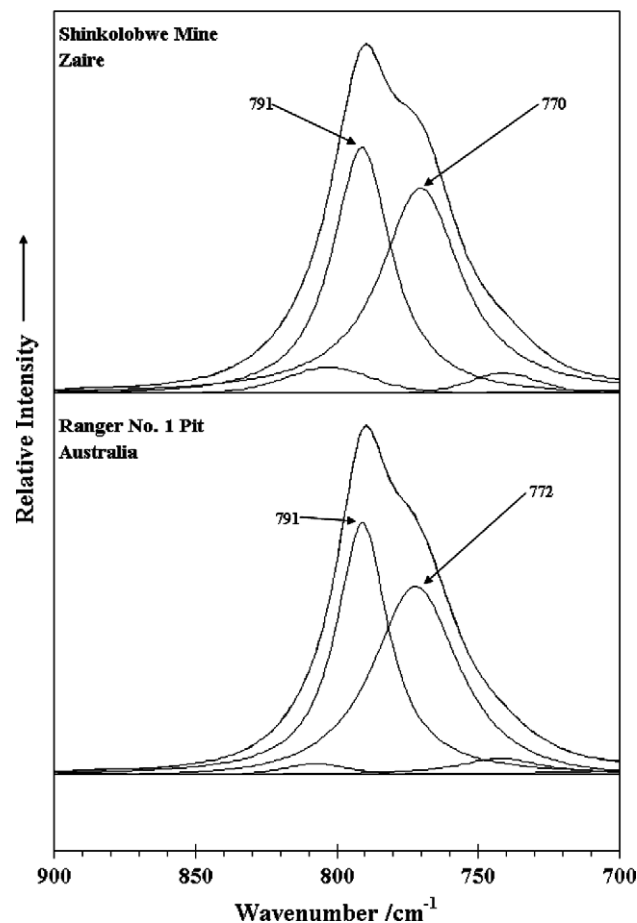


Fig. 1. Raman spectra of curite in the $700\text{--}900 \text{ cm}^{-1}$ region from The Ranger Uranium Mine and Shinkolobwe Mine.

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