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Thermal analysis and Hot-stage Raman spectroscopy of the basic copper arsenate mineral

Euchroite

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Abstract The thermal analysis of euchroite shows two mass loss steps in the temperature range 100–105 °C and 185–205 °C. These mass loss steps are attributed to dehydration and dehydroxylation of the mineral. Hot-stage Raman spectroscopy (HSRS) has been used to study the thermal stability of the mineral euchroite, a mineral involved in a complex set of equilibria between the copper hydroxy arsenates: euchroite $Cu_2(AsO_4)(OH)\cdot 3H_2O$ → olivenite $Cu_2(AsO_4)(OH)$ → strashimirite $Cu_8(AsO_4)_4(OH)_4\cdot 5H_2O$ → arhbarite $Cu_2Mg(AsO_4)(OH)_3$. HSRS inolves the collection of Raman spectra as a function of the temperature. HSRS shows that the mineral euchroite decomposes between 125 and 175 °C with the loss of water. At 125 °C, Raman bands are observed at 858 cm^{-1} assigned to the ν_1 AsO_4^{3-} symmetric stretching vibration and 801, 822, and 871 cm^{-1} assigned to the ν_3 AsO_4^{3-} (A_1) antisymmetric stretching vibrations. A distinct band shift is observed upon heating to 275 °C. At 275 °C, the four Raman bands are resolved at 762, 810, 837, and 862 cm^{-1}. Further heating results in the diminution of the intensity in the Raman spectra, and this is attributed to sublimation of the arsenate mineral. HSRS is the most useful technique for studying the thermal stability of minerals, especially when only very small amounts of mineral are available.

Keywords Copper · Arsenate · Olivenite · Cornwallite · Cornubite · Clinoclase thermal stage · Raman spectroscopy · Euchroite

Introduction

A quite large number of dark emerald green copper arsenate minerals [1, 2] exist, including euchroite $Cu_2(AsO_4)(OH)\cdot 3H_2O$ [3–5]. The mineral euchroite is orthorhombic and is widely distributed. Another related mineral is strashimirite $Cu_8(AsO_4)_4(OH)_4\cdot 5H_2O$, a hydrated hydroxyl divalent copper arsenate [6, 7]. The mineral is of monoclinic symmetry with space group $P2_1/m$ and may be compared with other hydroxyl copper arsenate minerals, olivenite $Cu_2(AsO_4)(OH)$, cornwallite $Cu_5(AsO_4)_2(OH)_4$.

The phase stability relationships between a range of diagenetically related minerals including the basic copper arsenates, have been studied by Williams [8]. Magalhaes et al. [9] reported the relative stabilities of the basic copper arsenates using estimated chemical parameters and experimentally determined solubility products [10, 11]. The difference in stability is attributed to pH, temperature of crystallization, and the relative redox potentials. The relative thermal stability of these minerals has not been reported. One possible set of relationships is as follows: euchroite $Cu_2(AsO_4)(OH)\cdot 3H_2O$ → olivenite $Cu_2(AsO_4)(OH)$ → strashimirite $Cu_8(AsO_4)_4(OH)_4\cdot 5H_2O$ → arhbarite $Cu_2Mg(AsO_4)(OH)_3$. A complex set of equilibria exists between these minerals. The presence of other cations in the solution such as Ca^{2+} has been shown to affect these equilibria [9]. The use of hot-stage Raman spectroscopy offers a technique for the study of the thermal stability of these types of minerals.

The aim of this research is to demonstrate the use of hot-stage Raman spectroscopy to assess the thermal stability of a selected copper hydroxy arsenate, namely euchroite, and to determine the changes in the molecular structure of the mineral as the mineral is thermally treated. Such research compliments the thermal analysis and differential

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thermogravimetric analysis of minerals [12–25]. This study forms a part of a comprehensive study of the molecular structure of minerals containing oxyanions using IR and Raman spectroscopy; we report the hot-stage Raman spectroscopy of the basic copper arsenate mineral euchroite.

Experimental

Mineral

The mineral euchroite was supplied by the Mineralogical Research Company and originated from L'ubietová, Slovak Republic. Anthony et al. have published the analysis of this mineral [26]. Eby and Hawthorne have published the structure of this mineral [4]. These authors [4] state that this mineral is orthorhombic, and consists of a fairly open heteropolyhedral framework consisting of edge-sharing chains of octahedrally coordinated Cu^{2+} cations that are cross-linked by sharing corners with arsenate tetrahedra.

