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Raman spectroscopic study of the uranyl titanate mineral holfertite $Ca_xU_{2-x}Ti(O_{8-x}OH_{4x})\cdot 3H_2O$ and the lack of metamictization

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Abstract

Raman spectra of the uranyl titanate mineral holfertite $Ca_xU_{2-x}Ti(O_{8-x}OH_{4x})\cdot 3H_2O$ were analysed and related to the mineral structure. Observed bands are attributed to the TiO and $(UO_2)^{2+}$ stretching and bending vibrations, U-OH bending vibrations, H_2O stretching, bending. The mineral holfertite is metamict as is evidenced by order/disorder of the mineral. Unexpectedly the Raman spectrum of holfertite does not show any metamictization. The intensity of the UO stretching and bending modes show normal intensity and the bands are sharp.

KEYWORDS: holfertite, uranyl, titanium, mineral, betafite, Raman spectroscopy, U-O bond length

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INTRODUCTION

In the uranium processing industry, certain minerals are difficult to convert to yellow cake because of their formulation. Among these uranium minerals are those which contain titanium. These minerals include absite $Ti_7U_2ThO_{20}\cdot 5H_2O$, betafite $(Ca,U)_2(Ti,Nb)_2O_6(OH)$, brannerite $(U^{4+},REE,Th,Ca)(Ti,Fe^{3+},Nb)_2(O,OH)_6$, davidite-(La) $(La,Ce)(Y,U,Fe^{2+})(Ti,Fe^{3+})_{20}(O,OH)_{38}$ and holfertite $Ca_xU_{2-x}Ti(O_{8-x}OH_{4x})\cdot 3H_2O$ [1, 2]. The presence of holfertite and related minerals is of particular importance at the Ranger Uranium Mine, at Kakadu, Northern Territory, Australia. Holfertite is an hydrated calcium uranyl hydroxy titanate with a trigonal structure and consists of small yellow rod-like needles [1, 2]. The mineral has probably been formed through Metamictization **(**sometimes called metamiction**).** The exact formula of the mineral is imprecise because of disorder-order in the structure [2]. According to Belakovskiy et al. the structure of holfertite is based upon chains of U and Ti polyhedra linking through common vertices to form a framework with channels along (001). The channels are ~8 Å wide and are occupied by Ca and H_2O.

Belakovskiy et al. Reported an infrared spectrum of holfertite [1]. These authors reported an infrared spectrum which they felt was ambiguous in relation to the presence of OH units. Intense infrared bands at 3390 and 1621 cm^{-1} were attributed to H_2O stretching and bending vibrations. Uranyl groups were identified by an infrared band at 892 cm-1, presumably attributable to the antisymmetric stretching vibration. TiO was identified through the infrared band at 622 cm^{-1}. No Raman spectrum of holfertite has been published, although a Raman spectrum exists in the RRUFF data base (http://rruff.info/holfertite/display=default/).
Raman spectroscopy has proven very useful for the study of minerals. Indeed Raman spectroscopy has proven most useful for the study of diagentically related minerals as often occurs with minerals containing uranyl groups [3-7]. This paper is a part of systematic studies of vibrational spectra of minerals of secondary origin in the oxide supergene zone and their synthetic analogs. In this work we attribute bands at various wavenumbers to vibrational modes of holfertite using Raman spectroscopy and relate the spectra to the molecular tructure of the mineral.

EXPERIMENTAL

Minerals

The holfertite mineral used in this work was obtained from Museum Victoria. The sample originated from the Holfertite pit, Stravation Canyon (Searles Canyon) Thomas Range, Juab County, Utah, USA. The chemical composition of the mineral has been published [1]. A Raman spectrum was also downloaded from the RRUFF data base (http://rruff.info/holfertite/display=default/).. The sample also originated from Searle Canyon, Thomas Range, Juab County, Utah, USA

Raman microprobe spectroscopy

The crystals of holfertite 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. Previous studies by the authors provide more details of the experimental technique.

Spectral manipulation such as baseline adjustment, smoothing and normalisation were performed using the Spectracalc software package GRAMS (Galactic Industries Corporation, NH, USA). Band component analysis was undertaken using the Jandel ‘Peakfit’ software package which enabled the type of fitting function to be selected and allows specific parameters to be fixed or varied accordingly. Band fitting was done using a Lorentz-Gauss cross-product function with the minimum number of component bands used for the fitting process. The Lorentz-Gauss ratio was maintained at values greater than 0.7 and fitting was undertaken until reproducible results were obtained with squared correlations of r^2 greater than 0.995.

