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A Raman spectroscopic study of the uranyl tellurite mineral schmitterite

Ray L. Frost*, Jiří Čejka[†], Matt Weier and Godwin A. Ayoko

Inorganic Materials Research Program, School of Physical and Chemical Sciences, Queensland University of Technology, GPO Box 2434, Brisbane Queensland 4001, Australia.

[†]) National Museum, Václavské náměstí 68, CZ-115 79 Praha 1, Czech Republic.

Abstract

Raman spectra of schmitterite measured at 298 and 77 K are presented and discussed in detail and in part in comparison with published IR spectrum of synthetic schmitterite. U-O bond lengths in uranyls, calculated with the empirical relations $R_{U-O} = f[v_1(\text{UO}_2)^{2+}] \text{ \AA}$ and $R_{U-O} = f[v_3(\text{UO}_2)^{2+}] \text{ \AA}$, are close to those inferred from the X-ray single crystal structure of synthetic schmitterite and agree also with the data for other natural and synthetic uranyl tellurites.

Key words: selenite, tellurite, Raman spectroscopy, U-O bond length, uranyl

Introduction

Schmitterite is the uranyl secondary mineral, the formula of which is $[\text{UO}_2\text{TeO}_3]$ [1]. Schmitterite was described from the Moctezuma Mine, Moctezuma, Sonora (Mexico) [2]. The second known locality is Shinkolobwe, Shaba region, Democratic Republic of Congo [3]. Its synthetic analogue was known since 1962 [4]. The mineral is orthorhombic with space group $Pmba$, a 7.860(4), b 10.089(2), c 5.363(2) Å [1, 2] or $Pbcm$ with cell parameters a 5.363(3), b 10.161(4), and c 7.862(3) Å as confirmed from the crystal structure studies of synthetic schmitterite [5-7]. There are four formula units in the unit cell. Other uranium minerals containing tellurium include cliffordite $[\text{UTe}_3\text{O}_9]$ and moctezumite $[\text{PbUO}_2(\text{TeO}_3)_2]$ [8-11]. Only few details are known about the formation of uranyl tellurite minerals. They occur where sulfides are undergoing oxidation which provide tellurium [12]. Thermodynamic data are reported for synthetic cliffordite and synthetic schmitterite [7, 13, 14]. Thermal stability of synthetic uranyl tellurites and tellurates including cliffordite and schmitterite was studied [15]. Infrared spectra of synthetic cliffordite [16] and synthetic schmitterite [17] have been published. Crystal structures of synthetic cliffordite [5, 18] synthetic schmitterite [6, 7, 19] and moctezumite [11] and of some synthetic uranyl tellurites [20-23] are known.

In schmitterite, the uranium shows a 2-5 coordination (UO_2O_5) and the tellurium is 4 coordinated. The uranyl polyhedra share edges to form chains, which are the main structural units [24]. According to Burns [25-27], uranyl anion sheet topology in schmitterite is related to the uranophane-type anion sheet topology, in which the pentagons are populated by uranyl ions thus forming uranyl pentagonal dipyramids and the squares of the anion topology contain Te^{4+}O_4 polyhedra [27]. Because of the lone pair of electrons on the Te^{4+} cation, all four oxygen ligands are

* Author to whom correspondence should be addressed (r.frost@qut.edu.au)

located at the same side of the cation. The composition of the sheets is $[(\text{UO}_2)(\text{TeO}_3)]$. These sheets are neutral. No interlayer constituents are present in the interlayer of the crystal structure of schmitterite. Adjacent sheets are held together by van der Waals forces and weak Te-O interactions over distances exceeding 3.1 Å [25, 27].

