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Raman spectroscopic study of the selenite mineral mandarinoite $\text{Fe}_2\text{Se}_3\text{O}_9 \cdot 6\text{H}_2\text{O}$

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Abstract

Selenites and tellurites may be subdivided according to formula and structure. There are five groups, based upon the formulae (a) $\text{A}(\text{XO}_3)$, (b) $\text{A}(\text{XO}_3) \cdot x\text{H}_2\text{O}$, (c) $\text{A}_2(\text{XO}_3)_3 \cdot x\text{H}_2\text{O}$, (d) $\text{A}_2(\text{X}_2\text{O}_5)$ and (e) $\text{A}(\text{X}_3\text{O}_8)$. Of the selenites, molybdomenite is an example of type (a); chalcomenite, clinochalcomenite, cobaltomenite and ahlfeldite are minerals of type (b); mandarinoite $\text{Fe}_2\text{Se}_3\text{O}_9 \cdot 6\text{H}_2\text{O}$ is an example of type (c). Raman spectroscopy has been used to characterise the mineral mandarinoite. The intense, sharp band at 814 cm^{-1} is assigned to the symmetric stretching $(\text{Se}_3\text{O}_9)^{6-}$ units. Three Raman bands observed at 695 , 723 and 744 cm^{-1} are attributed to the ν_3 $(\text{Se}_3\text{O}_9)^{6-}$ antisymmetric stretching modes. Raman bands at 355 , 398 and 474 cm^{-1} are assigned to the ν_4 and ν_2 bending modes. Raman bands are observed at 2796 , 2926 , 3046 , 3189 and 3507 cm^{-1} and are assigned to OH stretching vibrations. The observation of multiple OH stretching vibrations suggests the non-equivalence of water in the mandarinoite structure. The use of the Libowitzky empirical function provides hydrogen bond distances of $2.633(9) \text{ \AA}$ (2926 cm^{-1}), $2.660(0) \text{ \AA}$ (3046 cm^{-1}), $2.700(0) \text{ \AA}$ (3189 cm^{-1}) and $2.905(3) \text{ \AA}$ (3507 cm^{-1}). The observation of multiple water stretching bands supports the concept of non-equivalent water units in the mandarinoite structure. The sharp, intense band at 3507 cm^{-1} may be due to hydroxyl units. It is probable that some of the selenite units have been replaced by hydroxyl units.

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KEY WORDS: selenite, Raman spectroscopy, mandarinoite, schmiederite, chalcomenite, clinochalcomenite

INTRODUCTION

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 $Fe_2Se_3O_9 \cdot 6H_2O$ ² is an example of type (c). There are no known examples of selenite minerals of formula (d) and (e). Examples of these groups may be found with tellurite minerals. Mandarinoite is formed by the probable simultaneous oxidation of penroseite and pyrite. It is a yellowish green in appearance and has monoclinic structure with point group $2/m$.

Raman spectroscopy has proven very useful for the study of minerals³⁻²³. Indeed, Raman spectroscopy has proven most useful for the study of diagenetically related minerals, as often occurs with carbonates^{10,12,24-26}. 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 solutions²¹. The aim of this paper is to present Raman and infrared spectra of the natural selenite mineral mandarinoite 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 mandarinoite samples originated from El Dragon Mine, Potosi, Bolivia. The sample was analysed by X-ray diffraction and EDX measurements. No mineral impurities were detected. According to Anthony *et al.* the analysis of the mineral is SeO_2 59.53% and Fe_2O_3 28.68%. This provides a formula of $Fe_2Se_3O_9 \cdot 4H_2O$

Raman microprobe spectroscopy

The crystals of mandarinoite 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, filter system and 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 authors²⁷⁻³⁰.

Spectroscopic 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 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. Further details on the manipulation of the data has been published^{7-13,25-27}.

RESULTS AND DISCUSSION

Farmer states that very little research has been undertaken on selenates. No known minerals with the selenate ion SeO_4^{2-} have been discovered and reported³¹. The infrared spectra of $\text{CuSeO}_3 \cdot 2\text{H}_2\text{O}$ has been reported by Sathinadan *et al.*³² and Makutan *et al.*³³. 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 $2E$. Nakamoto³⁴ gives these as $807, 432\text{ cm}^{-1}$ (A_1), 737 and 374 cm^{-1} (E). The comment may be

made, that there is very little published on the vibrational spectroscopy of selenite minerals, especially the Raman spectroscopy of selenites.

