Raman and infrared spectroscopic study of kamphaugite-(Y)

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HIGHLIGHTS

- We have studied the carbonate mineral kamphaugite.
- Chemical analysis shows the presence of Ca, Y and C.
- Two distinct Raman bands provide evidence for the non-equivalence of the carbonate anion.

GRAPHICAL ABSTRACT

ABSTRACT

We have studied the carbonate mineral kamphaugite-(Y)(CaY(CO$_3$)$_2$(OH)·H$_2$O), a mineral which contains yttrium and specific rare earth elements. Chemical analysis shows the presence of Ca, Y and C. Back scattering SEM appears to indicate a single pure phase. The vibrational spectroscopy of kamphaugite-(Y) was obtained using a combination of Raman and infrared spectroscopy. Two distinct Raman bands observed at 1078 and 1088 cm^{-1} provide evidence for the non-equivalence of the carbonate anion in the kamphaugite-(Y) structure. Such a concept is supported by the number of bands assigned to the carbonate antisymmetric stretching mode. Multiple bands in the v_4 region offers further support for the non-equivalence of carbonate anions in the structure. Vibrational spectroscopy enables aspects of the structure of the mineral kamphaugite-(Y) to be assessed.

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Introduction

The mineral kamphaugite-(Y) is a calcium rare earth carbonate of formula Ca(Y,REE)(CO$_3$)$_2$(OH)·H$_2$O [1]. The mineral is known from a considerable number of locations worldwide [2–7]. The mineral is often found in association with other carbonates [8]. The composition of the mineral varies according to the origin of the mineral [3,4]. The carbon in kamphaugite-(Y) is said to be of a meteoritic origin [3]. The mineral is formed in a genesis at <50 °C during very low-temperature post-magmatic hydrothermal activity [3].

The mineral is tetragonal of point group 422. The mineral forms aggregates of rosettes and spherules up to 4 mm in size. The space group is $P4_12_12$ with $a = 7.434$ Å and $c = 21.793$ Å and $z = 8$.

It is important to understand the vibrational spectroscopy of the carbonate anion in different molecular environments. Nakamoto et al. first published and tabulated the selection rules for unidentate and bidentate anions including the carbonate anion [16,17]. The free ion, CO$_3^{2-}$ with D$_{3h}$ symmetry exhibits four normal vibrational modes; a symmetric stretching vibration (v_1), an out-of-plane bend (v_2), a doubly degenerate asymmetric stretch (v_3) and another doubly degenerate bending mode (v_4). The symmetries of these modes are A_1' (R) + A_2'' (IR) + E' (R, IR) + E'' (R, IR) and occur at 1063, 879, 1415 and 680 cm^{-1} respectively. Generally, strong Raman modes appear around 1100 cm^{-1} due to the symmetric stretching vibration (v_1), of

the carbonate groups, while intense IR and weak Raman peaks near 1400 cm^{-1} are due to the antisymmetric stretching mode (ν_3). Infrared modes near 800 cm^{-1} are derived from the out-of-plane bend (ν_2). Infrared and Raman modes around 700 cm^{-1} region are due to the in-plane bending mode (ν_4). This mode is doubly degenerate for undistorted CO_3^{2-} groups [17]. As the carbonate groups become distorted from regular planar symmetry, this mode splits into two components [17]. Infrared and Raman spectroscopy provide sensitive test for structural distortion of CO_3^{2-}.

It is important to study the vibrational spectroscopy of kamphaugite-(Y) as there have been very few studies of this mineral as is evidenced in the literature [2–7]. In addition, kamphaugite-(Y) is part of a complex paragenesis of carbonate minerals. Vibrational spectroscopy has proved an important tool for the study of minerals [9–14]. Due to the large variety of minerals, vibrational spectroscopy methods can be an important tool in the study of alkaline deposits. The objective of this research is to report the Raman and infrared spectra of kamphaugite-(Y) and to relate the spectra to the mineral structure.

