Vibrational spectroscopy of the multianion mineral kemmlitzite $(Sr,Ce)Al_3(AsO_4)(SO_4)(OH)_6$

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Abstract

Some minerals are colloidal and show no X-ray diffraction patterns. Vibrational spectroscopy offers one of the few methods for the assessment of the structure of these types of mineral. Among this group of minerals is kemmlitzite $(Sr,Ce)Al_3(AsO_4)(SO_4)(OH)_6$. The objective of this research is to determine the molecular structure of the mineral kemmlitzite using vibrational spectroscopy. Raman microscopy offers a useful method for the analysis of such colloidal minerals.

Raman and infrared bands are attributed to the AsO_4^{3-} , SO_4^{2-} and water stretching vibrations. The Raman spectrum is dominated by a very intense sharp band at 984 cm^{-1} assigned to the SO_4^{2-} symmetric stretching mode. Raman bands at 690, 772 and 825 cm^{-1} may be assigned to the AsO_4^{3-} antisymmetric and symmetric stretching modes. Raman bands observed at 432 and 465 cm^{-1} are attributable to the doubly degenerate $\nu_2 (SO_4)^{2-}$ bending mode. Vibrational spectroscopy is important in the assessment of the molecular structure of the kemmlitzite, especially when the mineral is non-diffracting or poorly diffracting.

Keywords: Raman spectroscopy, kemmlitzite, beudantite, arsenate, sulphate

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Introduction

Kemmlitzite is a rare secondary mineral found in the zone of oxidized over lead-bearing deposits. Kemmlitzite $(Sr,Ce)Al_3(AsO_4)(SO_4)(OH)_6$ [1] is a multi-anion mineral containing hydroxyl, sulphate and arsenate groups and is a member of the beudantite subgroup of alunites [2-4]. The mineral is a source or rare earth elements. The mineral is hexagonal with Point Group 3 2/*m* and Space Group *[R3m]* [2, 5]. Kemmlitzite was originally described as hidalgoite. It occurs as trigonal, pseudo cubic, colourless to white crystals of 0.2 to 3 mm. Kemmlitzite is found together with albite, quartz, cabalzarite, tripuhyite, tilasite and arseniosiderite. The mineral has the potential to act as a gas sensor.

The reason for this research is that minerals such as kemmlitzite are found in soils and in old mine sites. Further, the formation of kemmlitzite can be used as the basis for arsenic accumulation. Therefore, this research focuses on the spectroscopic determination of kemmlitzite and consequential molecular structure. Raman spectroscopy has proven very useful for the study of minerals [6-13]. Indeed Raman spectroscopy has proven most useful for the study of diagenetically related minerals as often occurs with minerals containing arsenate and sulphate groups, including pitticite and zykaite. Raman spectroscopy is especially useful when the minerals are X-ray non-diffracting or poorly diffracting and very useful for the study of amorphous and colloidal minerals. Kemmlitzite is a mineral which falls into this category. This paper is a part of systematic studies of vibrational spectra of minerals of secondary origin in the oxide supergene zone. In this work we attribute bands at various wavenumbers to vibrational modes of kemmlitzite using Raman spectroscopy and relate the spectra to the structure of the mineral.

Experimental

Minerals

The mineral kemmlitzite was supplied by The Mineralogical research Company. The mineral originated from Kemmlitz Deposit, Oschatz, Sachsen, Germany. Details of the mineral have been published [14].

Raman spectroscopy

Crystals of kemmlitzite were placed on a polished metal surface on the stage of an Olympus BHSM microscope, which is equipped with 10x, 20x, and 50x objectives. The microscope is part of a Renishaw 1000 Raman microscope system, which also includes a monochromator, a filter system and a CCD detector (1024 pixels). The Raman spectra were excited by a Spectra-Physics model 127 He-Ne laser producing highly polarised light at 633 nm and collected at a nominal resolution of 2 cm^{-1} and a precision of ± 1 cm^{-1} in the range between 100 and 4000 cm^{-1}. Repeated acquisition on the crystals using the highest magnification (50x) was accumulated to improve the signal to noise ratio in the spectra. Spectra were calibrated using the 520.5 cm^{-1} line of a silicon wafer.