RESULTS AND DISCUSSION

It is noted that the XRD patterns show a disordered structure. Yet quality Raman spectra may be obtained indicating that the disorder does not occur at the molecular level. The Raman spectrum of holfertite is displayed in Figure 1. An intense sharp band is observed at 828 cm^{-1} and is assigned to the UO_2^{2+} symmetric stretching mode. In the infrared spectrum a broadish band was observed at 892 cm^{-1} and is assigned to the UO_2^{2+} antisymmetric stretching mode. The Raman spectrum of holfertite downloaded from the RRUFF data base is given in Figure 2. A sharp intense band is observed at 812 cm^{-1} and corresponds to the 828 cm^{-1} band observed in this work.

The Raman spectrum displays a sharp band at 749 cm^{-1}. It is likely that this band is due to the TiO stretching vibration of TiO_4 units in the holfertite structure. In the RRUFF spectrum a Raman band at 733 cm^{-1} is observed. In the infrared spectrum of Belakovskiy et al. [1] A quite broad band at 622 cm^{-1} was assigned to the TiO stretching vibrations. These authors proposed that an infrared band at 3420 cm^{-1} was due to overtones of the TiO stretching vibration. Such an assignment seems unlikely. A low intensity Raman band at 641 cm^{-1} is observed. This band may be also associated with TiO vibrations. A Raman band at 628 cm^{-1} was observed in the RRUFF spectrum. A very intense sharp band is observed at 389 cm^{-1} (Figure 1) and at 384 cm^{-1} (Figure 2). This band is associated with OTiO bending vibrations. Other low intensity bands are observed at 328, 257, 201 and 144 cm^{-1}. The latter three bands are associated with OUO bending vibrations. An intense band at 159 cm^{-1} was observed in the RRUFF spectrum and is the bending mode of the OUO units.

The Raman spectrum in the 1000 to 3800 cm^{-1} region is reported in Figure 3. The spectrum suffers a little from a lack of signal to noise, nevertheless Raman bands may be resolved as shown. An intense sharp band is observed at 3500 cm^{-1} with a shoulder at 3406 cm^{-1}. There are two possible assignemnts for these bands a) the bands are due to water stretching vibrations and b) the bands are due to stretching vibrations iof the OH units. In the infrared spectrum reported by Belakovskiy et al. The band at 3390 cm^{-1} was assigned to a water stretching vibration. These authors also observed an infrared band at 3240 cm^{-1}. Two Raman bands are observed at 2866 and 2925 cm^{-1}. These bands may be due to organic molecules on the surface of the mineral. A Raman band at 1628 cm^{-1} is observed and is assigned to a water bending vibration. A Raman band at 1128 cm^{-1} is also observed and the position of this band suggests it may be assigned to a UOH bending mode.

The effect of metamictization

Metamictization is a natural process in which a mineral self destructs, usually through the loss of an alpha particle. This process involves the random expansion of the unit cell with consequent lengthening of the UO bonds. This results in a decrease in the expected intensity of the Raman bands associated with UO_2^{2+} units and also a significant broadening of the bands. Metamictization causes the disorder in the holfertite mineral. However in the Raman spectra of holfertite the peaks are sharp and intense, suggesting at least at the molecular level that metamictization has not affected the structure. Our studies have shown that uranyl containing minerals including absite $Ti_7U_2ThO_{20}\cdot 5H_2O$, betafite $(Ca,U)_2(Ti,Nb)_2O_6(OH)$, brannerite $(U^{4+},REE,Th,Ca)(Ti,Fe^{3+},Nb)_2(O,OH)_6$, davidite-(La) $(La,Ce)(Y,U,Fe^{2+})(Ti,Fe^{3+})_{20}(O,OH)_{38}$ all show the effect of metamictization with a large decrease in the intensity of bands associated with UO_2^{2+} units and broadening of the bands.