Experimental

Samples description and preparation

The kamphaugite-(Y) sample studied in this work originated from Poudrette Quarry, Mont Saint-Hilaire, Québéc, Canada. This is the location of the 'type' mineral. The compositions have been reported by Anthony et al. (page 348) [15]. The sample was incorporated to the collection of the Geology Department of the Federal University of Ouro Preto, Minas Gerais, Brazil, with sample code SAD-046. The sample was gently crushed and the associated minerals were removed under a stereomicroscope Leica MZ4. Qualitative and semiquantitative chemical analyses via SEM/EDX were applied to the mineral characterization.

Scanning electron microscopy (SEM)

Experiments and analyses involving electron microscopy were performed in the Center of Microscopy of the Universidade Federal de Minas Gerais, Belo Horizonte, Minas Gerais, Brazil (http://www.microscopia.ufmg.br).

Kamphaugite-(Y) crystals were coated with a 5 nm layer of evaporated carbon. Secondary Electron and Backscattering Electron images were obtained using a JEOL JSM-6360LV equipment. Qualitative and semi-quantitative chemical analyses in the EDS mode were performed with a ThermoNORAN spectrometer model Quest and were applied to support the mineral characterization.

Raman microprobe spectroscopy

Crystals of kamphaugite-(Y) 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 acquisitions on the crystals using the highest magnification (50×) were accumulated to improve the signal to noise ratio of the spectra. Raman Spectra were calibrated using the 520.5 cm^{-1} line of a silicon wafer. The Raman spectrum of at least 10 crystals was collected to ensure the consistency of the spectra.

An image of the kamphaugite-(Y) crystals measured is shown in the Supplementary information as Fig. S1. Clearly the crystals of

kamphaugite-(Y) are readily observed, making the Raman spectroscopic measurements readily obtainable.

Infrared spectroscopy

Infrared spectra of kamphaugite-(Y) 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.

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 Lorentzian–Gaussian 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

Chemical characterization

The SEM image of kamphaugite-(Y) sample studied in this work is shown in Fig. S1. The image shows a fragment of a crystal aggre-
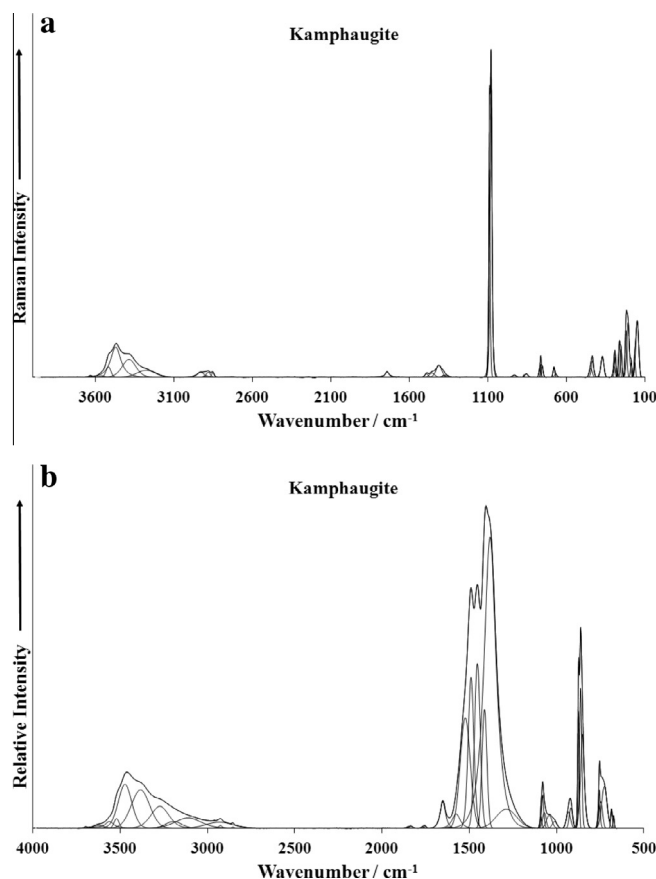