Infrared spectrum of synthetic schmitterite was described and partly interpreted by Botto [17]. The Raman spectrum of synthetic schmitterite was only shortly mentioned in Botto's paper without any details. According to Botto [17], bands of the $\nu_3 (\text{UO}_2)^{2+}$ lie at 937 and 882 cm^{-1} . Evidently, the presence of two bands assigned to the $\nu_3 (\text{UO}_2)^{2+}$ must be due to the difference between the two U-O bond lengths, which lowers the symmetry. The infrared band at 818 cm^{-1} is assigned to the ν_1 symmetric stretching mode and is purportedly found at 830 cm^{-1} in the Raman spectrum. According to Čejka [28] for the pyramidal selenite and tellurite ions with point symmetry C_{3v} there are six normal vibrations with four fundamentals. For the $(\text{TeO}_3)^{2-}$ unit, the $\nu_1 (A_1)$ mode occurs at 740 cm^{-1} , the $\nu_2 (A_2)$ mode at 400 cm^{-1} , the $\nu_3 (E)$ mode at 665 cm^{-1} . The $\nu_4 (E)$ mode was not defined but was suggested that the vibration may be found at 345 cm^{-1} . All vibrational modes should be both infrared and Raman active. Solomonik and Marenich [29, 30] presented structure, force fields and vibrational spectra of alkali tellurites via ab initio calculations. Day et al. [31] discussed matrix-isolation studies on the vaporization of alkali-metal tellurites on the basis of their infrared spectra.

The aim of this paper to present the Raman spectrum of natural schmitterite, to interpret the observed bands and shoulders, and to infer the U-O bond lengths from the wavenumbers of the bands attributed to the $(\text{UO}_2)^{2+}$ stretching vibrations which enables their comparison with the data from the X-ray single crystal structure analysis of synthetic schmitterite. The paper is a part of our systematic study of the Raman and infrared spectra related crystal chemistry of the uranyl minerals .

Experimental

Minerals

Two schmitterite samples (Registered numbers M25802 and M30643) were obtained from Museum Victoria. The schmitterite originated from the Shinkolobwe mine, Shaba, Democratic Republic of Congo.

Raman microprobe spectroscopy

The crystals of schmitterite were placed and orientated on the stage of an Olympus BHSM microscope, equipped with 10x and 50x 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 order to ensure that the correct spectra are obtained, the incident excitation radiation was scrambled.

It should be noted that because of the very small amount of sample supplied on loan from the museum, it was not possible to run the infrared spectrum. This does show a major advantage of Raman spectroscopy in the study of uranium minerals is the ability to study very small amounts of mineral. Spectra at liquid nitrogen temperature were obtained using a Linkam thermal stage (Scientific Instruments Ltd, Waterfield, Surrey, England). Details of the technique have been published elsewhere by the authors [32-35].

The reason for collecting spectral data at 77 K is several fold (a) the technique enables better band separation and makes the attribution of the bands easier (b) collecting spectral data at 77 K acts as a check on the 298 K spectra. This is important when IR data are not obtainable because of the sample size. The spatial resolution in infrared spectroscopy is at best 25 microns where as in Raman microscopy the spatial resolution is between 0.8 and 1.0 microns. (c) any significant changes in spectra give an indication of phase or structure transitions at 77 K. It is noted that almost no Raman spectral data are available for tellurites and especially uranyl tellurites.

Results and discussion

Raman spectroscopy

The $D_{\infty h}$ symmetry lowering of the uranyl and C_{3v} of the tellurite units in the crystal structure of schmitterite causes activation of all uranyl vibrations in the Raman spectra and splitting of the doubly degenerate ν_2 (δ) $(UO_2)^{2+}$ bending vibration, and also the splitting of the both doubly degenerate ν_3 $(TeO_3)^{2-}$ antisymmetric stretching and ν_4 $(TeO_3)^{2-}$ bending vibrations.

The observed Raman spectra of schmitterite may be divided in at least three or four regions. Bands observed at wavenumbers higher than 800 cm^{-1} were attributed to the $(UO_2)^{2+}$ stretching vibrations. U-O bond lengths in uranyls calculated with the empirical relations by Bartlett and Cooney [36] are given in parentheses. Botto [17] assigned bands at 937 (1.759 \AA) and 882 (1.798 \AA) cm^{-1} in the IR spectrum of synthetic schmitterite to the ν_3 $(UO_2)^{2+}$ antisymmetric stretching vibrations. The corresponding weak band was observed at 876.3 (1.802 \AA) cm^{-1} in the Raman spectrum. The Raman band at 837.6 (1.774 \AA) cm^{-1} is related to the IR band at 818 (1.793 \AA) cm^{-1} and may be attributed to the ν_1 $(UO_2)^{2+}$ symmetric stretching vibration. Botto [17] also mentioned a very strong Raman band at 830 cm^{-1} and assigned this band to the uranyl symmetric stretching vibration. However, Botto does not publish any other details of the Raman spectrum of synthetic schmitterite.