Thermal analysis

Thermal decomposition of euchroite was carried out in a TA® Instrument incorporating a high-resolution thermo gravimetric analyzer (series Q500) in a flowing nitrogen atmosphere (60 cm^3 min^{-1}). Approximately 5 mg of euchroite underwent thermal analysis, with a heating rate of 5 °C min^{-1}, with resolution of 6 from 25 to 1000 °C.

Raman spectroscopy

Crystals of euchroite were placed on a polished metal surface on the stage of an Olympus BHSM microscope, which is equipped with 10×, 20×, and 50× 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 polarized 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 200 and 4000 cm^{-1}. Repeated acquisition on the crystals using the highest magnification (50×) 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. Spectra at elevated temperatures were obtained using a Linkam thermal stage (Scientific Instruments Ltd., Waterford Surrey, England). Spectra were taken from 50 °C at 100 °C intervals up to a temperature of 300 °C. Intervals of 50 °C were used where there was no evident change in the mass or the mass derivative. Spectral manipulation such as baseline correction/adjustment and smoothing were performed using the Spectracalc software package GRAMS (Galactic Industries Corporation, NH, USA). Band component analysis was undertaken using the Jandel "Peakfit" software package that 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 Lorentzian–Gaussian cross-product function with the minimum number of component bands used for the fitting process. The Gaussian–Lorentzian 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

Thermal analysis

The thermal analysis of euchroite shows two mass loss steps in the temperature range 100–105 °C and 185–205 °C. These mass loss steps are attributed to

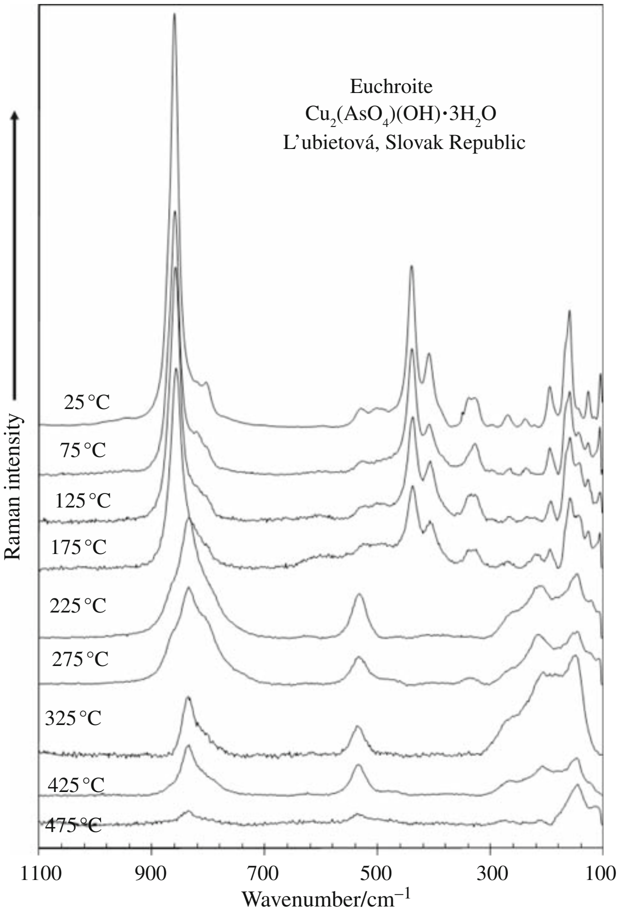

Fig. 1 Raman spectra of euchroite in the 100–1100 cm^{-1} over the temperature range 25–425 °C

dehydration and dehydroxylation of the mineral. The following reactions are proposed:

$$Cu_2(AsO_4)(OH) \cdot 3H_2O \rightarrow Cu_2(AsO_4)(OH) + 3H_2O$$

and

$$2Cu_2(AsO_4)(OH) \rightarrow 2Cu_2O(AsO_4) + H_2O$$

Mass losses of 15.2 and 4.7% are observed, which compare well with the theoretical mass losses of 16.05 and 5.0%.

Hot-stage Raman spectroscopy

The hot-stage Raman spectra of euchroite over the temperature range from ambient to 425 °C is shown in Fig. 1. Changes in the Raman spectra are clearly observed. The Raman spectrum undergoes changes after 125 °C. The spectrum obtained at 125 °C is very different from the spectrum at 175 °C. The intensity of the bands decreases as a function of temperature until no intensity remains after 425 °C. It is proposed that in the first step, the water is lost, and a reaction such as the following is proposed: $Cu_2(AsO_4)(OH) \cdot 3H_2O \rightarrow Cu_2(AsO_4)(OH) + 3H_2O$. At higher temperatures, it is proposed that the mineral sublimes, and after 425 °C, no material remains.