The Raman spectra of the mandarinoite mineral in the 100 to 1000 cm^{-1} region are shown in Fig. 1. The intense sharp band at 814 cm^{-1} is assigned to the symmetric stretching $(\text{Se}_3\text{O}_9)^{6-}$ units. In contrast, the values for the ν_3 antisymmetric stretching mode occur at 740, 713 and 714 cm^{-1} respectively. A comparison may be made with the band positions of chalcomenite and clinochalcomenite at 813 cm^{-1} and 811 cm^{-1} respectively. There is a small difference between the band position of the two polymorphs. 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 modes³⁵. The values for 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 depend upon the degree of hydration^{36,37}. Three Raman bands are observed for mandarinoite at 695, 723 and 744 cm^{-1} . These bands are attributed to the ν_3 $(\text{SeO}_3)^{2-}$ antisymmetric stretching modes. A comparison may be made with the spectra of chalcomenite and clinochalcomenite. Three bands are found for chalcomenite at 685, 710 and 727 cm^{-1} and two bands for the clinochalcomenite at 709 and 749 cm^{-1} .

The Raman spectrum of mandarinoite (Fig. 1) displays bands at 355, 398 and 474 cm^{-1} . The first two bands are assigned to the ν_4 bending modes whilst the latter band is assigned to the ν_2 bending mode. The value for ν_2 bands occurs between 449 and 461 cm^{-1} and ν_4 bands between 387 and 427 cm^{-1} ³⁵. 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 $680 \leq \nu_3 \text{ SeO}_3 \leq 775 \text{ cm}^{-1}$ ³⁸. Khandelwal and Verma 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 ν_3 $(\text{UO}_2)^{2+}$ modes, respectively^{39,40}. 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} ³⁵, where the band at around 472 cm^{-1} is attributed to ν_2 bending mode. An intense sharp band at 398 cm^{-1} for schmiederite is

assigned to this ν_2 bending mode. Some variation in band position is observed for clinochalcomenite where the band is found at 489 cm^{-1} . Two bands are observed for cobaltomenite at 512 and 443 cm^{-1} . The latter band is assigned to the ν_2 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 spectra of mandarinoite in the 1450 to 1800 cm^{-1} is shown in Fig. 2. The spectrum suffers from a lack of signal to noise. It should be noted that the spectrum has been multiplied by 9000 to be displayed. It is not unexpected to have very low intensity bands for water in the Raman spectrum. Water is a very poor Raman scatterer. Nevertheless, two bands may be observed at around 1666 and 1563 cm^{-1} . The first band is assigned to the water bending mode. The position of this band suggests that the water is strongly hydrogen bonded. The position of this band is quite sensitive to hydrogen bond strength. Weakly hydrogen bonded water occurs at 1595 cm^{-1} as may be observed for the band position of water vapour. Strongly hydrogen bonded water occurs at positions greater than 1640 cm^{-1} . The band at 1563 cm^{-1} is not defined or attributed. It is possibly an overtone band.

The Raman spectrum of the water OH stretching region of mandarinoite in the 2650 to 3500 cm^{-1} region is shown in Fig. 3. Three intense bands are observed at 2926 , 3189 and 3507 cm^{-1} . Two other band components may be resolved at 2796 and 3046 cm^{-1} . The first two bands are assigned to the water OH stretching vibrations. The third band is very sharp and it is suspected that it can be attributed to OH stretching vibrations. Dunn *et al.* found the formula to contain 4 water units⁴¹. Hawthorne² reported that the formula of mandarinoite contains 6 water units rather than 4. However, Anthony *et al.* (page 427) confirmed the formula to contain 6 water units. In the crystal structure, Hawthorne stated that there are three unique FeF_6 octahedra ($\text{F}_6 = \text{unspecified anion}$) linked by corner-sharing to form a $\text{M}_2\text{T}_3\text{F}_{12}$ framework. Large voids in this framework are occupied by the H_2O molecules, which participate in a hydrogen bonding scheme that is essential to the anion bond-valence requirements. The previously mentioned assignment of the sharp Raman band at 3507 cm^{-1} to the stretching vibration of OH units is likely. In other words, some of the Se_3O_9 units have been replaced by hydroxyl units. The observation of multiple

water stretching vibrations supports the concept of non-equivalent water units in the structure of mandarinoite.

Studies have shown a strong correlation between OH stretching frequencies and both O···O bond distances and H···O bond distances⁴²⁻⁴⁵. Libowitzky (1999) showed that a regression function can be employed, relating the hydroxyl stretching frequencies with regression coefficients better than 0.96 using infrared spectroscopy⁴⁶. The function is described as: $\nu_1 = (3592 - 304) \times 109^{\frac{-d(O-O)}{0.1321}} \text{ cm}^{-1}$. Thus OH···O bond distances may be calculated using the Libowitzky empirical function. The values for the OH stretching vibrations, as shown in Fig. 3, provide hydrogen bond distances of 2.633(9) Å (2926 cm⁻¹), 2.660(0) Å (3046 cm⁻¹), 2.700(0) Å (3189 cm⁻¹) and 2.905(3) Å (3507 cm⁻¹). Hawthorne² suggested that water acted as a space filler in the voids of the mandarinoite structure. If this is the case then the water is very strongly hydrogen bonded.