Infrared spectroscopy

Infrared spectra were obtained using a Nicolet Nexus 870 FTIR spectrometer with a smart endurance single bounce diamond ATR cell. Spectra over the 4000–525 cm^{-1} range were obtained by the co-addition of 128 scans with a resolution of 4 cm^{-1} and a mirror velocity of 0.6329 cm/s. Spectra were co-added to improve the signal to noise ratio.

Band component analysis was undertaken using the Jandel 'Peakfit' (Erkrath, Germany) software package which enabled the type of fitting function to be selected and allowed 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 (r^2) greater than 0.995. Band fitting of the spectra is quite reliable providing there is some band separation or changes in the spectral profile.

Results and discussion

The Raman spectrum of kemmlitzite in the 550 to 1150 cm^{-1} region and of a second kemmlitzite crystal in the 500 to 900 cm^{-1} region are displayed in Figures 1a and 1b. The spectra are different and this is attributed to an orientation effect. In Figure 1a the intense peak at 984 cm^{-1} with a shoulder at 957 cm^{-1} is assigned to the SO_4^{2-} ν_1 symmetric stretching mode. In Figure 1b, the intense peaks are due to the AsO_4^{3-} antisymmetric and symmetric stretching modes. It is probable that the band at 825 cm^{-1} is attributed to the AsO_4^{3-} symmetric stretching vibration. The other two bands are assigned to the antisymmetric

stretching vibrations. The infrared spectrum of kemmlitzite in the 500 to 1800 cm-1 region is shown in Figure 2. The spectrum is dominated by two intense bands at 851 and 962 cm^{-1}. These bands may be attributed to the AsO_4^{3-} and SO_4^{2-} stretching vibrations. The bands at 574, 595 and 614 cm^{-1} are due to the ν_4 $(SO_4)^{2-}$ bending modes.

The Raman spectrum of kemmlitzite in the 100 to 600 cm^{-1} range is reported in Figure 3. The Raman bands observed at 388 and 427 cm^{-1} are attributable to the doubly degenerate ν_2 $(SO_4)^{2-}$ bending mode. There is also the possibility that the band at 427 cm-1 is due to the triply degenerate bending vibration (F_2, ν_4). The strong Raman band at 342 cm^{-1} is assigned to the doubly degenerate bending vibration (E, ν_2). The Raman spectrum in the 1000 to 1800 cm^{-1} region is reported in Figure 4. Three bands may be defined at 1356, 1524 and 1591 cm^{-1}. These bands are attributed to OH deformation modes of OH bonded to large cations.

The Raman spectrum of kemmlitzite in the 3000 to 3800 cm^{-1} region and the infrared spectrum in the 2700 to 3100 cm^{-1} region are displayed in Figures 5a and 5b. In the Raman spectrum, component bands are found at 3047, 3374, 3441 and 3566 cm^{-1}. According to the formula $(Sr,Ce)Al_3(AsO_4)(SO_4)(OH)_6$ no water is present in the structure, otherwise a water bending mode at around 1630 cm^{-1} would be expected. These bands are attributed to OH stretching modes. The observation of multiple OH stretching vibrations suggests that the OH units are not equivalent. The infrared spectrum shows bands at 2851, 2894, 2923 and 2954 cm^{-1}.

Studies have shown a strong correlation between OH stretching frequencies and both O···O bond distances and H···O hydrogen bond distances [15-18]. Libowitzky (1999) showed that a regression function can be employed relating the hydroxyl stretching wavenumbers with regression coefficients better than 0.96 using infrared spectroscopy [19]. The function is described as: $\nu_1 = (3592 - 304) \times 109^{\frac{-d(O-O)}{0.1321}}$ cm^{-1}. Thus OH---O hydrogen bond distances may be calculated using the Libowitzky empirical function. The values for the OH stretching vibrations from the Raman spectra shown in the figures provide hydrogen bond distances of 2.6604 Å (3047 cm^{-1}), 2.7814 Å (3374 cm^{-1}), 2.82899 Å (3441 cm^{-1}), 3.0623 Å (3566 cm^{-1}) and from the infrared data 2.6253 Å (2881 cm^{-1}), 2.6277 Å (2894 cm^{-1}), 2.6333 Å (2923 cm^{-1}), 2.6396Å (2954 cm^{-1}). The large hydrogen bond distances which are present in kemmlitzite can also be seen in other mixed anion minerals such as pitticite and zykaite where the distances ranging 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 of hydrogen bonding contributes to the stability of the mineral.