The band at 823.3 (1.787 \AA) cm^{-1} may be assigned to the ν_1 $(UO_2)^{2+}$. The observed U-O bond lengths in uranyls are close to the average value 1.815 \AA [19] and 1.805 \AA [6] and agree also with the values proposed by Burns [25-27] for the uranyl natural and synthetic compounds having the uranyl pentagonal dipyramidal coordination polyhedra in their crystal structures. The number of the uranyl stretching vibrations observed in Raman and infrared spectra of schmitterite is not in disagreement with the asymmetry of the $(O-U-O)^{2+}$ bonds, FGA and number of molecules in the unit cell of schmitterite. Bands observed in the region $600\text{-}800\text{ cm}^{-1}$ are connected with the $(Te-O)$ stretching vibrations in $(TeO_3)^{2-}$. IR bands at 740 and 665 cm^{-1} were assigned to the ν $(Te-O)$ stretching vibrations [17]. Raman bands at

749.5, 677 and 606.3 cm^{-1} (298 K) and 736.4, 685 and 591.3 cm^{-1} (77 K) were attributed to the split doubly degenerate antisymmetric stretching vibration ν_3 (TeO_3)²⁻. A very strong Raman band at 723.7 (298 K) and 723.2 (77 K) cm^{-1} is assigned to the symmetric stretching vibration ν_1 (TeO_3)²⁻. The band width decreases significantly on obtaining the spectra at 77 K: the band width decreases from 17.7 to 11.9 cm^{-1} .

Botto [1984] attributed the IR band close to 400 cm^{-1} to the bending vibration δ (Te-O_n) [17]. Raman bands in the range 300 to 500 cm^{-1} are assigned to the ν_2 and the split doubly degenerate ν_4 (TeO_3)²⁻ bending vibrations, 504.2, cm^{-1} and 429.3, and 401.3 and 313.1 cm^{-1} (298 K), respectively, and 506.2 cm^{-1} and 431.7, and 403.8 and 315.1 cm^{-1} (77 K), respectively. Botto does not give any details on the interpretation of the IR bands in the region of wavenumbers lower than 400 cm^{-1} . Raman bands at 274.4 and 258.3 cm^{-1} (298 K) and 281.3 and 260.3 cm^{-1} (77 K) may be assigned to the ν_2 (δ) (UO_2)²⁺ bending vibrations. These Raman bands at 274.4, 258.3, 238.5 (298 K) show band widths of 16.0, 11.4 and 7.7 cm^{-1} . The band widths decrease to 7.1, 6.5 and 5.5 cm^{-1} at 77 K. Raman bands with lower wavenumbers are connected with lattice vibrations. Raman bands at 606.3 and 504.2 (298 K) and 591.3 and 506.2 (77 K) cm^{-1} may be probably connected with the ν (U-O_{lig}) vibrations. There may be assumed their coincidence with the split ν_3 (TeO_3)²⁻ vibrations. Botto also assigned IR bands at 565 and 537 cm^{-1} to the ν (U-O_{II}) vibrations [17].

Conclusions

Raman spectra of the secondary uranyl mineral schmitterite, UO_2TeO_3 , at 298 and 77 K are presented and interpreted and compared with the IR spectrum of schmitterite published by Botto [17]. U-O bond lengths in uranyl are calculated with two empirical relations $R_{\text{U-O}} = f[\nu_1(\text{UO}_2)^{2+}] \text{ \AA}$ and $R_{\text{U-O}} = f[\nu_3(\text{UO}_2)^{2+}] \text{ \AA}$. The empirical relations by Bartlett and Cooney are used [36]. Obtained U-O bond lengths are close to those inferred from the X-ray single crystal structure of synthetic schmitterite [6, 19] and in agreement with those observed in other natural or synthetic uranyl tellurites.

