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Raman spectroscopic study of the selenite mineral -ahlfeldite $\text{NiSeO}_3 \cdot 2\text{H}_2\text{O}$

Ray L. Frost^{*} and Eloise C. Keeffe

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

Raman spectroscopy has been used to study the selenite mineral ahlfeldite. A comparison is made with the Raman spectra of chalcomenite, cobaltomenite and clinochalcomenite. Selenite minerals are characterised by the position of the symmetric stretching mode which is observed at higher wavenumbers than the antisymmetric stretching mode. The selenite ion has C_{3v} symmetry and four modes, $2A_1$ and $2E$. These modes are observed at $813, 472 \text{ cm}^{-1}$ (A_1) and $685, 710, 727$ and 367 and 396 cm^{-1} (E). Bands assigned to the water stretching vibrations are observed for ahlfeldite at 3385 cm^{-1} , for chalcomenite at $2953, 3184$ and 3506 cm^{-1} and for clinochalcomenite at $2909, 3193$ and 3507 cm^{-1} . A comparison of the Raman spectra of chalcomenite, clinochalcomenite and cobaltomenite is made. The position of these bands enabled hydrogen bond distances in the selenite structure to be estimated. Hydrogen bond distances for ahlfeldite, chalcomenite and clinochalcomenite were determined to be similar.

KEYWORDS: selenite, Raman spectroscopy, ahlfeldite, chalcomenite,
clinochalcomenite, cobaltomenite, marthozite, mandarinoite

INTRODUCTION

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

Selenites and tellurites may be subdivided according to formula and structure¹. There are five groups, based upon the formulae (a) $A(XO_3)$, (b) $A(XO_3) \cdot xH_2O$, (c) $A_2(XO_3)_3 \cdot xH_2O$, (d) $A_2(X_2O_5)$ and (e) $A(X_3O_8)$. Of the selenites, molybdomenite is an example of type (a); chalcomenite, clinochalcomenite, cobaltomenite and ahlfeldite are minerals of type (b); mandarinoite is an example from group (c). There are no known examples of selenite minerals with formula (d) and (e). Examples of these groups are found with tellurite minerals. Of the selenites is the mineral chalcomenite and its dimorph clinochalcomenite. Chalcomenite, $CuSeO_3 \cdot 2H_2O$, is a rare secondary mineral found in the oxidised deposits of Cu-Se bearing minerals. This mineral in comparison with ahlfeldite, is orthorhombic with point group 222²⁻⁴. Chalcomenite is dimorphous with the monoclinic clinochalcomenite and is normally found as powdery crusts or massive films with crystal growth along the (001) direction. The mineral ahlfeldite $(Ni,Co)SeO_3 \cdot 2H_2O$ is monoclinic and point group 2/m.⁵ The mineral forms part of a series between ahlfeldite $(Ni,Co)SeO_3 \cdot 2H_2O$ and cobaltomenite $(Co)SeO_3 \cdot 2H_2O$. The mineral displays large crystals elongated along the 001 axis superimposed upon the host matrix.

Raman spectroscopy has proven very useful for the study of minerals. In deed, Raman spectroscopy has proven most useful for the study of diagenetically related minerals, as often occurs with many minerals. Some previous studies have been undertaken by the authors, in which Raman spectroscopy was used to study complex secondary minerals formed by crystallisation from concentrated sulphate solutions⁶⁻¹⁰. The aim of this paper is to present Raman spectra of a natural selected selenite, namely ahlfeldite, and to discuss the spectra from a structural point of view. It is a part of systematic studies on the vibrational spectra of minerals of secondary origin in the oxide supergene zone and their synthetic analogs.

EXPERIMENTAL

Minerals

The ahlfeldite mineral was supplied by the Mineralogical Research Company and originated from the Pacajake Mine, Bolivia. The analysis of the mineral has been

published by Anthony *et al.*⁵. The mineral contains 50.0 SeO₂, 3.55% CoO and 30.24% NiO.