Fig. 1. (a) Raman spectrum of kamphaugite-(Y) over the 100–4000 cm^{-1} spectral range (upper spectrum). (b) Infrared spectrum of kamphaugite-(Y) over the 500–4000 cm^{-1} spectral range (lower spectrum).
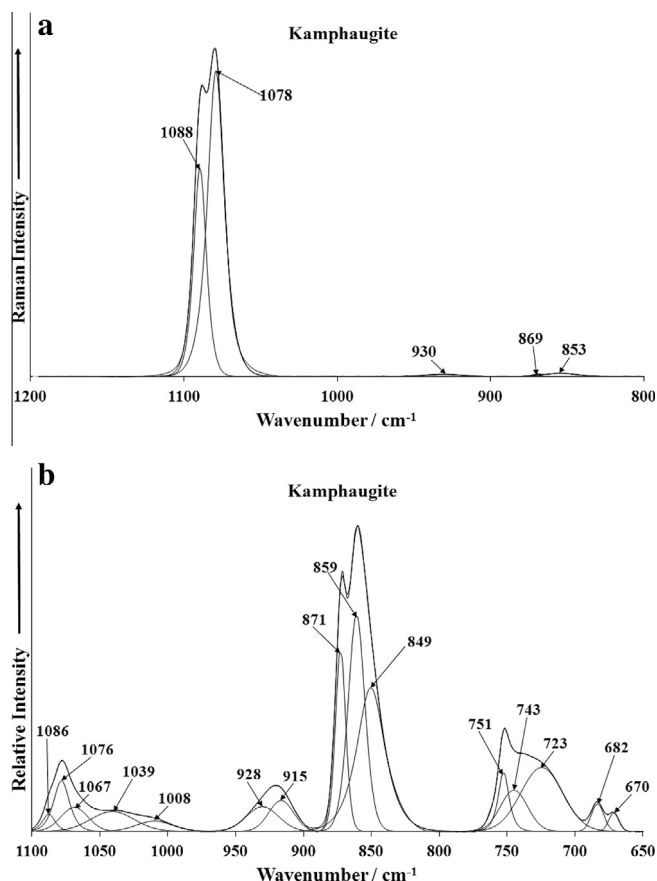
Fig. 2. (a) Raman spectrum of kamphaugite-(Y) over the 800–1200 cm^{-1} spectral range (upper spectrum). (b) Infrared spectrum of kamphaugite-(Y) over the 650–1100 cm^{-1} spectral range (lower spectrum).

Fig. 3. (a) Raman spectrum of kamphaugite-(Y) over the 400–800 cm^{-1} spectral range. (b) Raman spectrum of kamphaugite-(Y) over the 100–400 cm^{-1} spectral range.

gate. This image shows the spheroidal nature of the mineral. The chemical analysis is provided in Fig. S2. Chemical analysis shows the presence of Ca, Al, Y and C. The carbon is present because the sample is carbon coated for SEM and EDX analysis.

Vibrational spectroscopy of kamphaugite-(Y)

The Raman spectrum of kamphaugite-(Y) in the 100–4000 cm^{-1} spectral range is displayed in Fig. 1a. This spectrum shows the position and relative intensities of the Raman bands. It is noted that there are large parts of the spectrum where no intensity or minimal intensity is observed. Thus, the spectrum is subdivided into subsections depending upon the type of vibration being studied. The infrared spectrum of kamphaugite-(Y) in the 500–4000 cm^{-1} spectral region is shown in Fig. 1b. This figure shows the position of the infrared bands and their relative intensities. This spectrum displays the position and relative intensities of the infrared bands. As for the Raman spectrum, there are parts of the spectrum where little or no intensity is observed. Thus the spectrum is subdivided into sections depending on the type of vibration being studied.

The Raman spectrum of kamphaugite-(Y) over the 800–1200 cm^{-1} spectral range is illustrated in Fig. 2a. The spectral region centered upon 1080 cm^{-1} is complex with a number of overlapping bands. Two distinct Raman bands are observed at 1078 and 1088 cm^{-1}. These bands are attributed to the carbonate ν_1 symmetric stretching modes. According to Farmer [18], the structure of kamphaugite-(Y) is stated to be quite regular. The structural analysis of kamphaugite-(Y) suggests that the $(CO_3)^{2-}$ ion is regular and