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List of Figures

Figure 1 Raman spectrum of schmitterite at 298 and 77 K in the 600 to 1000 cm^{-1} region.

Figure 2 Raman spectrum of schmitterite at 298 and 77 K in the 300 to 600 cm^{-1} region.

Figure 3 Raman spectrum of schmitterite at 298 and 77 K in the 100 to 300 cm^{-1} region.

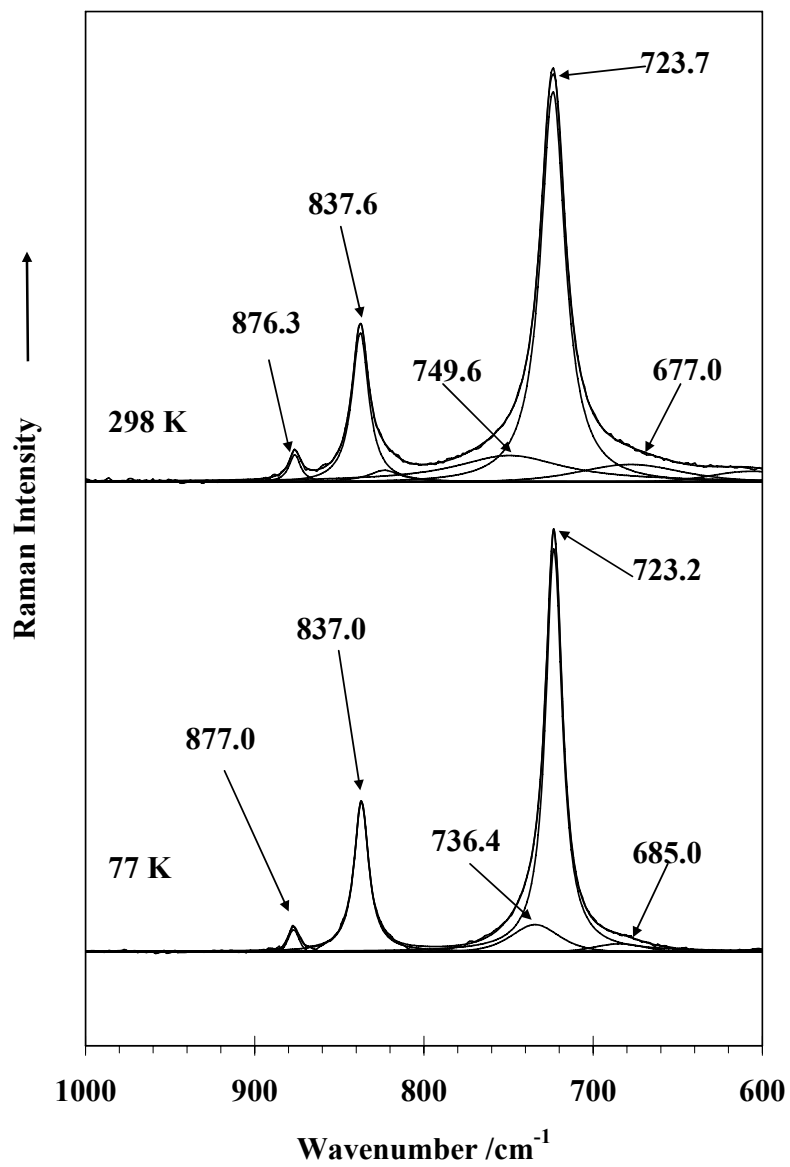


Figure 1

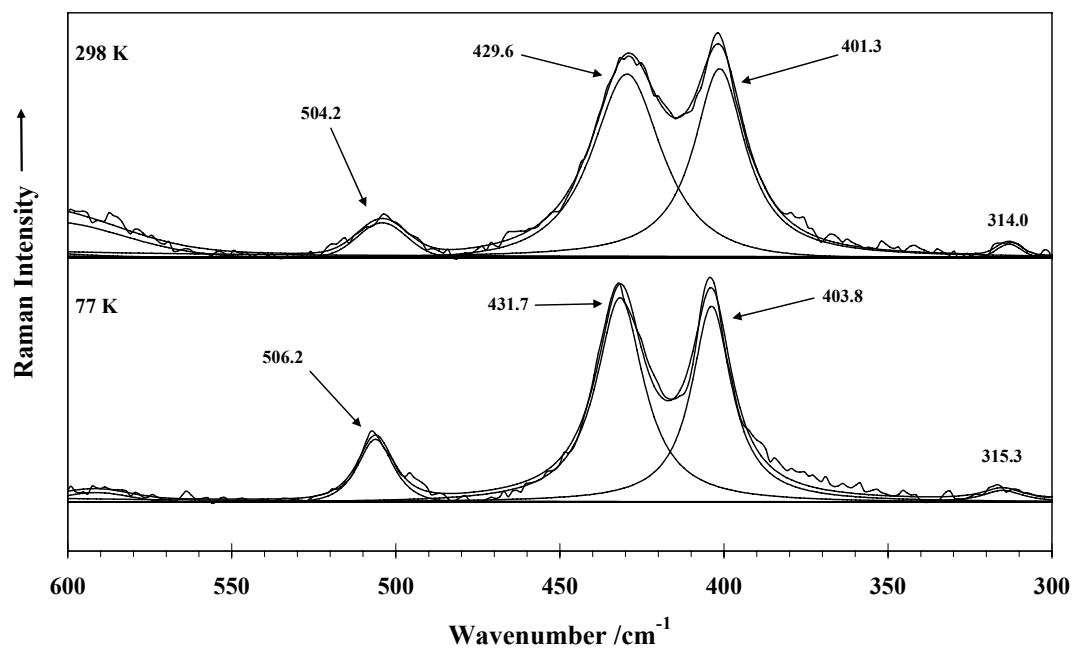


Figure 2

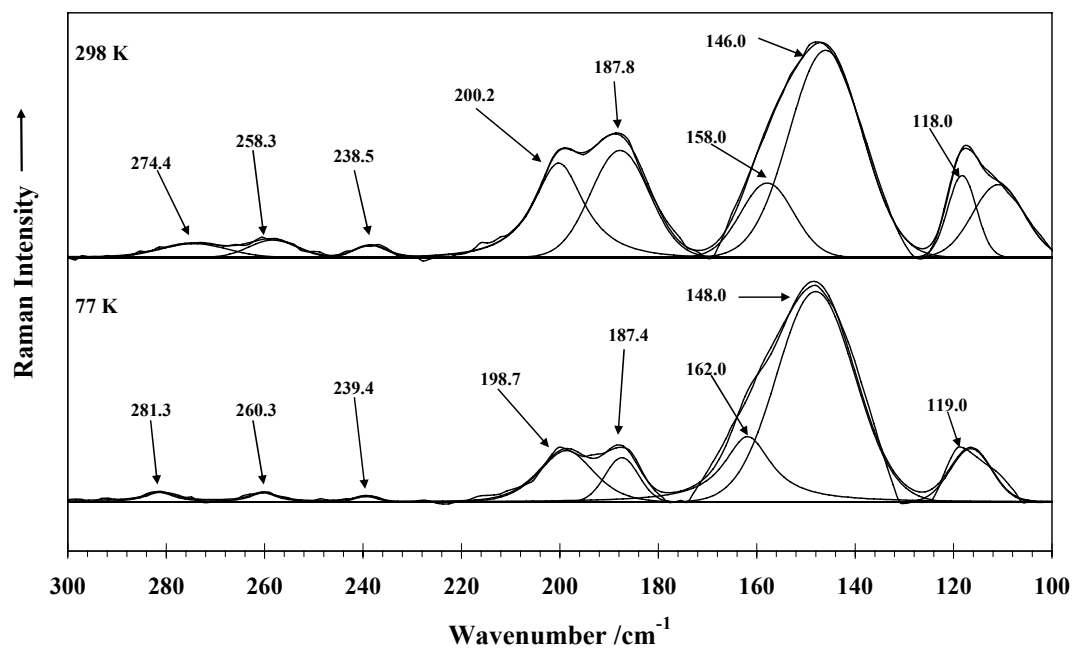


Figure 3

