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Raman spectroscopic study of the mineral qingheiite $Na_2(Mn^{2+},Mg,Fe^{2+})_2(Al,Fe^{3+})(PO_4)_3$, a pegmatite phosphate mineral from Santa Ana pegmatite, Argentina

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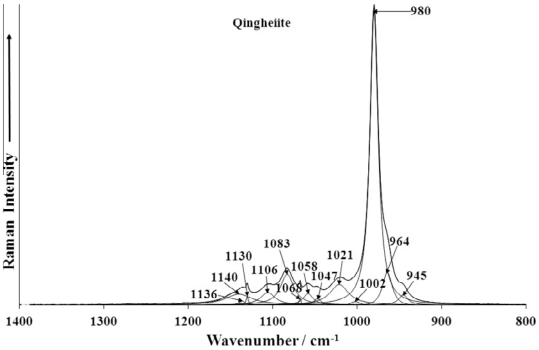
HIGHLIGHTS

- We have studied the pegmatite phosphate mineral qingheiite.
- The formula was determined as $Na_{1.39}(Mn_{1.42}, Mg_{0.87}, Fe^{2+}_{0.64}, Zn_{0.01})_{\sum 2.94}(Al_{0.43}, Fe^{3+}_{0.35})_{\sum 0.78}(PO_4)_{2.99}$.
- The Raman spectra shows the phosphate anion is very strongly distorted.
- The presence of water was determined by infrared spectroscopy.

GRAPHICAL ABSTRACT



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ABSTRACT

The pegmatite mineral qingheiite $Na_2(Mn^{2+},Mg,Fe^{2+})_2(Al,Fe^{3+})(PO_4)_3$ has been studied by a combination of SEM and EMP, Raman and infrared spectroscopy. The studied sample was collected from the Santa Ana pegmatite, Argentina. The mineral occurs as a primary mineral in lithium bearing pegmatite, in association with beausite and lithiophilite. The Raman spectrum is characterized by a very sharp intense Raman band at 980 cm^{-1} assigned to the PO_4^{3-} symmetric stretching mode.

Multiple Raman bands are observed in the PO_4^{3-} antisymmetric stretching region, providing evidence for the existence of more than one phosphate unit in the structure of qingheiite and evidence for the reduction in symmetry of the phosphate units. This concept is affirmed by the number of bands in the v_4 and v_2 bending regions. No intensity was observed in the OH stretching region in the Raman spectrum but significant intensity is found in the infrared spectrum. Infrared bands are observed at 2917, 3195, 3414 and 3498 cm^{-1} are assigned to water stretching vibrations. It is suggested that some water is coordinating the metal cations in the structure of qingheiite.

Introduction

Qingheiite is a rare Na, Mn and Al phosphate mineral and belongs to the wyllieite group. This mineral group shows general chemical formula given as: $Na_2(M1)(M2)(X)(PO_4)_6$, where M1 can be occupied by Mn and Fe; M2 by Fe, Mg and Mn and X by Al and Fe. The group also includes a number of minerals such as bobfergusonite, ferrorosemaryite, ferrowyllieite, qingheiite-(Fe^{2+}) and rosemaryite [1].

Qingheiite is the Mg end-member of the wyllieite subgroup and is typically found in granitic pegmatites. The chemical formula can be written as $Na_2(Mn^{2+},Mg,Fe^{2+})_2(Al,Fe^{3+})(PO_4)_3$. The mineral crystallizes in the monoclinic crystal system, space group $P2_1/b$,

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unit cell parameter: a = 11.85 Å, b = 12.41 Å, c = 6.42 Å, β = 114.45°, V = 859.45 Å^3. The mineral was discovered in a muscovite-bearing granitic pegmatite of Qinghe County, Altai Prefecture, Uygur Autonomous Region of Xinjiang, China [2]. Despite the type locality, qingheiite was also described from Santa Ana pegmatite, Argentina [3], and Sowie Mountains, Poland [4].

Raman spectroscopy has proven very useful for the study of minerals. Indeed Raman spectroscopy has proven most useful for the study of secondary minerals as often occurs with minerals containing phosphate groups. In the infrared study of triploidite, a basic manganese phosphate, S.D. Ross (in Framer's treatise page 383) reports the infrared spectrum with the (ν_1) at 957 cm^{-1}, (ν_3) at 1090, 1058, 1030 and 1010 cm^{-1}, (ν_2) at 420 cm^{-1} and the ν_4 mode at 595, 570, 486 cm^{-1} [5–7]. An hydroxyl stretching wavenumber of 3509 cm^{-1} was given. In the Raman spectroscopic study of strengite, in the region below 400 cm^{-1}, Frost and Weier [8,9] described the metal stretching vibrations for FeO and also the OFeO bending modes.