Two types of water units can be identified in the structure of mandarinoite. The hydrogen bond distances previously established can be used to predict the location of hydroxyl stretching. The spectrum of mandarinoite may be divided into two regions containing evidence of OH stretching; namely 3100–3600 cm⁻¹ and 2500–3100 cm⁻¹. This distinction suggests that the strength of the hydrogen bonds, as measured by the hydrogen bond distances, can also be divided accordingly into two groups. An arbitrary cut-off point may be 2.700 Å, based upon the wavenumber ~3190 cm⁻¹. Thus, the first two bands of mandarinoite listed above may be described as strong hydrogen bonds and the last two bands as relatively weak hydrogen bonds. The infrared spectra of the mandarinoite gave bands in similar positions and identical hydrogen bond distances. It should be noted that a quite weak band at 1666 cm⁻¹ is assigned to the water HOH bending mode. For normal hydrogen-bonded water, this band occurs at around 1630 cm⁻¹. Thus, the position of this band also indicates strong hydrogen bonding within the mandarinoite mineral. A comparison of hydrogen bond distances may be made with other secondary minerals such as perhamite and peisleyite. The large hydrogen bond distances present in perhamite⁴⁷ can be seen in other mixed anion minerals, such as peisleyite⁴⁸ where the distances range between 3.052(5) and 2.683(6) Å. 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 contributes to the stability of the mineral.

CONCLUSIONS

Raman spectroscopy has been used to characterise the selenite mineral known as mandarinoite. The Raman spectra show clearly resolved bands with good band separation enabling identification and assignment of the bands. Bands are identified in terms of the structure and symmetry of the $(\text{Se}_3\text{O}_9)^{6-}$ units. OH bond lengths are inferred from the Raman spectra. The observation of multiple water stretching bands supports the concept of non-equivalent water units in the mandarinoite structure. The sharp intense band at 3507 cm^{-1} may be due to hydroxyl units. It is probable that some of the selenite units have been replaced by hydroxyl units.