The free arsenate ion has tetrahedral symmetry and, thus, should have four bands, of which two are infrared active with theoretical values of ν_3 (F_2) 887 cm^{-1} and ν_4 (F_2) 463 cm^{-1}. The Raman active modes are observed at 837 (A_1) and 349 (E) cm^{-1}. Upon coordination of the arsenate ion to the copper atom, the symmetry of the arsenate ion reduces to C_{3v} and may be further reduced to C_{2v}. As a consequence of this symmetry reduction, all the bands will be both infrared and Raman active. The Raman spectra of the tetrahedral anions in aqueous systems are well known. The symmetric stretching vibration of the arsenate anion (ν_1) is observed at 810 cm^{-1} and coincides with the position of the asymmetric stretching mode (ν_3). The symmetric bending mode (ν_2) is observed at 342 cm^{-1}, and the out-of-plane bending mode (ν_4) is observed at 398 cm^{-1}.

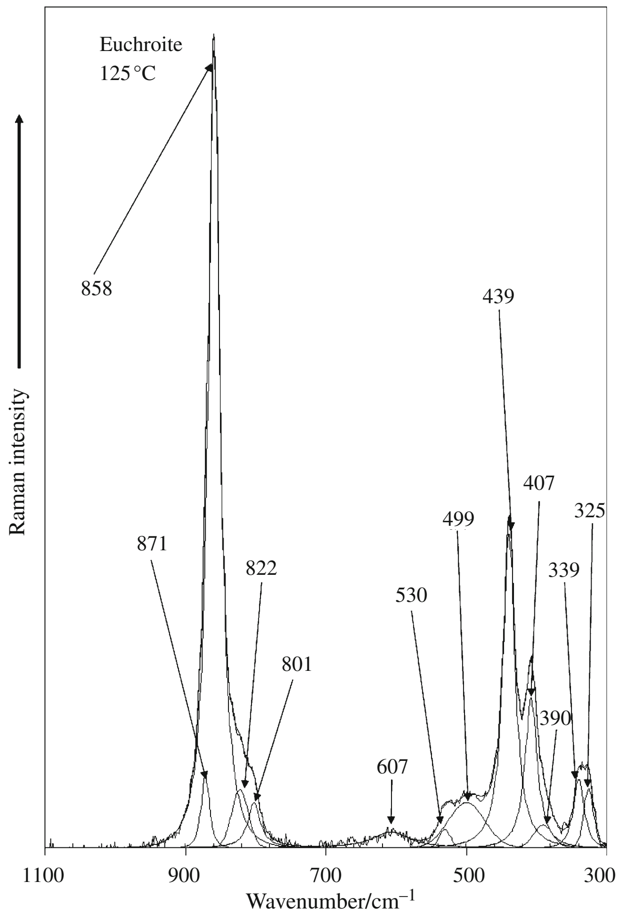

Fig. 2 Raman spectrum of euchroite at 125 °C in the 300–1100 cm^{-1} region with fitted curves

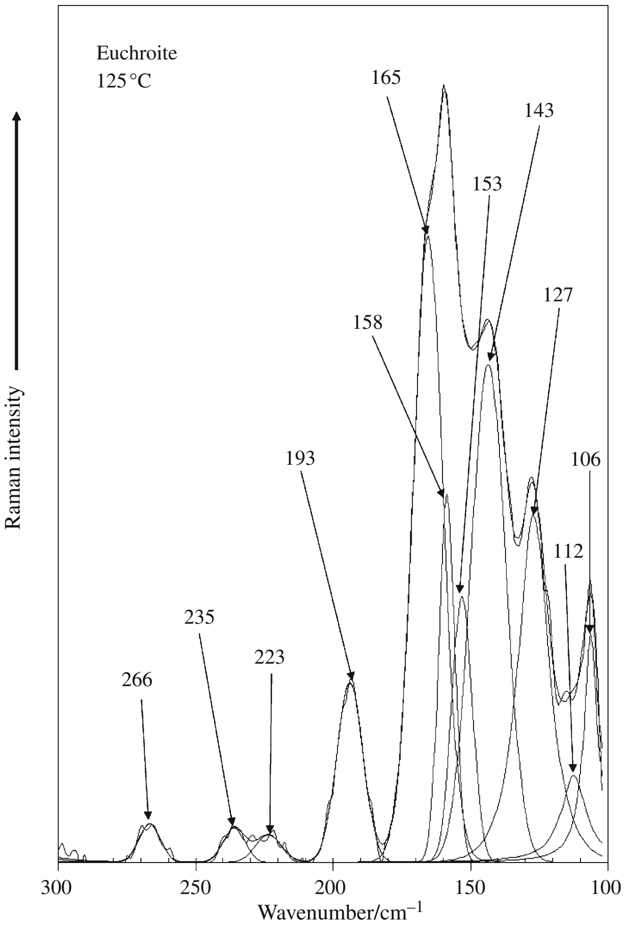

Fig. 3 Raman spectrum of euchroite at 125 °C in the 100–300 cm^{-1} region with fitted curves