Two types of OH units can be identified in the structure of kemmlitzite. The hydrogen bond distances previously established above can be used to predict the hydroxyl stretching wavenumbers. The spectrum of kemmlitzite may be divided into two groups of OH stretching wavenumbers; namely 3300–3700 cm^{-1} and 2900–3300 cm^{-1}. This distinction suggests that the strength of the hydrogen bonds as measured by the hydrogen bond distances can also be divided into two groups according to the H-bond distances. An arbitrary cut-off point may be 2.74 Å based upon the wavenumber 3300 cm^{-1}. Thus the first three bands at 3374, 3441 and 3566 cm^{-1} may be described as weak hydrogen bonds and the two bands at 3047 and 3269 cm^{-1} as relatively strong hydrogen bonds. All of the infrared bands are described as due to strong hydrogen bonding.

Conclusions

Kemmlitzite is an example of a mineral which resembles a gel and as such shows poor X-ray diffraction patterns. The application of vibrational spectroscopy is of importance as it offers one of the only methods for the assessment of the molecular structure of the mineral.

The Raman spectrum of kemmlitzite is dominated by a very intense sharp band at 984 cm^{-1} assigned to the SO_4^{2-} symmetric stretching mode. The same vibrational mode is observed in the infrared spectrum as a sharp band at 962 cm^{-1}. Raman bands at 690, 772 and 825 cm^{-1} are assigned to AsO_4^{3-} antisymmetric and symmetric stretching modes. Infrared bands were observed at 760, 851 and 962 cm^{-1}.

The observation of multiple bands in the ν_4 $(SO_4)^{2-}$ spectral region at 574, 595, 604 and 614 cm^{-1} in the infrared spectrum supports the concept of reduction in symmetry of the sulphate anion in the structure of kemmlitzite. Raman bands observed at 427and 482 cm^{-1} are attributable to the doubly degenerate ν_2 $(SO_4)^{2-}$ bending mode.

Vibrational spectroscopy is important in the assessment of the molecular structure of the kemmlitzite, especially when the mineral is non-diffracting or poorly diffracting.

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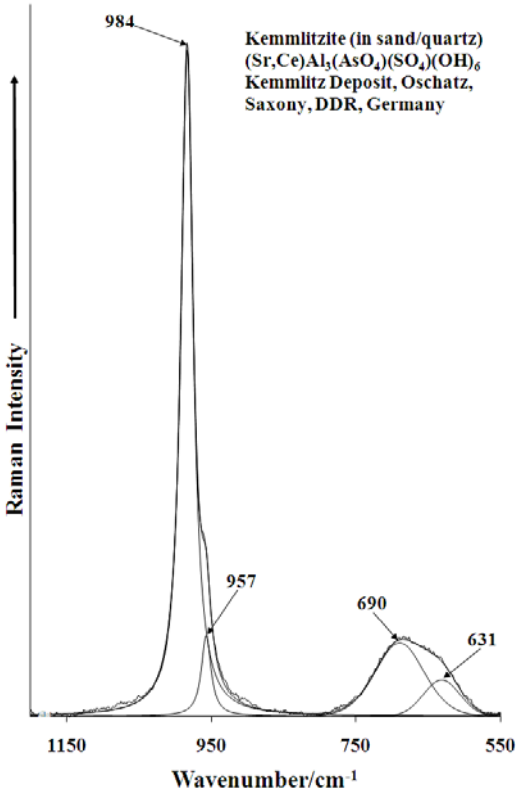