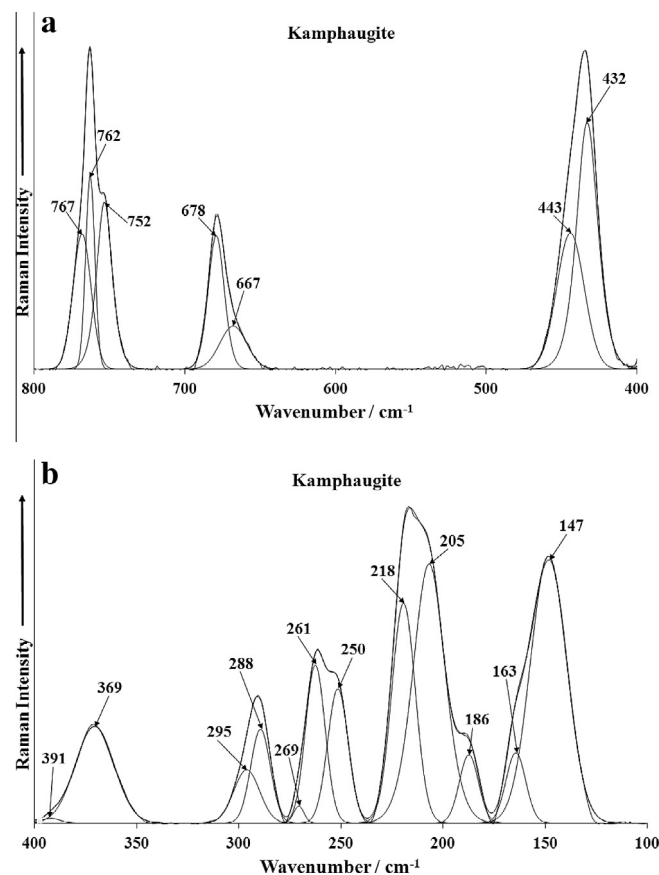is not involved with bonding [19–21]. This suggestion is not consistent with the Raman spectrum as multiple bands are observed in the $(CO_3)^{2-}$ stretching region. Farmer also reported the ν_1 band to be two quite distinct bands which is unusual for a single $(CO_3)^{2-}$ ion [18]. A very low intensity Raman band is found at 1366 cm^{-1} which is assigned to the ν_3 antisymmetric stretching mode. This band is of a low intensity and it is highly likely to be a multiple component band. Two bands are observed in the Raman spectra for kamphaugite-(Y) at 853 and 930 cm^{-1}. Frueh and Golightly reported two infrared bands at 950 and 930 cm^{-1} [22] and Farmer assigned these bands to OH deformation modes. Thus, the two Raman bands at 898 and 936 cm^{-1} are attributed to the OH deformation bands of kamphaugite-(Y). Two Raman bands are observed at 820 and 824 cm^{-1} and are attributed to the ν_4 bending mode.