The chalcocite samples originated from El Dragon Mine, Potosi, Bolivia and Eagle Claims, Beaverlodge Lake Area, Saskatchewan, Canada. The clinochalcocite sample also originated from El Dragon Mine, Potosi, Bolivia. The cobaltocite samples originated from Parco Mine, Thompson's District, Grand County, Utah, USA and from El Dragon Mine, Potosi, Bolivia. Anthony *et al.* reported the typical composition of these minerals⁶ to be 48.9% SeO₂, 35.1% CuO and 15.9% H₂O. Clinochalcocite, a dimorphous mineral, has a similar composition; as does the cobalt analogue, cobaltocite.

Raman microprobe spectroscopy

The crystals of chalcocite were placed and orientated on the stage of an Olympus BHSM microscope, equipped with 10x and 50x objectives as 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. Details of the technique have been published by the authors¹¹⁻¹⁸.

Spectroscopic manipulation such as baseline adjustment, smoothing and normalisation were performed using the Spectralcalc 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 Gauss-Lorentz cross-product function with the minimum number of component bands used for the fitting process. The Gauss-Lorentz 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

Farmer states that very little research has been undertaken on selenates. No minerals with the selenate ion SeO_4^{2-} have been discovered and reported¹⁹. The infrared spectra of $\text{CuSeO}_3 \cdot 2\text{H}_2\text{O}$ has been reported by Sathinadan *et al.*²⁰ and Makutan *et al.*²¹. Farmer reports that the band positions of selenates are readily distinguished from that of selenites. The selenite ion should show a maximum of six bands. The free ion will have C_{3v} symmetry and four modes, $2A_1$ and $2E$. Nakamoto²² gives these as $807, 432 \text{ cm}^{-1}$ (A_1) and $737, 374 \text{ cm}^{-1}$ (E). The comment may be made that there is very little published on the vibrational spectroscopy of selenite or selenate minerals, especially the Raman spectroscopy of selenites, including ahlfeldite.

The Raman spectra of the ahlfeldite mineral in the 700 to 1200 cm^{-1} region are shown in Fig. 1. The intense band at 832 cm^{-1} is assigned to the symmetric stretching $(\text{SeO}_3)^{2-}$ units. The Raman bands at 1055 and 1093 cm^{-1} are assigned to carbonate bands. The carbonate mineral is the host matrix upon which the ahlfeldite mineral formed. The spectrum of ahlfeldite may be compared with the other selenite minerals chalcomenite, clinochalcomenite and cobaltomenite. Intense Raman bands at 813 cm^{-1} for chalcomenite and 811 cm^{-1} for clinochalcomenite have been observed and assigned to the symmetric stretching $(\text{SeO}_3)^{2-}$ units. There is a small difference between the band position of the two polymorphs. The symmetric stretching $(\text{SeO}_3)^{2-}$ of cobaltomenite is observed at 813 cm^{-1} . The spectroscopy of selenites is interesting in that, like many mineral arsenates, the symmetric stretching mode is observed at higher wavenumbers than the antisymmetric stretching mode. The values of ν_1 based upon infrared spectra for sodium, calcium and copper selenites are $788, 784$ and 774 cm^{-1} . Vlaev has shown that the band positions in the infrared spectra of cobalt selenites depends upon the degree of hydration^{23,24}.

Raman bands are observed at 719 and 751 cm^{-1} and assigned to the ν_3 $(\text{SeO}_3)^{2-}$ antisymmetric stretching mode. The spectrum of ahlfeldite may be compared with the other selenite minerals chalcomenite, clinochalcomenite and cobaltomenite. Raman bands for chalcomenite are observed in each of the spectra within the 685 to 750 cm^{-1} region. The chalcomenite mineral from Canada shows three bands at $685, 710$ and

727 cm^{-1} . Two Raman bands are resolved at 690 and 720 cm^{-1} for the Bolivian chalcomenite. Two Raman bands are also observed for the clinochalcomenite at 709 and 749 cm^{-1} . These bands are attributed to the ν_3 $(\text{SeO}_3)^{2-}$ antisymmetric stretching modes. The Raman spectrum of cobaltomenite shows a single band at 716 cm^{-1} , which is assigned to the ν_3 $(\text{SeO}_3)^{2-}$ antisymmetric stretching mode. It is suggested that the selenate anion is in a perturbed state in the mineral ahlfeldite as more than one ν_3 $(\text{SeO}_3)^{2-}$ antisymmetric stretching mode is observed. This distortion is less for cobaltomenite as only a single band is observed.