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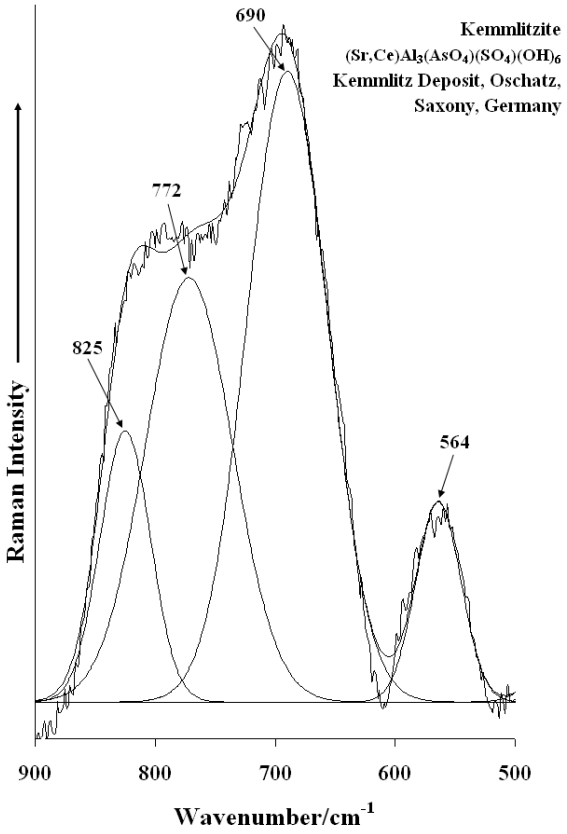

Figure 1b

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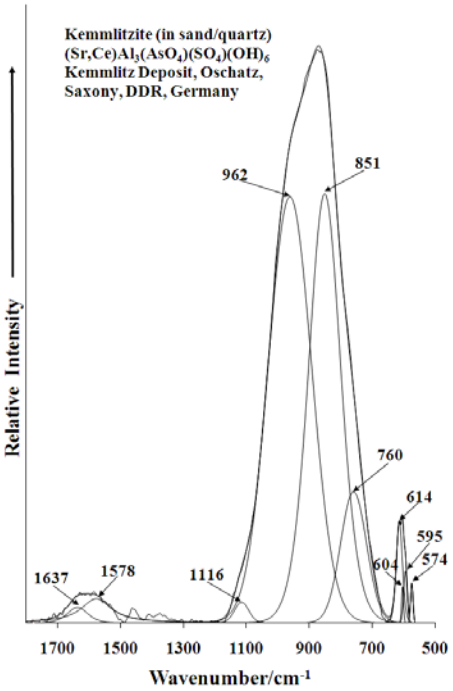

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238 **Figure 2**

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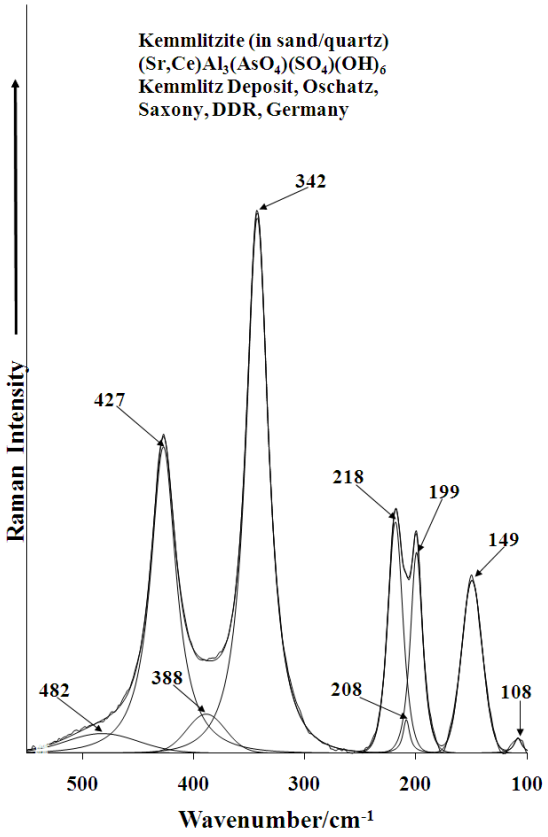