Acknowledgements

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List of Fig.s

Fig. 1 Raman spectrum of mandarinoite in the 100 to 1100 cm^{-1} region

Fig. 2 Raman spectrum of mandarinoite in the 1200 to 1800 cm^{-1} region

Fig. 3 Raman spectrum of mandarinoite in the 2900 to 3700 cm^{-1} region

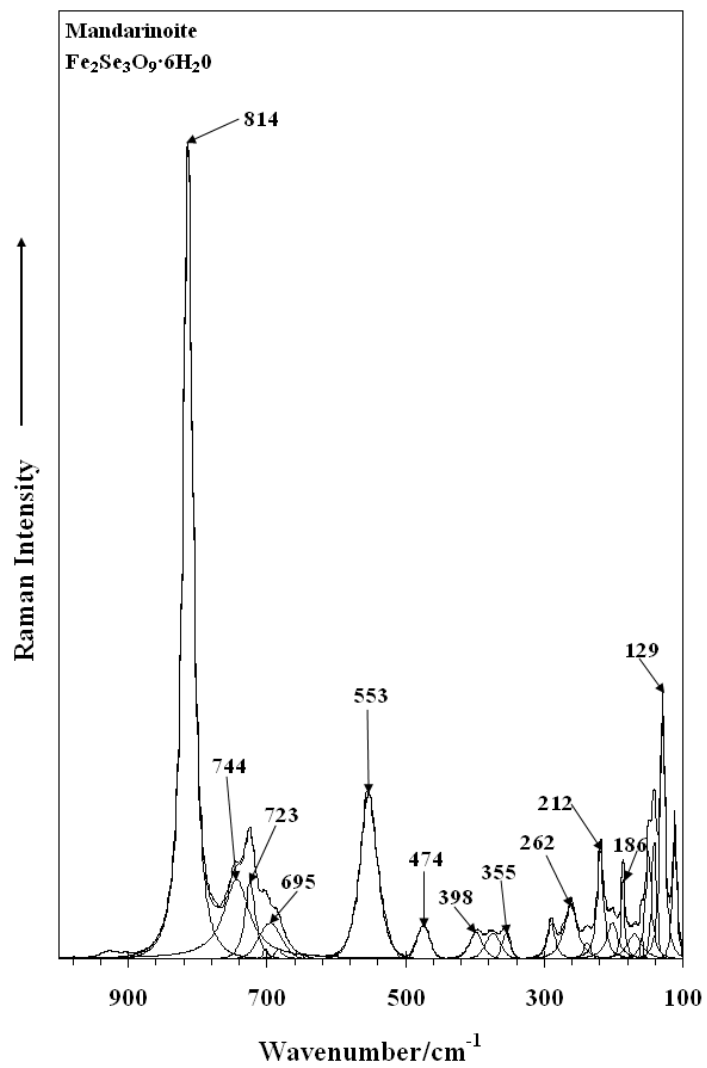


Fig. 1

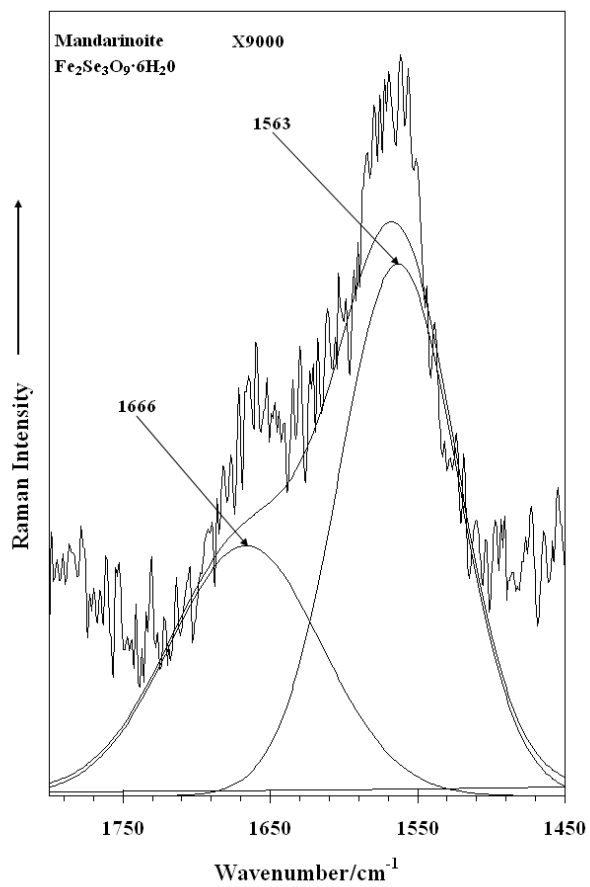


Fig. 2

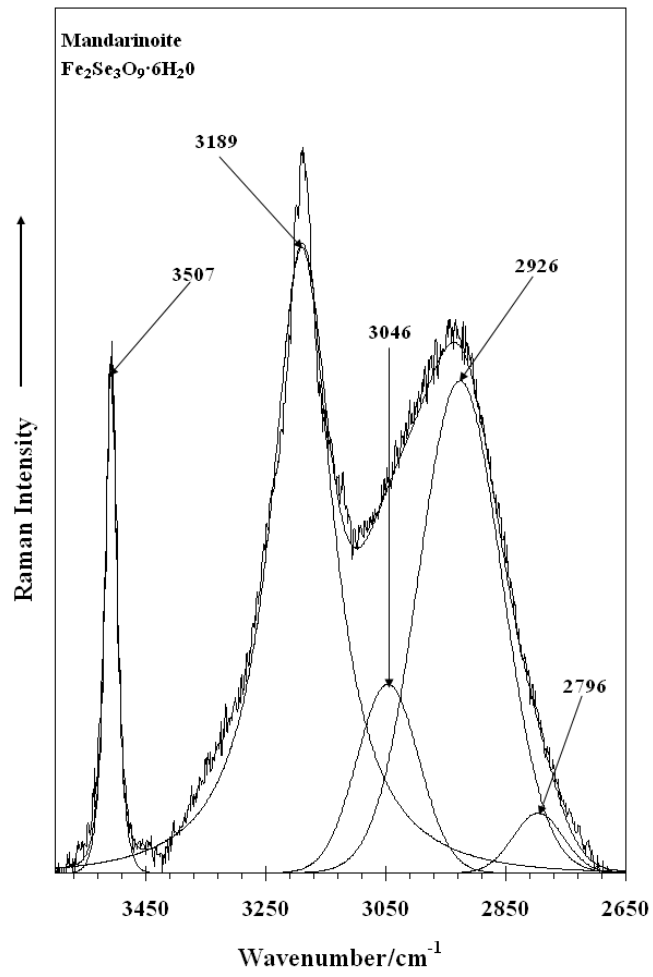


Fig. 3