



Vibrational spectroscopic characterization of the phosphate mineral hureaulite – $(\text{Mn, Fe})_5(\text{PO}_4)_2(\text{HPO}_4)_2 \cdot 4(\text{H}_2\text{O})$

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ABSTRACT

This research was done on hureaulite samples from the Cigana claim, a lithium bearing pegmatite with triphylite and spodumene. The mine is located in Conselheiro Pena, east of Minas Gerais. Chemical analysis was carried out by Electron Microprobe analysis and indicated a manganese rich phase with partial substitution of iron. The calculated chemical formula of the studied sample is: $(\text{Mn}_{3.23}, \text{Fe}_{1.04}, \text{Ca}_{0.19}, \text{Mg}_{0.13})(\text{PO}_4)_{2.7}(\text{HPO}_4)_{2.6}(\text{OH})_{4.78}$. The Raman spectrum of hureaulite is dominated by an intense sharp band at 959 cm^{-1} assigned to PO stretching vibrations of HPO_4^{2-} units. The Raman band at 989 cm^{-1} is assigned to the PO_4^{3-} stretching vibration. Raman bands at 1007, 1024, 1047, and 1083 cm^{-1} are attributed to both the HOP and PO antisymmetric stretching vibrations of HPO_4^{2-} and PO_4^{3-} units. A set of Raman bands at 531, 543, 564 and 582 cm^{-1} are assigned to the ν_4 bending modes of the HPO_4^{2-} and PO_4^{3-} units. Raman bands observed at 414, and 455 cm^{-1} are attributed to the ν_2 HPO_4^{2-} and PO_4^{3-} units. The intense A series of Raman and infrared bands in the OH stretching region are assigned to water stretching vibrations. Based upon the position of these bands hydrogen bond distances are calculated. Hydrogen bond distances are short indicating very strong hydrogen bonding in the hureaulite structure. A combination of Raman and infrared spectroscopy enabled aspects of the molecular structure of the mineral hureaulite to be understood.

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1. Introduction

Hureaulite is a manganese hydrated acid phosphate mineral with general chemical formula expressed by $(\text{Mn, Fe})_5(\text{PO}_4)_2(\text{HPO}_4)_2 \cdot 4(\text{H}_2\text{O})$. It was first discovered and named by Alluaud [1] in 1826 in samples from Huréaux quarry, St. Sylvestre, Haute-Vienne, France, and was first described by Dufrenoy in 1829 [2]. The mineral belongs to the hureaulite group that also includes: miguelromeroite [3], nyholmite [4], sainfeldite [5] and villyaellenite [6]. A comparison among the members of the hureaulite group suggest a general chemical formula expressed by $(\text{M1})(\text{M2})_2(\text{M3})_2(\text{XO}_4)_2(\text{HXO}_4)_2 \cdot 4(\text{H}_2\text{O})$, where M1 = Mn, Ca, Cd; M2 = Fe, Mn, Cd, Ca; M3 = Fe, Mn, Zn, Ca and X can be occupied by P and As.

The crystal structure of hureaulite was solved by Moore and Araki [7]. The mineral crystallizes in monoclinic crystal system, C2/c space group with unit-cell parameters $a = 17.594(10) \text{ \AA}$, $b = 9.086(5) \text{ \AA}$, $c = 9.404(5) \text{ \AA}$, $\alpha = 90^\circ$, $\beta = 96.67(8)^\circ$, $\gamma = 90^\circ$, $V = 1493.14 \text{ \AA}^3$ and $Z = 4$. Hureaulite structure consists of an

open three-dimensional network formed by octahedral pentameric entities that share vertices with the $[\text{PO}_4]$ and $[\text{PO}_3(\text{OH})]$ tetrahedra. Mössbauer spectroscopy characterization was carried out by Moreira et al. [8], who described a complete Mn^{2+} – Fe^{2+} solid solution.