Figure 3

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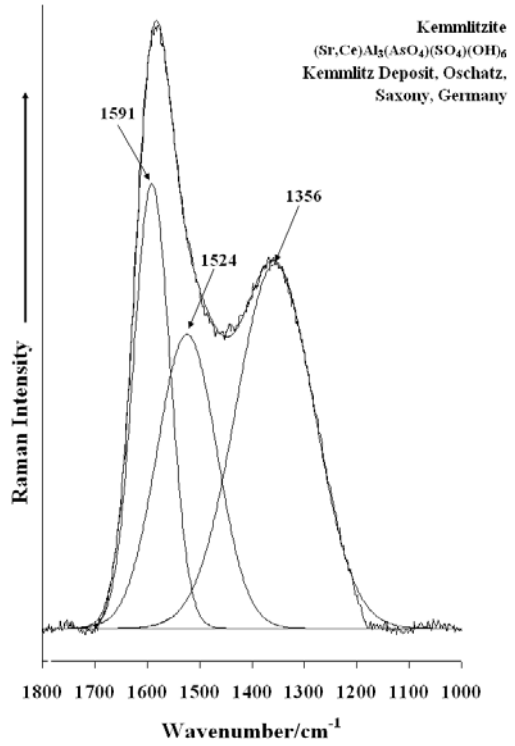

Figure 4

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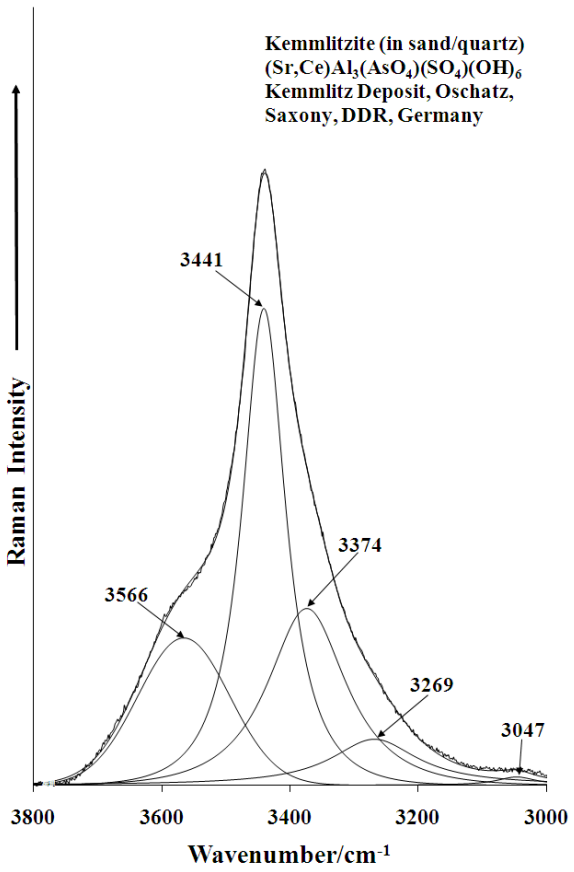

Figure 5a

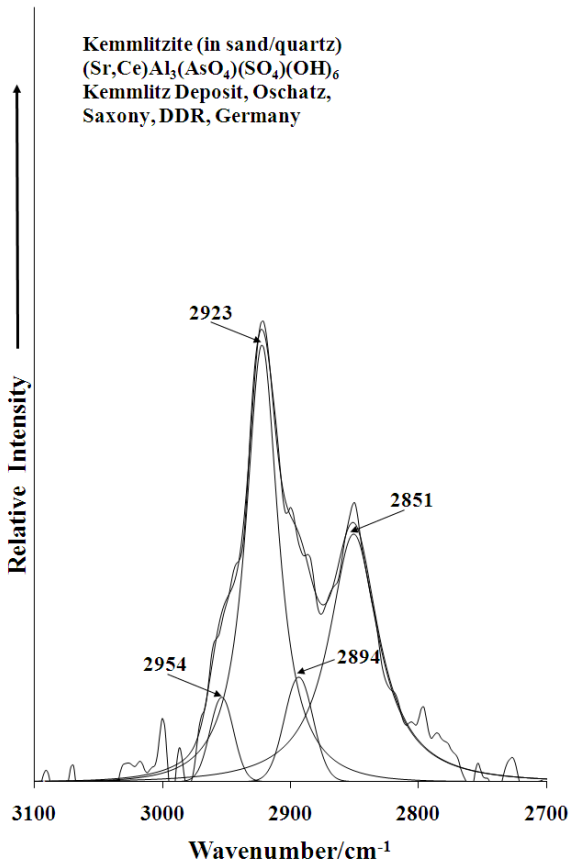

Figure 5b

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