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Raman and infrared spectroscopic study of kamphaugite-(Y)

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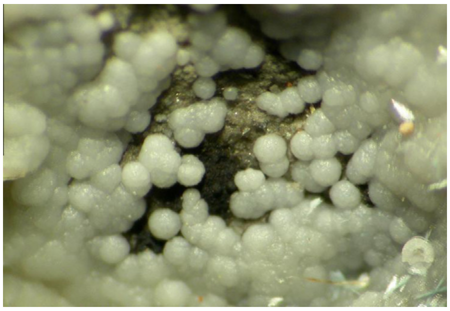
HIGHLIGHTS

- 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



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ABSTRACT

We have studied the carbonate mineral kamphaugite-(Y)($CaY(CO_3)_2(OH){\cdot}H_2O$), 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 ν_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.

Introduction

The mineral kamphaugite-(Y) is a calcium rare earth carbonate of formula $Ca(Y,REE)(CO_3)_2(OH){\cdot}H_2O$ [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 unidenate 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 (ν_1), an out-of-plane bend (ν_2), a doubly degenerate asymmetric stretch (ν_3) and another doubly degenerate bending mode (ν_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 (ν_1), of

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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-

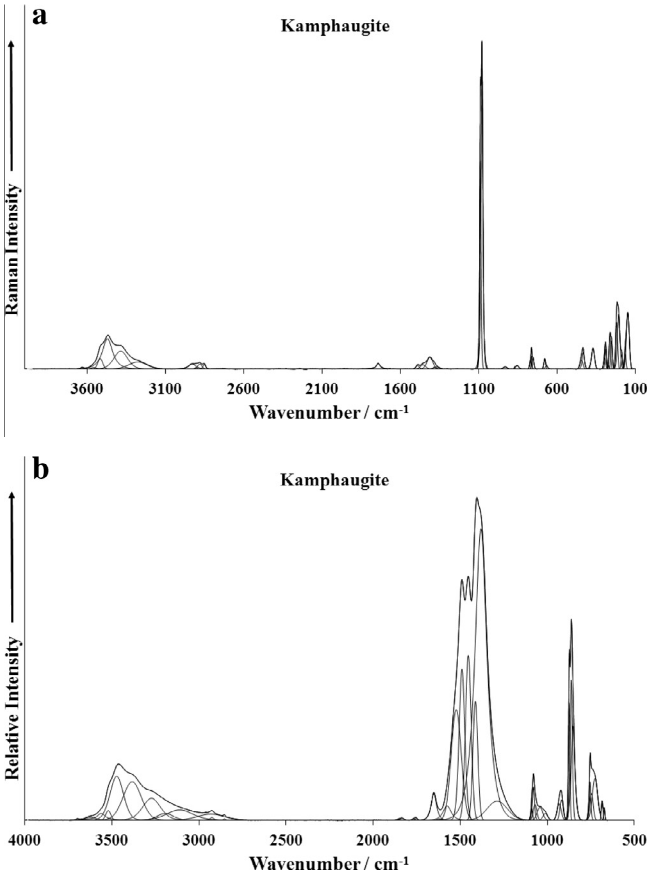

Fig. 1. (a) Raman spectrum of kamphaugite-(Y) over the 100–4000 cm^{-1} spectral range (upper spectrum). (b) Infrared spectrum of kamphaugite-(Y) over the 500–4000 cm^{-1} spectral range (lower spectrum).