CONCLUSIONS

The minerals containing the uranyl group and titanium as an oxide are of interest because of their difficulty in mineral processing. These minerals include holfertite, davidite, bannerite, betafite. Observed Raman bands are attributed to the $(UO_2)^{2+}$ and TiO stretching and bending vibrations, U-OH and OTiO bending vibrations. Minerals such as holfertite undergo a process of metamictization, a process of crystal self destruction. This process involves the expansion of the unit cell in a random manner. This expansion causes a lengthening in the UO bond length. This effect is probably responsible for the disorder/ order in the mineral holfertite and the lack of a precise formula for the mineral. At the molecular level the effect of metamictization is not observed. The Raman spectra of holfertite do not appear to show the effects of metamictization. No decrease in intensity of bands associated with $(UO_2)^{2+}$ units is observed.

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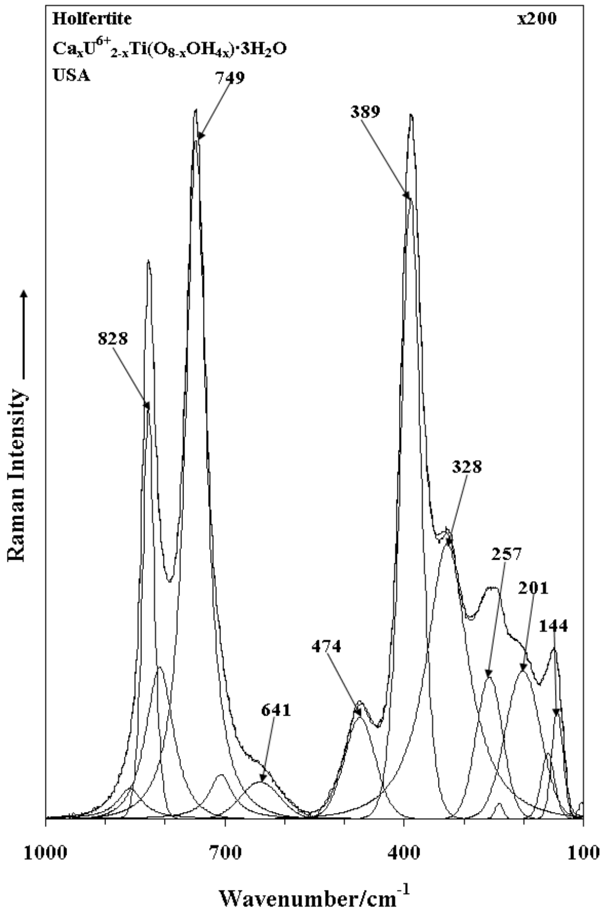
Holfertite
$Ca_xU^{6+}_{2-x}Ti(O_{8-x}OH_{4x})\cdot 3H_2O$
USA
x200
749
389
828
328
257
201
144
474
641
Raman Intensity
1000
700
400
100
Wavenumber/cm^{-1}