The Raman spectrum of ahlfeldite in the 100 to 700 cm^{-1} region is displayed in Fig. 2. Raman bands are observed for ahlfeldite at 408 cm^{-1} . This band is assigned to the $(\text{SeO}_3)^{2-}$ ν_2 bending mode. Two other bands are observed at 508 and 532 cm^{-1} . These bands may be assigned to this mode but another likely assignment is to the water librational modes. The band at 348 cm^{-1} is ascribed to the $(\text{SeO}_3)^{2-}$ ν_4 bending mode. A previous study gave the values for ν_2 bands as occurring between 449 and 461 cm^{-1} and the ν_4 bands between 387 and 427 cm^{-1} , where the band at around 472 cm^{-1} was attributed to ν_2 bending mode. Some variation in band position is observed for clinocomenite where the band is found at 489 cm^{-1} . It is suggested that the difference in band position may be attributed to the differing crystallographic systems in the structure of chalcomenite and clinochalcomenite. Two bands are observed for cobaltomenite at 512 and 443 cm^{-1} . The latter band is assigned to the ν_2 bending mode. A second band for cobaltomenite is observed at 421 cm^{-1} which is also assigned to this bending mode. Bands are observed at 367 and 396 cm^{-1} for chalcomenite and 349, 361 and 378 cm^{-1} for clinochalcomenite. These bands are ascribed to the ν_4 bending mode. The Raman band at 570 cm^{-1} for chalcomenite and clinochalcomenite is assigned to a water librational mode. The band is observed at 512 cm^{-1} for cobaltomenite.

The spectroscopy of selenites is interesting in that, like many mineral arsenates, the symmetric stretching mode is observed at higher wavenumbers than the antisymmetric stretching mode. The values of ν_1 for sodium, calcium and copper selenites are at 788, 784 and 774 cm^{-1} . In contrast, the values for the ν_3 antisymmetric stretching mode occur at 740, 713 and 714 cm^{-1} . The value for ν_2 bands occurs between 449 and 461 cm^{-1} and ν_4 bands between 387 and 427 cm^{-1} . Bäumer *et al.*

proved that in the case of infrared spectra of M^{2+} selenite monohydrates, the stretching vibrations of selenite units are located in the regions $760 \leq \nu_1 \text{ SeO}_3 \leq 855 \text{ cm}^{-1}$ and $680 \leq \nu_3 \text{ SeO}_3 \leq 775 \text{ cm}^{-1}$. These authors attributed the Raman (infrared) bands in the spectra of UO_2SeO_3 at 381 and 389 (390) cm^{-1} to the $\nu_4 (\text{SeO}_3)^{2-}$, at 497 (500) cm^{-1} to the $\nu_2 (\text{SeO}_3)^{2-}$, as 724 and 731 (700) cm^{-1} to the $\nu_3 (\text{SeO}_3)^{2-}$, 829 (820-840) cm^{-1} to the $\nu_1 (\text{SeO}_3)^{2-}$, and bands at 878 (875 sh) and 884 (920-940) cm^{-1} to the ν_1 and $\nu_3 (\text{UO}_2)^{2+}$, respectively. The same authors assigned observed Raman and infrared bands for $(\text{NH}_4)_2(\text{UO}_2)_2(\text{SeO}_3)_3 \cdot 6\text{H}_2\text{O}$ at 384, 390 (395), 475 (498), 731 and 829 (700 and 830), and 800 (808) cm^{-1} to the ν_4 , ν_2 , ν_3 and ν_1 modes, respectively, and those at 879 and 883 (872), and (900) cm^{-1} to the ν_1 and $\nu_3 (\text{UO}_2)^{2+}$ modes, respectively. Similar spectra were observed and interpreted for $\text{K}_2(\text{UO}_2)_2(\text{SeO}_3)_3 \cdot 2\text{H}_2\text{O}$, $(\text{NH}_4)_2(\text{UO}_2)(\text{SeO}_3)_2$, and $\text{K}_2(\text{UO}_2)(\text{SeO}_3)_2 \cdot 3\text{H}_2\text{O}$. The results of the Raman spectrum of chalcomenite fit well with the published results