Hureaulite is a common mineral in lithium bearing pegmatites and is related to the hydrothermal alteration after triphylite–lithiophilite or some other Fe–Mn primary phosphate. Hureaulite also can originate from the hydrothermal reaction of Mn-rich phosphatic solutions. Moore described hureaulite as an early to late hydrothermal mineral in the phosphate paragenesis of granitic pegmatites [9]. Hureaulite has been synthesized by different methods. Hydrothermal synthesis and treatment in different physical and chemical conditions were used to obtain single and doped hureaulite crystals [10–12]. In recent studies, hureaulite crystals have produced by reflux process at ambient temperature and pressure [13–15].

Hureaulite has potential to application in different ways in industry, such as magnetics, optics, and electrochemistry. In addition, hureaulite is widely used as an additive to obtain highly corrosion-resistant surfaces in order to improve the wear resistance of steels (3, 7, 8, 9). A dense, finely-structured phosphate layer firmly attaches to the substrate when hureaulite is

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used to form corrosion-resistant surfaces [8,10,11]. Recently, the synthesis and physicochemical properties of hureaulite have garnered widespread attention in mineralogy and materials science [5,12–14]. In recent years, spectroscopic studies concerning phosphate minerals are increasing, especially due to their industrial and technological importance, however, only Near-infrared vibrational spectroscopic data are available on hureaulite [16].

Farmer [17] divided the vibrational spectra of phosphates according to the presence, or absence of water and hydroxyl units in the minerals. In aqueous systems, Raman spectra of phosphate oxyanions show a symmetric stretching mode (ν_1) at 938 cm^{-1} , the antisymmetric stretching mode (ν_3) at 1017 cm^{-1} , the symmetric bending mode (ν_2) at 420 cm^{-1} and the ν_4 mode at 567 cm^{-1} [18–20]. The value for the ν_1 symmetric stretching vibration of PO_4 units as determined by infrared spectroscopy was given as 930 cm^{-1} (augelite), 940 cm^{-1} (wavellite), 970 cm^{-1} (rockbridgeite), 995 cm^{-1} (dufrenite) and 965 cm^{-1} (beraunite). The position of the symmetric stretching vibration is mineral dependent and a function of the cation and crystal structure. The fact that the symmetric stretching mode is observed in the infrared spectrum affirms a reduction in symmetry of the PO_4 units.

The value for the ν_2 symmetric bending vibration of PO_4 units as determined by infrared spectroscopy was given as 438 cm^{-1} (augelite), 452 cm^{-1} (wavellite), 440 and 415 cm^{-1} (rockbridgeite), 455 , 435 and 415 cm^{-1} (dufrenite) and 470 and 450 cm^{-1} (beraunite). The observation of multiple bending modes provides an indication of symmetry reduction of the PO_4 units. This symmetry reduction is also observed through the ν_3 antisymmetric stretching vibrations. Augelite shows infrared bands at 1205 , 1155 , 1079 and 1015 cm^{-1} ; wavellite at 1145 , 1102 , 1062 and 1025 cm^{-1} ; rockbridgeite at 1145 , 1060 and 1030 cm^{-1} ; dufrenite at 1135 , 1070 and 1032 cm^{-1} ; and beraunite at 1150 , 1100 , 1076 and 1035 cm^{-1} .

In the infrared study of triploidite, a basic manganese phosphate, Farmer 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} [12]. A hydroxyl stretching frequency of 3509 cm^{-1} was given. In the spectroscopic study of strengite, in the region below to 400 cm^{-1} , Frost and Weier [21] described the metal stretching vibrations for MnO and also the OMnO bending modes.

In this work, samples of a monomineral hureaulite from the Cigana pegmatite, located in the municipality of Conselheiro Pena, Minas Gerais, Brazil have been characterized. Studies include chemistry and backscattering images via SEM in the EDS mode and electron probe microanalysis in the WDS mode (EPMA), spectroscopic characterization of the structure with infrared and Raman.