Of all the tetrahedral oxyanions spectra, the positions of the arsenate vibrations occur at lower wavenumbers than any of the other naturally occurring mineral oxyanions spectra. Farmer lists a number of spectra of arsenates including the basic copper arsenates olivenite and euchroite [27]. The effect of the arsenate ion in a crystal will be to remove the degeneracy and allow splitting of the bands according to factor group analysis. The ν_1 and ν_3 infrared bands of olivenite and euchroite were observed at 860, 828, and 790 cm^{-1}, and 830 and 770 cm^{-1}, respectively. The bending modes were found at 493 and 452 cm^{-1} for olivenite and at 475 and 410 cm^{-1} for euchroite. No ν_2 bands were shown. This is no doubt related to the fact that the bands are found below 400 cm^{-1}, which makes the measurement by infrared spectroscopy difficult.

The Raman spectrum of euchroite in the 300–1100 cm^{-1} region at 125 °C is illustrated in Fig. 2. The very intense Raman band is observed at 858 cm^{-1} and is assigned to the ν_1 AsO_4^{3-} (A_1) symmetric stretching vibration. The band shows some slight asymmetry, and low-intensity component bands may be resolved at 801, 822, and 871 cm^{-1}. This band is observed at 836 cm^{-1} at 25 °C, and a significant shift is observed as the mineral is heated. The low-intensity bands at 801 and 822 cm^{-1} are assigned to the ν_3 AsO_4^{3-} (A_1) antisymmetric stretching vibration.

In the spectral region 300–500 cm^{-1} of euchroite, four Raman bands at 125 °C are observed at 325, 339, 407, and 439 cm^{-1}. The first two bands are attributed to the ν_2 AsO_4^{3-} bending mode. Farmer did not report the position of the ν_2 AsO_4^{3-} bending modes. No doubt, because the position of these bands lies below 400 cm^{-1}. The ν_2 bending vibration should be common to all copper hydroxy arsenates, and the spectra should be relatively intense. Raman bands are observed at 350 cm^{-1} for olivenite, 340 cm^{-1} for cornwallite, and at 380 cm^{-1}. These bands are all assigned to the ν_2 AsO_4^{3-} symmetric bending vibration. Four Raman bands at 25 °C are observed at 358, 385, 441, and 474 cm^{-1}. The two bands at 358 and 385 cm^{-1} are ascribed to the ν_2 AsO_4^{3-} bending mode. The low wavenumber region of the Raman spectrum of euchroite at 125 °C is shown in Fig. 3. Intense bands are observed at 127, 143, 158, and

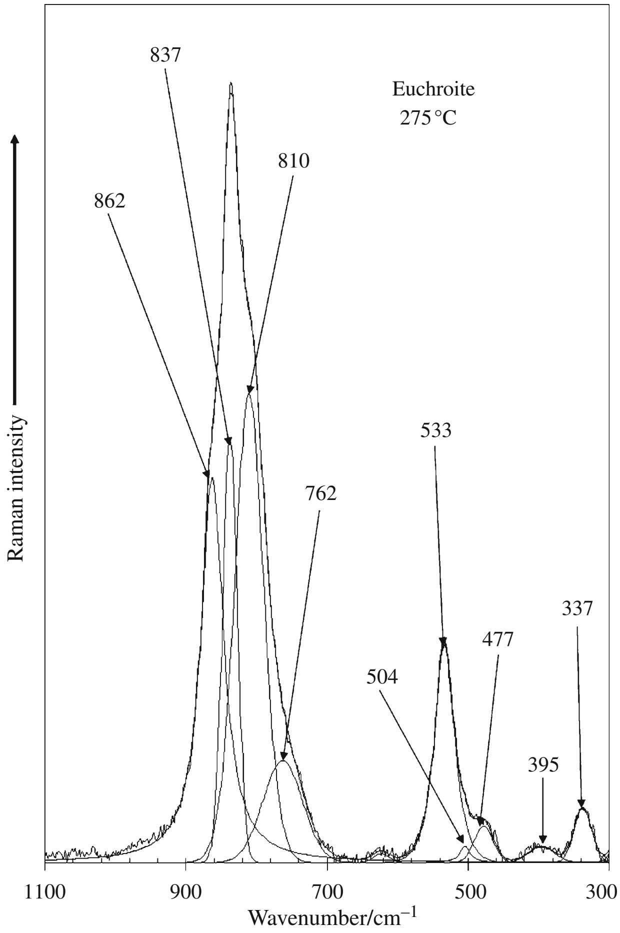

Fig. 4 Raman spectrum of euchroite at 275 °C in the 300–1100 cm^{-1} region with fitted curves