The Raman spectra of ahlfeldite in the 1900 to 3700 cm^{-1} region are shown in Fig. 3. The spectra suffer from low signal to noise. This no doubt due to water being a very poor Raman scatterer. A Raman band at 3388 cm^{-1} is observed. The band is not symmetric and may be resolved into component bands as is shown in the Fig.. Studies have shown a strong correlation between OH stretching frequencies and both O...O bond distances and H...O hydrogen bond distances. Libowitzky showed that a regression function can be employed, relating the hydroxyl stretching frequencies with regression coefficients better than 0.96 using infrared spectroscopy²⁵. The function is described as: $\nu_1 = (3592 - 304) \times 109^{\frac{-d(O-O)}{0.1321}} \text{ cm}^{-1}$. Thus OH...O hydrogen bond distances may be calculated using the Libowitzky empirical function.

For chalcomenite, three bands are observed at 2953, 3184 and 3506 cm^{-1} . For clinochalcomenite bands at 2909, 3193 and 3507 cm^{-1} are observed in similar positions. Three bands may be resolved at 2962, 3209 and 3450 cm^{-1} . The values for the OH stretching vibrations listed above provide hydrogen bond distances of 2.630 (0) Å (2909 cm^{-1}), 2.701(5) Å (3193 cm^{-1}) and 2.906(6) Å (3507 cm^{-1}) for clinochalcomenite and 2.639(3) Å (2953 cm^{-1}), 2.6986(1) Å (3184 cm^{-1}) and 2.904(7) Å (3506 cm^{-1}) for chalcomenite. The hydrogen bond distances for cobaltomenite are 2.641(2) Å (2962 cm^{-1}), 2.707(0) Å (3209 cm^{-1}) and 2.838(0) Å (3450 cm^{-1}).

Differences in the hydrogen bond distances between the cobaltomenite and chalcomenite are observed. Such hydrogen bond distances are typical of secondary minerals. A range of hydrogen bond distances are observed from reasonably strong to weak hydrogen bonding. This range of hydrogen bonding contributes to the stability of the mineral.

CONCLUSIONS

It is interesting that, in nature, selenites are formed as opposed to selenates. Thus, minerals based upon $(\text{SeO}_3)^{2-}$ units are formed. Among these naturally occurring selenite minerals are ahlfeldite, chalcomenite and clinochalcomenite as well as a significant number of uranyl selenate minerals. Raman spectroscopy has been used to characterise these selenite minerals, probably for the first time. Intense Raman bands for ahlfeldite are observed at 832 and 803 cm^{-1} . These bands are assigned to the symmetric and antisymmetric stretching modes of $(\text{SeO}_3)^{2-}$ units. A comparison may be made with the other selenite minerals chalcomenite and clinochalcomenite. Intense Raman bands at 813 cm^{-1} for chalcomenite and at 811 cm^{-1} for clinochalcomenite are assigned to the symmetric stretching $(\text{SeO}_3)^{2-}$ units. Low intensity bands at 685, 710 and 727 cm^{-1} are attributed to the ν_3 $(\text{SeO}_3)^{2-}$ antisymmetric stretching mode.

The intense Raman band of ahlfeldite at 430 cm^{-1} is assigned to the $(\text{SeO}_3)^{2-}$ ν_2 bending mode. The Raman band for chalcomenite and clinochalcomenite at around 472 cm^{-1} is attributed to the ν_2 bending modes. Some variation in band position is observed for clinocomenite where the band is found at 489 cm^{-1} . It is proposed that the difference in the band position may be attributed to the differing crystallographic structural system of chalcomenite and clinochalcomenite. In the OH stretching region an intense band is observed for ahlfeldite at 33856 cm^{-1} . For chalcomenite three bands are observed at 2953, 3184 and 3506 cm^{-1} and for clinochalcomenite they are observed at 2909, 3193 and 3507 cm^{-1} . These bands are assigned to the water stretching vibrations. These values have been used to determine hydrogen bond distances which range from reasonably strong to weak hydrogen bonding. This range of hydrogen bonding contributes to the stability of the mineral.