Figure 1

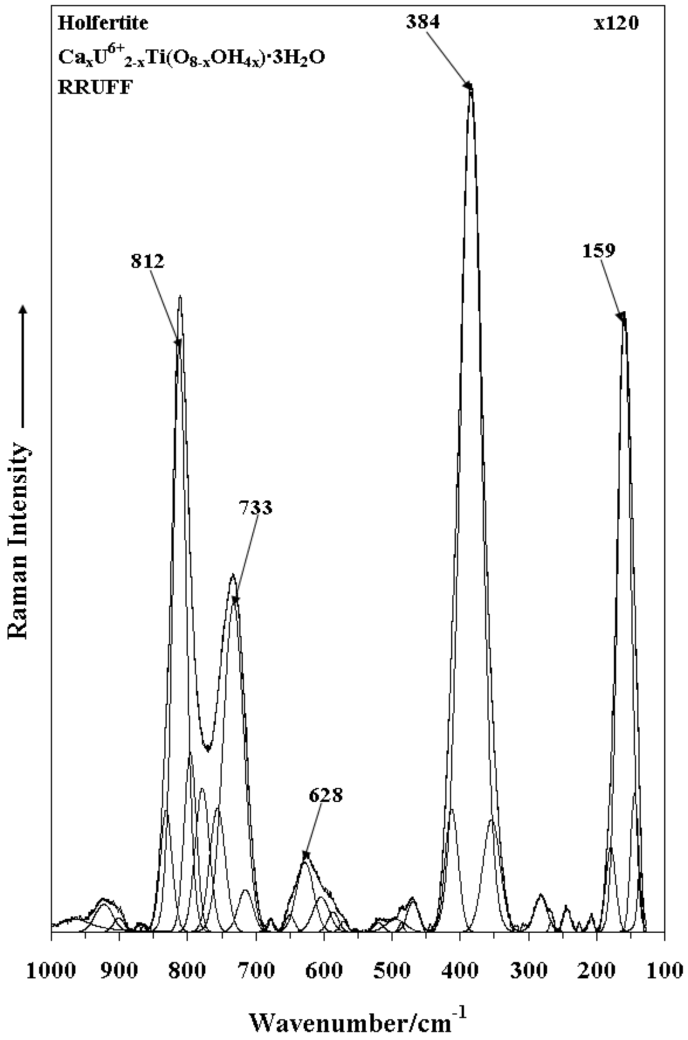

Figure 2 RRUFF

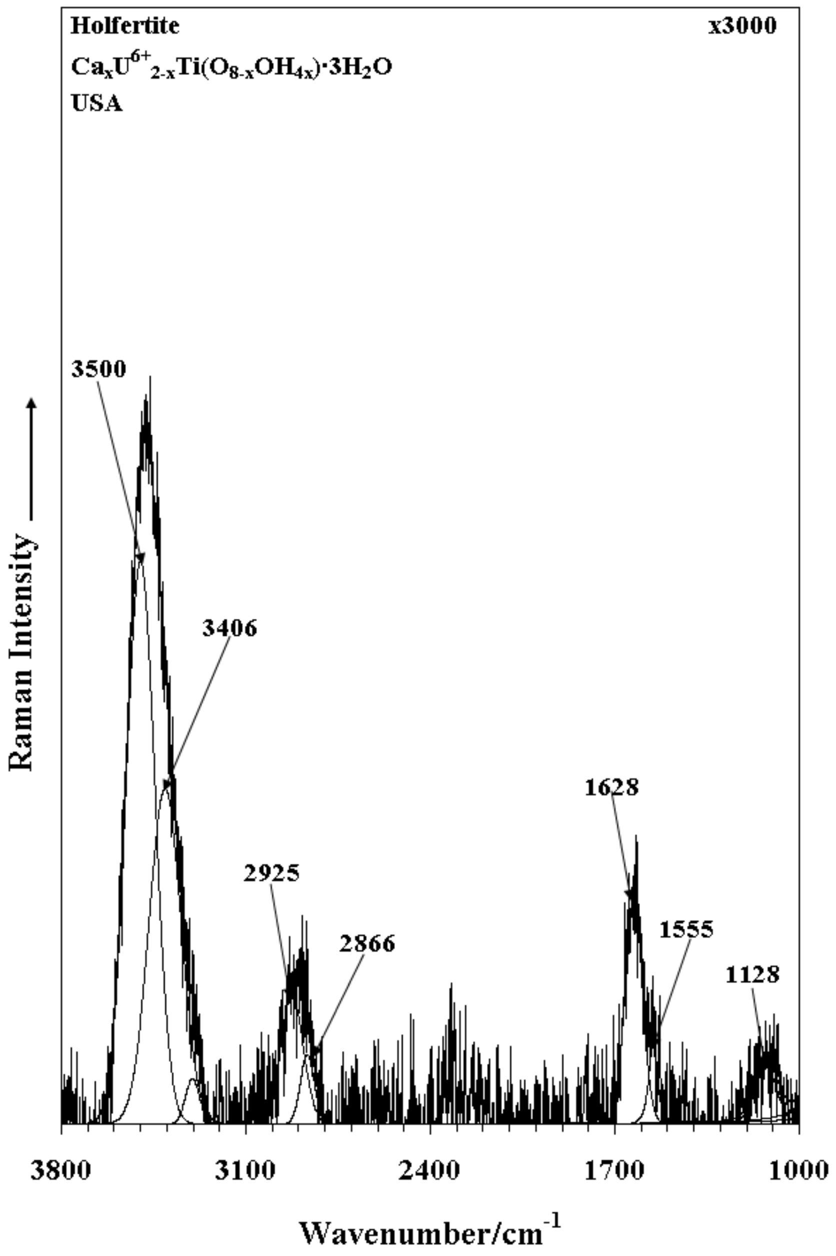
Holfertite
$Ca_xU^{6+}_{2-x}Ti(O_{8-x}OH_{4x})\cdot 3H_2O$
USA
x3000
Raman Intensity
3500
3406
2925
2866
1628
1555
1128
3800
3100
2400
1700
1000
Wavenumber/cm^{-1}

Figure 3