2. Geological setting, occurrence and general appearance

The Cigana mine, located in the municipality of Conselheiro Pena, is a well-known pegmatite in Brazil, being an important source of rare phosphates. The pegmatite is located in the Conselheiro Pena pegmatite district, one of the subdivisions of the Eastern Brazilian Pegmatite province (EBP) [22]. The Conselheiro Pena pegmatite district covers an area of about 5000 km^2 , in the middle part of the Doce River basin, about 360 km NE of the city of Belo Horizonte.

The Cigana mine in the past was mined for industrial feldspar and with minor importance gemstones and samples for the collectors market. The pegmatite is heterogeneous with well-developed mineralogical and textural zoning. It has symmetric lens shape with the longer axis trending to NW–SE and body dips sub vertically. The minimum extension is of about 50 m and 20 m thickness.

The pegmatite is hosted by quartz–mica schist with garnet, staurolite and sillimanite of the São Tomé Formation. Tourmalinization is observed in the contact between the pegmatite and the host rock. Hydrothermal and metasomatic fluids were responsible for the albitization and development of miarolitic cavities, and a complex secondary phosphate assemblage was described by Chaves et al. [23].

The primary mineral association is represented by quartz, muscovite, microcline, schorl, almandine-spessartine, spodumene and triphylite. The secondary association is mainly composed by albite, Ta and Nb oxides, hydrothermal beryl, cassiterite, pyrite and a complex paragenesis of phosphates formed as a result of hydrothermal alteration of triphylite [23]. In the Cigana pegmatite, secondary phosphates, namely eosphorite, fairfieldite, fluorapatite, frondelite, gormanite, hureaulite, lithiophilite, reddingite and vivianite are common minerals in miarolitic cavities and in massive blocks formed after the aggregates of primary triphylite. Hureaulite crystals up to 5.0 mm along the c axis with monoclinic prismatic morphology occur in miarolitic cavities and after triphylite, in association with vivianite, lithiophilite and reddingite.

3. Experimental

3.1. Samples and preparation

Pink hureaulite single crystals from granitic pegmatite from Minas Gerais were obtained from the collection of the Geology Department of the Federal University of Ouro Preto, Minas Gerais, Brazil, with sample code SAA-081. The sample is from Cigana claim (also named João claim), a lithium bearing pegmatite with triphylite and spodumene. The mine is located in Conselheiro Pena, east of Minas Gerais. To remove contaminate phases, with the support of a Stereomicroscope Leica Model EZ4, hureaulite crystals were handily selected from a sample in association with reddingite, lithiophilite, triphylite and vivianite. The hureaulite crystals were phase analyzed by X-ray powder diffraction and scanning electron microscopy in the EDS mode (SEM/EDS).

3.2. Scanning electron microscopy (SEM)

Hureaulite samples were coated with a thin layer of evaporated carbon. Secondary electron images and backscattering electron images were obtained using a JEOL-5510 scanning electron microscope (SEM) from the Geology Department of the Federal University of Ouro Preto. Qualitative chemical analysis by SEM in the EDS mode was produced to support the mineral characterization and determine the elements to be analyzed by Electron probe micro-analysis.

3.3. Electron probe micro-analysis (EPMA)

A quantitative chemical analysis was carried via EPMA. Hureaulite single crystal selected for this study was analyzed with the performance of five spots. The chemical analysis was carried out with a Jeol JXA8900R spectrometer from the Physics Department of the Federal University of Minas Gerais, Belo Horizonte. For each selected element was used the following standards: Fe – magnetite, Mg – olivine, Mn – rhodonite, P and Ca – Apatite Astimex, Al – Corundum and F – Fluorite. The epoxy embedded hureaulite sample was polished in the sequence of $9\text{ }\mu\text{m}$, $6\text{ }\mu\text{m}$ and $1\text{ }\mu\text{m}$ diamond paste MetaDI® II Diamond Paste–Buhler, using water as a lubricant, with a semi-automatic MiniMet® 1000 Grinder–Polisher–Buehler. Finally, the epoxy embedded hureaulite was coated with a thin layer of evaporated carbon. The electron probe microanalysis in the WDS (wavelength dispersive spectrometer) mode was obtained at

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