The infrared spectrum of kamphaugite-(Y) over the 650–1100 cm^{-1} spectral range is reported in Fig. 2b. This figure displays a number of spectral features including a number of infrared bands at 1039, 1067, 1076 and 1086 cm^{-1}, which are attributed to the carbonate ν_3 antisymmetric stretching mode. The broadish infrared band at 1008 cm^{-1} may be the carbonate ν_1 symmetric stretching mode. Such a vibration should not be observed in the infrared spectrum for a perfect carbonate anion, one which is not distorted in any way. If the carbonate anion shows some reduction in symmetry, then the vibrational mode will be activated and the band observed in the infrared spectrum. A series of infrared bands are observed at 915 and 928 cm^{-1} and are the equivalent of the Raman bands in similar positions and are assigned to hydroxyl deformation modes. In the infrared spectrum, three bands are noted at 849, 859 and 871 cm^{-1} and are assigned to the carbonate ν_4
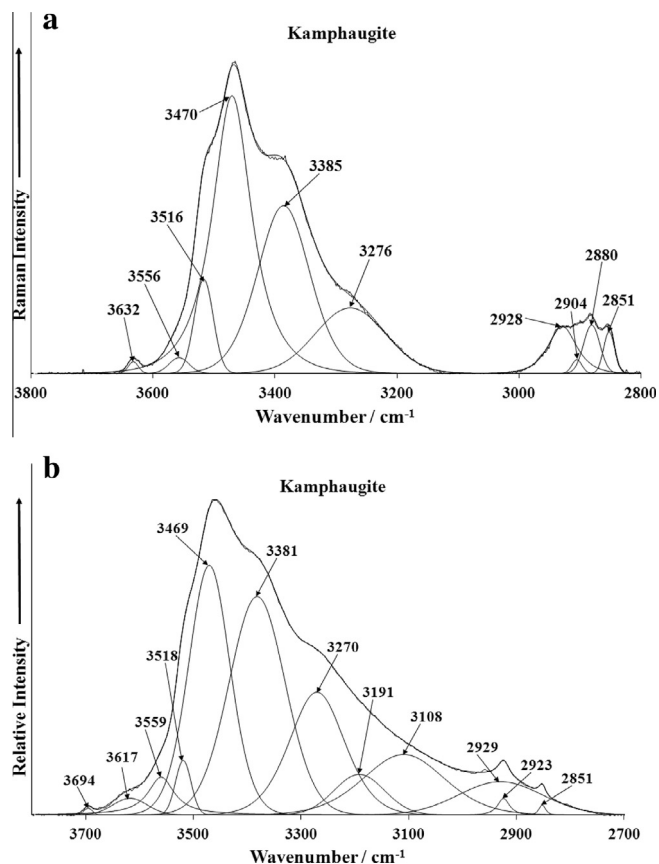
Fig. 4. (a) Raman spectrum of kamphaugite-(Y) over the 2800–3800 cm^{-1} spectral range (upper spectrum). (b) Infrared spectrum of kamphaugite-(Y) over the 2700–3800 cm^{-1} spectral range (lower spectrum).

Fig. 5. (a) Raman spectrum of kamphaugite-(Y) over the 1300–1800 cm^{-1} spectral range. (b) Infrared spectrum of kamphaugite-(Y) over the 1700–1900 cm^{-1} spectral range.

bending mode. The observation of multiple bands in the v_4 region provides further evidence for the nonequivalence of the carbonate units in the kamphaugite-(Y) structure.

The Raman spectrum of kamphaugite-(Y) over the 400–800 cm^{-1} spectral range is shown in Fig. 3a. Bands in this figure are well below the position of any carbonate bands.

An intense band observed at 678 cm^{-1} and is assigned to an AlO stretching vibration. Frueh and Golightly reported a band at 685 cm^{-1} and assigned the band to this vibrational mode [22]. Serna et al. attributed most of the vibrational bands below 700 cm^{-1} to AlO modes [23]. It is probable that the band at 432 with a shoulder at 443 cm^{-1} is also attributable to an AlO symmetric stretching vibration. Two bands are observed at ~361, 374 and 389 cm^{-1} and may be assigned to OAlO bending modes. The Raman spectrum of kamphaugite-(Y) over the 100–400 cm^{-1} spectral range is shown in Fig. 3b. A number of Raman bands are observed at 147, 163, 186, 205, 218, 250, 261, 288, 295 and 369 cm^{-1}. These bands are defined as external vibrations.

The Raman spectrum of kamphaugite-(Y) over the 2800–3800 cm^{-1} spectral region is given in Fig. 4a. Raman bands are observed at 3276, 3385, 3470, 3516, 3556 and 3632 cm^{-1} with other low intensity bands at 2851, 2880, 2904 and 2928 cm^{-1}. These latter bands are attributed to CH bands of some organic impurity. The other bands are attributed to water stretching vibrations. A Raman band in a high wavenumber position is also noted at 3632 cm^{-1}. This band is assigned to the stretching vibration of the OH units.