The objective of this research is to report the vibrational spectra of qingheiite and to relate the spectra to the molecular structure of the mineral. Chemical characterization was done with support of Electron Probe Micro Analysis (EMP).

Experimental

Occurrence, samples description and preparation

The qingheiite sample studied in this work was collected from the Santa Ana pegmatite, Argentina. The mineral occurs as a primary mineral in lithium bearing pegmatite, in association with beausite and lithiophilite. The mineral occurs as millimetric to centimetric veins in a matrix beauzite and lithiophilite exsolution. Qingheiite shows deep green color and vitreous luster. The sample was incorporated in the mineral collection of the Geology Department of the Federal University of Ouro Preto, Minas Gerais, Brazil, with sample code SAA-095. The Santa Ana pegmatite is located in the Cerro La Torre pegmatite group, Totoral pegmatite field of the Pampean pegmatite province. A detailed geological and mineralogical study of the pegmatite was carried out by Galliski et al. [3].

The qingheiite sample was gently crushed and to remove contaminant phases, the fragments were carefully hand-picked using a Stereomicroscope Leica Model EZ4. The fragments were prepared to be analyzed by different methods. The qingheiite sample was phase analyzed by X-ray diffraction. Scanning electron microscopy in the EDS mode (SEM/EDS) was applied to support the mineralogical 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).

A fragment of a qingheiite single crystal was prepared in a carbon tape. Due to the low vacuum conditions the sample was not metalized. Secondary Electron and Backscattering Electron images were obtained using a JEOL JSM-6360LV equipment. Qualitative and semi-quantitative chemical analysis in the EDS mode were performed with a ThermoNORAN spectrometer model Quest and was applied to support the mineral characterization.

Electron microprobe analysis (EMP)

EMP was performed in a qingheiite single crystal. The chemical analysis was done using a Jeol JXA8900R with four WDS spectrometers at the Physics Department of the Federal University of Minas Gerais, Belo Horizonte. For each selected element the following standards were applied: Mn (rhodonite), Fe (magnetite), Ca ($Ca_2P_2O_7$), Mg (MgO), Zn (Sphalerite), Na (Albite) and P ($Ca_2P_2O_7$). Samples of qingheiite embedded in an epoxy resin were coated with a thin layer of evaporated carbon. The EMP analysis was performed at 15 kV of accelerating voltage and beam current of 10 nA.

Raman spectroscopy

Crystals of qingheiite 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.

Infrared spectroscopy

Infrared spectra were obtained using a Nicolet Nexus 8700 FTIR spectrometer with a Smart Endurance single bounce diamond ATR

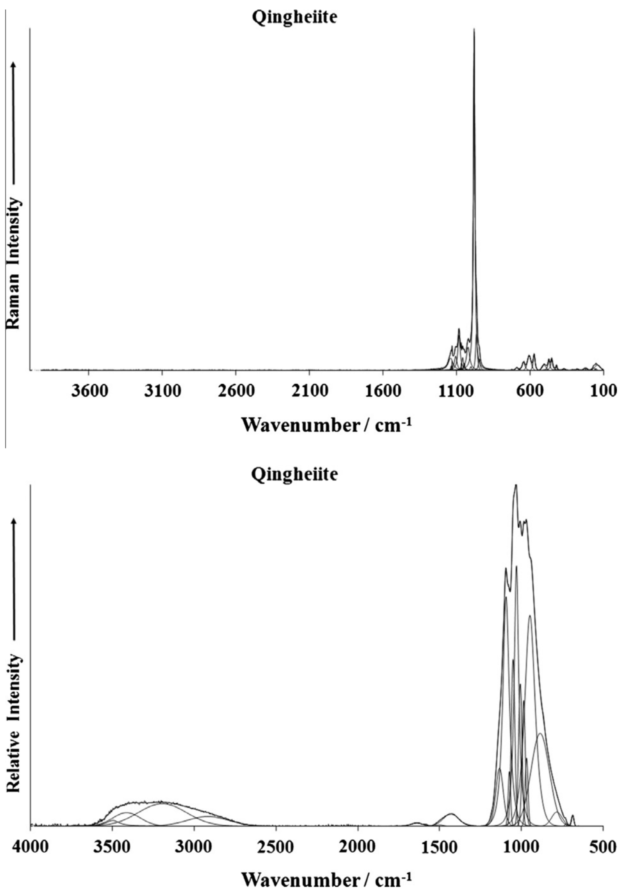

Fig. 1. (a) Raman spectrum of qingheiite over the 100–4000 cm^{-1} spectral range. (b) Infrared spectrum of qingheiite over the 500–4000 cm^{-1} spectral range.