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A Raman and infrared spectroscopic analysis of the phosphate mineral wardite $\text{NaAl}_3(\text{PO}_4)_2(\text{OH})_4 \cdot 2(\text{H}_2\text{O})$ from Brazil

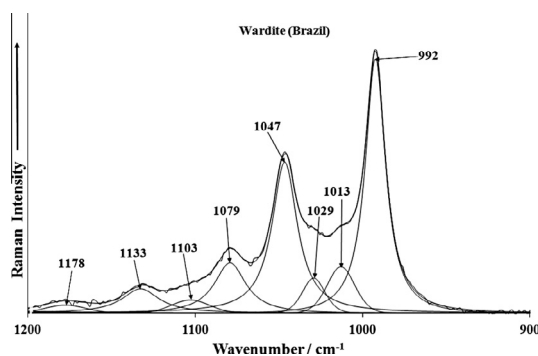
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HIGHLIGHTS

- A wardite mineral sample from Lavra Da Ilha, Minas Gerais, Brazil was analysed.
- Using SEM with EDX and vibrational spectroscopy.
- The calculated formula is $(\text{Na}_{0.97}\text{Ca}_{0.03})_{\Sigma 1.00}\text{Al}_3(\text{PO}_4)_2(\text{OH})_4 \cdot 2(\text{H}_2\text{O})$.
- Observation of multiple bands supports the concept of non-equivalent phosphate units in the structure.

GRAPHICAL ABSTRACT



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ABSTRACT

A wardite mineral sample from Lavra Da Ilha, Minas Gerais, Brazil has been examined by vibrational spectroscopy. The mineral is unusual in that it belongs to a unique symmetry class, namely the tetragonal-trapezohedral group. The structure of wardite contains layers of corner-linked OH bridged MO_6 octahedra stacked along the tetragonal C-axis in a four-layer sequence and linked by PO_4 groups. Consequentially not all phosphate units are identical. Two intense Raman bands observed at 995 and 1051 cm^{-1} are assigned to the ν_1 PO_4^{3-} symmetric stretching mode. Intense Raman bands are observed at 605 and 618 cm^{-1} with shoulders at 578 and 589 cm^{-1} are assigned to the ν_4 out of plane bending modes of the PO_4^{3-} . The observation of multiple bands supports the concept of non-equivalent phosphate units in the structure. Sharp infrared bands are observed at 3544 and 3611 cm^{-1} are attributed to the OH stretching vibrations of the hydroxyl units. Vibrational spectroscopy enables subtle details of the molecular structure of wardite to be determined.

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Introduction

Wardite is a mineral found in many parts of the world, including Brazil. Wardite [1] is a hydrated hydroxyl sodium aluminium phosphate $\text{NaAl}_3(\text{PO}_4)_2(\text{OH})_4 \cdot 2(\text{H}_2\text{O})$ [2,3]. Wardite is a poorly known

mineral, but of special interest to mineralogists. Some studies of wardite and the structurally related mineral cyrilovite have been undertaken by the authors [4,5]. Hence, we have carried out this study to further our understanding of the structure of the mineral wardite. Crystals of wardite show the lower symmetry by displaying squashed pseudo-octahedrons with striated faces. The mineral is unusual in that it belongs to a unique symmetry class, namely the tetragonal-trapezohedral group [2]. This class has only a 4-fold rotational axis and two 2-fold rotational axes and nothing else. Such

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unique symmetry will influence the vibrational spectrum. Crystals of wardite show the lower symmetry by displaying squashed pseudo-octahedrons with striated faces. The crystal structures of natural wardite and of the isomorphous cyrilovite are published [2,6]. The structure of cyrilovite was further refined by Cooper et al. [7]. The cell dimensions are *Space Group*: $P4_12_12$ or $P4_32_12$. $a = 7.03(1) \text{ \AA}$, $c = 19.04(1) \text{ \AA}$ and $Z = 4$. The structures contain layers of two kinds of corner-linked –OH bridged MO_6 octahedra ($M = \text{Al, Fe}$), stacked along the tetragonal C -axis in a four-layer sequence and linked by PO_4 groups. Within a layer, e.g. around the (001) plane, two independent pairs of symmetry-correlated –OH groups are arranged in the equatorial pseudo-planes of one kind of MO_6 octahedra [2,6]. The mineral is white to colourless, to pale green to blue-green and other colours depending upon the composition of the mineral. Wardite is an Al based mineral but replacement of the Al by Fe will affect the exact colour of wardite. The mineral is known from many localities in Australia including at the Iron Monarch quarry, Iron Knob, South Australia, from Wycheproof, Victoria, and on Milgun Station, Western Australia.