The infrared spectrum over the 2700–3500 cm^{-1} spectral range is reported in Fig. 4b. The spectral profile is broad and bands may
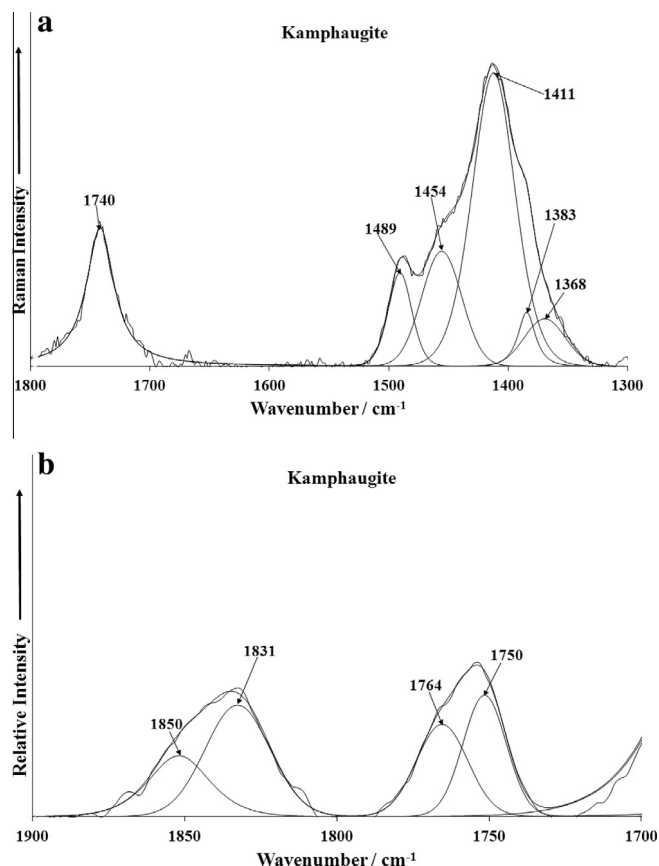
be resolved at 3108, 3191, 3270, 3381, 3649, 3518, 3559, 3617 and 3694 cm^{-1}. The latter two bands are assigned to OH stretching vibrations whilst the remaining bands are ascroibed to water stretching vibrations. Studies have shown a strong correlation between OH stretching frequencies and both O···O bond distances and H···O hydrogen bond distances [24–27]. Libowitzky showed that a regression function can be employed relating the hydroxyl stretching wavenumbers with regression coefficients better than 0.96 using infrared spectroscopy [28]. The function is described as: $v_1 = (3592 - 304) \times 109^{\frac{-d(O-O)}{0.1321}}$ cm^{-1}. Thus OH···O hydrogen bond distances may be calculated using the Libowitzky empirical function. The values for the OH stretching vibrations detailed above provide hydrogen bond distances of 0.2732 pm (3276 cm^{-1}), 0.27170 pm (3237 cm^{-1}). Frueh and Golightly suggested some hydrogen bonding exists for kamphaugite-(Y) [22]. The values calculated here, support the concept of strong hydrogen bonding between the OH units and the carbonate anions in the kamphaugite-(Y) structure.

The Raman spectrum of kamphaugite-(Y) over the 1300–1800 cm^{-1} spectral range is reported in Fig. 5a. The series of Raman bands at 1368, 1383, 1411, 1454 and 1489 cm^{-1} are assigned to the v_3 $(CO_3)^{2-}$ antisymmetric stretching mode. The observation of a large number of bands offers further support for the concept of non-equivalence of the carbonate anion in the kamphaugite-(Y) structure. Another band is observed at 1740 cm^{-1}. The assignment of this band is not known. One possibility is that it is due to the carbonate anion bonded to a hydroxyl unit. Similar bands at 1750 and 1764 cm^{-1} are noted in the infrared spectrum (Fig. 5b).

Conclusions

The mineral kamphuagite-(Y) has been analyzed using a combination of SEM with EDX and vibrational spectroscopy. Chemical analysis shows the presence of Ca, Y and C.

SEM and XRD shaped the mineral was a reasonably pure phase. The Al and Si found in low concentrations in the EDX analysis probably result from the presence of clay in the mineral sample.

Raman bands at 1078 and 1088 cm^{-1} are assigned to the carbonate ν_1 symmetric stretching modes. A very low intensity Raman band found at 1366 cm^{-1} is assigned to the ν_3 antisymmetric stretching mode. Two Raman bands at 898 and 936 cm^{-1} are attributed to the OH deformation bands of kamphaugite-(Y). Raman bands are observed at 820 and 824 cm^{-1} and are attributed to the ν_4 bending mode. Raman spectroscopy offers support for the non-equivalence of carbonate units in the kamphaugite-(Y) structure.

Acknowledgements

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.saa.2015.02.017.

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