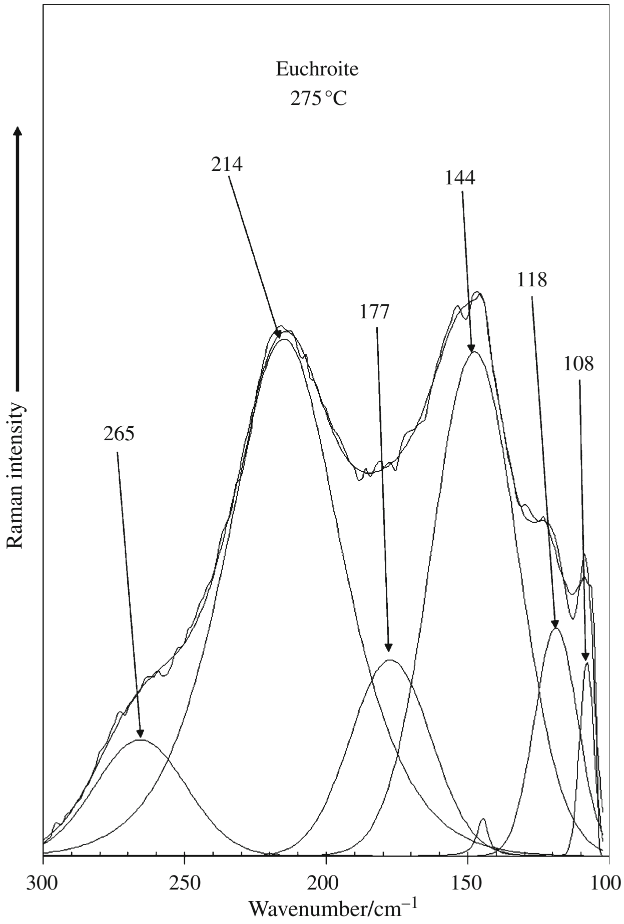

Fig. 5 Raman spectrum of euchroite at 275 °C in the 100–300 cm^{-1} region with fitted curves

165 cm^{-1}. Other bands of lower intensity are found at 106, 223, 235, and 266 cm^{-1}.

The Raman spectrum of euchroite at 275 °C is displayed in Figs. 4 and 5. This spectrum is very different to the Raman spectrum at 125 °C. All of the Raman spectra taken above 125 °C may be represented by the spectrum collected at 275 °C. In the AsO_4^{3-} stretching region, four Raman bands are resolved at 762, 810, 837, and 862 cm^{-1}. The sharp band at 837 cm^{-1} may be assigned to the ν_1 AsO_4^{3-} (A_1) symmetric stretching vibration. The band on the higher wavenumber side may be due to the $HAsO_4^{2-}$ units, and therefore, the band at 862 cm^{-1} is the symmetric stretching mode of this unit. It is proposed that at the higher temperatures, the OH units and AsO_4^{3-} units are interacting to give acid arsenate units $HAsO_4^{2-}$. The two low-intensity bands at 337 and 395 cm^{-1} are described as ν_2 AsO_4^{3-} bending modes. The three bands at 477, 504, and 533 cm^{-1} may be assigned ν_4 AsO_4^{3-} bending modes. Low wavenumber bands with significant intensity may be observed at 144, 214, and 265 cm^{-1}.

Conclusions

Hot-stage Raman spectroscopy is a technique in which Raman spectra are collected as a function of temperature using a thermal stage. Such a technique enables changes in the Raman spectra to be collected with increasing temperature, and the changes in the spectra are related to the changes in the molecular structure of a mineral. The mineral euchroite $Cu_2(AsO_4)(OH)\cdot 3H_2O$ is one of several copper hydroxy arsenate minerals including strashimirite, olivenite, and arhbarite which are involved in a complex set of equilibria, which are a function of a number of parameters including pH, temperature of crystallization, and the relative redox potentials. Hot-stage Raman spectroscopy offers a technique for studying the relative thermal stability of these minerals. Euchroite was found to decompose between 125 and 175 °C. The technique is most useful when only very small amounts of material are available as may occur for minerals in museum collections.

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