There have been some studies of the vibrational spectroscopy of wardite [8,9]. Tarte et al. collected the infrared spectra of five samples of cyrilovite $\text{NaFe}_3(\text{PO}_4)_2(\text{OH})_4 \cdot 2(\text{H}_2\text{O})$ and wardite [9]. Cyrilovite is analogous to wardite, with ferric iron replacing the aluminium in the structure. It is likely that solid solutions of the two minerals are formed with varying amounts of ferric ion and aluminium in the structure, thus influencing the colour and appearance of the mineral. The mineral wardite is capable of crystallizing in a similar form to that of cyrilovite because of their closely related chemical compositions. Between wardite's composition, $\text{NaAl}_3(\text{PO}_4)_2(\text{OH})_4 \cdot 2(\text{H}_2\text{O})$, and cyrilovite composition, $\text{NaFe}_3(\text{PO}_4)_2(\text{OH})_4 \cdot 2(\text{H}_2\text{O})$, these minerals are able to form end members of a series of solid solutions. Either of the two minerals can occur in various proportions in a series of solid solutions in the wardite mineral group. Cyrilovite is a rare accessory mineral in some oxidizing phosphate-bearing granite pegmatites and iron deposits, such as are found in Brazil [4]. The vibrational spectrum is dependent upon the ratio of the Al/Fe. Tarte et al. found that the two minerals wardite and cyrilovite can be distinguished by the spectral patterns of the OH stretching region in the infrared spectrum [9]. These workers did not interpret the spectra of the phosphate because of complexity and no detailed assignment was given. Breitingner et al. reported the combined vibrational spectra of a natural wardite. Breitingner and co-workers used a full array of techniques including inelastic neutron scattering, infrared, Raman and near infrared techniques [8] to study the properties of the mineral. These workers used a natural wardite with significant amounts of ferric iron in the structure. In other words the sample analysed was fundamentally a solid solution of wardite and cyrilovite, but at the wardite end. The original papers on the infrared spectrum of isolated phosphate units was published by Lazarev [10]. Of course, Phosphates structures are different. Usually they have rather low symmetry: orthorhombic, monoclinic, or even triclinic [11]. Farmer based upon the work of Petrov et al. [12–14] made a comparison of the results of the vibrational spectrum of a series of phosphates.

Raman spectroscopy has proven very useful for the study of minerals, especially minerals containing oxyanions such as phosphate. Indeed, Raman spectroscopy has proven most useful for the study of diagenetically related minerals where isomorphic substitution may occur as with wardite and cyrilovite, as often occurs with minerals containing phosphate groups. This paper is a part of systematic studies of vibrational spectra of minerals of secondary origin in the oxide supergene zone. The objective of this research is to report the Raman and infrared spectra of wardite and to relate the spectra to the molecular structure of the mineral.

Experimental

Samples description and preparation

The mineral wardite studied in this work was obtained from the collection of the Geology Department of the Federal University of Ouro Preto, Minas Gerais, Brazil, with sample code SAD-008. The wardite originated from Lavra Da Ilha, Minas Gerais, Brazil. Details of the mineral have been published (page 643) [15]. Crystals of wardite can make nice specimens with their colourless or light green colour and glassy lustre. Massive green wardite is associated with variscite nodules where it formed from the alteration of the variscite. The mineral is an uncommon species in complex zoned pegmatites.

The sample was gently crushed and the associated minerals were removed under a stereomicroscope Leica MZ4. Scanning electron microscopy (SEM) was applied to support the mineral chemistry.

Scanning electron microscopy (SEM)

Wardite cleavage fragments were coated with a 5 nm layer of evaporated Au. 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 spectroscopy

Crystals of wardite were placed on a polished metal surface on the stage of an Olympus BHSM microscope, which is equipped with 10 \times , 20 \times , and 50 \times 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 $\pm 1 \text{ cm}^{-1}$ in the range between 200 and 4000 cm^{-1} . Some of these mineral fluoresced badly at 633 nm; as a consequence other laser excitation wavelengths were used especially the 785 nm laser. Repeated acquisitions on the crystals using the highest magnification (50 \times) were accumulated to improve the signal to noise ratio of the spectra. Spectra were calibrated using the 520.5 cm^{-1} line of a silicon wafer. Previous studies by the authors provide more details of the experimental technique [4,16–19]. Alignment of all crystals in a similar orientation has been attempted and achieved. However, differences in intensity may be observed due to minor differences in the crystal orientation.

Infrared spectroscopy

Infrared spectra were obtained in reflectance mode, 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. Using the reflectance technique, the mineral sample is not destroyed. This is important as many mineral samples are from museum collections, as is this sample.

Spectral manipulation such as baseline correction/adjustment and smoothing were performed using the Spectralcalc software package GRAMS (Galactic Industries Corporation, NH, USA). Band component analysis was undertaken using the Jandel 'Peakfit'

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