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List of Figs

Fig. 1 Raman spectrum of ahlfeldite in the 700 to 900 cm^{-1} region

Fig. 2 Raman spectrum of ahlfeldite in the 100 to 700 cm^{-1} region

Fig. 3 Raman spectrum of ahlfeldite in the 1900 to 3700 cm^{-1} region

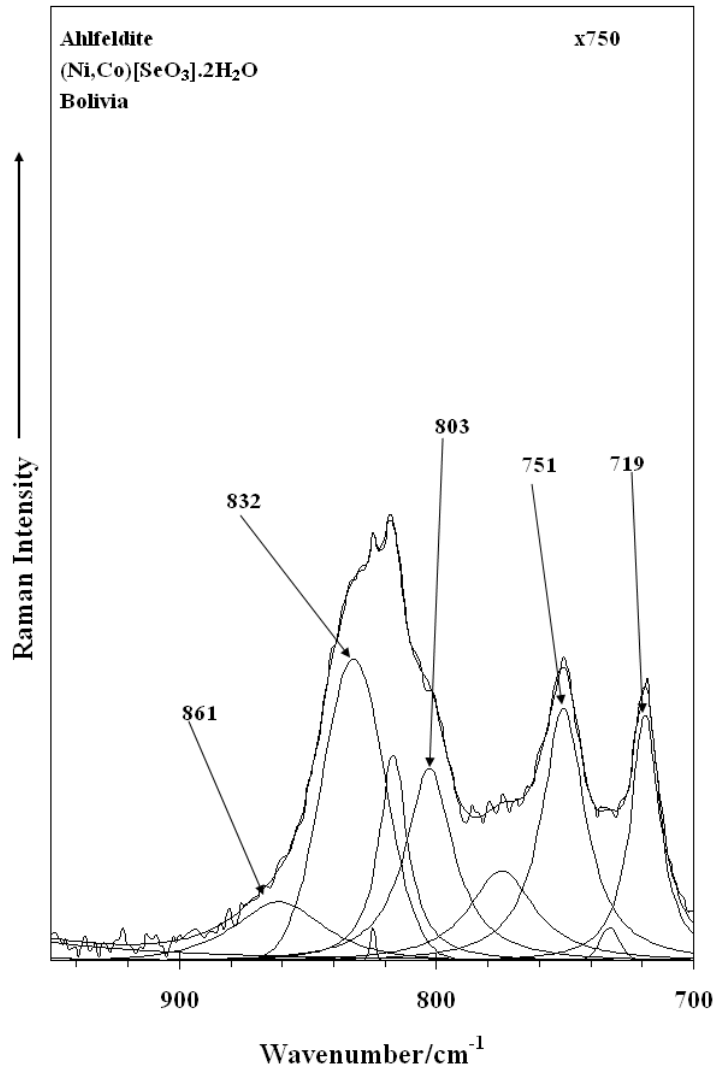


Fig. 1

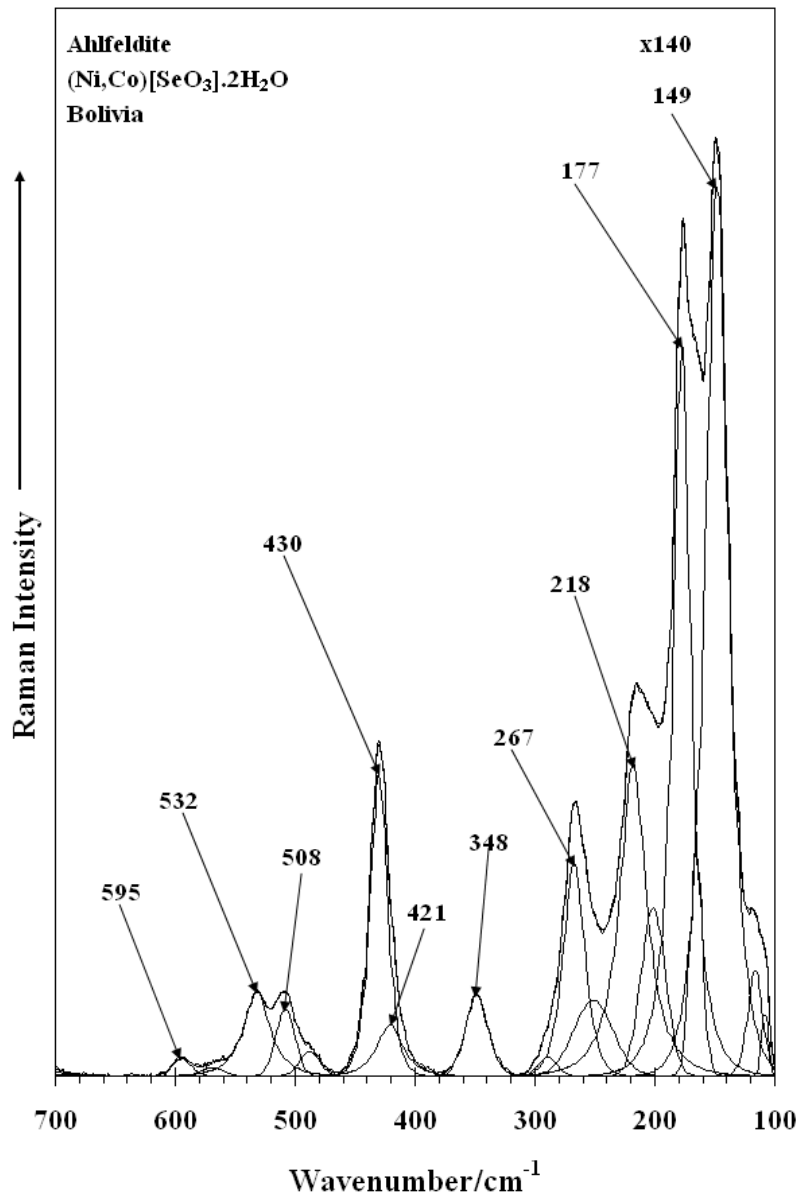


Fig. 2

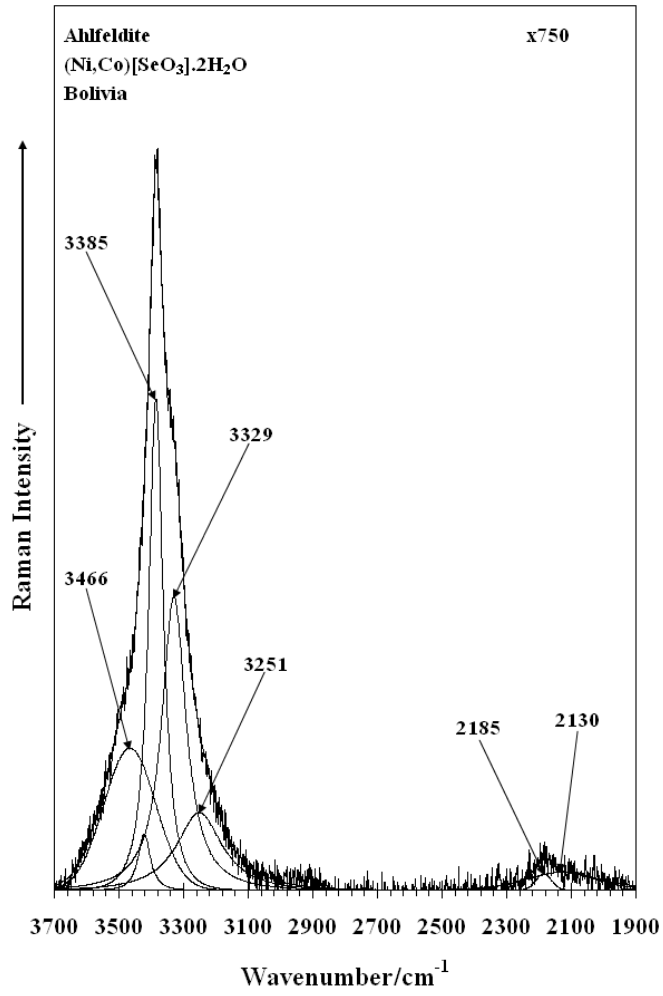


Fig. 3