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Raman, infrared and near-infrared spectroscopic characterization of the herderite–hydroxylherderite mineral series

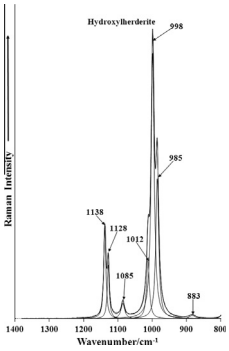
Ray L. Frost [a,*], Ricardo Scholz [b], Andrés López [a], Yunfei Xi [a], Camila de Siqueira Queiroz [b], Fernanda M. Belotti [c], Mauro Cândido Filho [d]

[a] School of Chemistry, Physics and Mechanical Engineering, Science and Engineering Faculty, Queensland University of Technology, GPO Box 2434, Brisbane, Queensland 4001, Australia
[b] Geology Department, School of Mines, Federal University of Ouro Preto, Campus Morro do Cruzeiro, Ouro Preto, MG 35400-00, Brazil
[c] Federal University of Itajubá, Campus Itabira, Itabira, MG, Brazil
[d] Mining Engineering Department, School of Mines, Federal University of Ouro Preto, Campus Morro do Cruzeiro, Ouro Preto, MG 35400-00, Brazil

HIGHLIGHTS

- We have studied herderite–hydroxylherderite series from Brazil.
- $CaBePO_4(F,OH)$ was investigated by an electron microprobe.
- The minerals occur as secondary products in granitic pegmatites.
- We studied the minerals using vibrational spectroscopy.
- Hydrogen bond distances were calculated.

GRAPHICAL ABSTRACT



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ABSTRACT

Natural single-crystal specimens of the herderite–hydroxylherderite series from Brazil, with general formula $CaBePO_4(F,OH)$, were investigated by electron microprobe, Raman, infrared and near-infrared spectroscopies. The minerals occur as secondary products in granitic pegmatites. Herderite and hydroxylherderite minerals show extensive solid solution formation. The Raman spectra of hydroxylherderite are characterized by bands at around 985 and 998 cm^{-1}, assigned to v_1 symmetric stretching mode of the $HOPO_3^{3-}$ and PO_4^{3-} units. Raman bands at around 1085, 1128 and 1138 cm^{-1} are attributed to both the HOP and PO antisymmetric stretching vibrations. The set of Raman bands observed at 563, 568, 577, 598, 616 and 633 cm^{-1} are assigned to the v_4 out of plane bending modes of the PO_4 and H_2PO_4 units. The OH Raman stretching vibrations of hydroxylherderite were observed ranging from 3626 cm^{-1} to 3609 cm^{-1}. The infrared stretching vibrations of hydroxylherderites were observed between 3606 cm^{-1} and 3599 cm^{-1}. By using a Libowitzky type function, hydrogen bond distances based upon the OH stretching bands were calculated. Characteristic NIR bands at around 6961 and 7054 cm^{-1} were assigned to the first overtone of the fundamental, whilst NIR bands at 10,194 and 10,329 cm^{-1} are assigned to the second overtone of the fundamental OH stretching vibration. Insight into the structure of the herderite–hydroxylherderite series is assessed by vibrational spectroscopy.

Introduction

Beryllium is a typical chemical element found in granitic pegmatites, especially in the structure of silicates such as beryl [$Be_3Al_2(Si_6O_{18})$], phenakite (Be_2SiO_4), euclase [$(BeAl(SiO_4)(OH)$]

* Corresponding author. Tel.: +61 7 3138 2407; fax: +61 7 3138 1804.
E-mail address: r.frost@qut.edu.au (R.L. Frost).

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and bertrandite [$Be_4(Si_2O_7)(OH)_2$], and the oxide chrysoberyl ($BeAl_2O_4$). Beryllium metal is an important element in industry with different applications in metallurgy especially in the production of copper, aluminum and magnesium alloys; however, the use is limited due to the high price and toxicity. Beryllium has also importance for the defence and aerospace industry, due to its stiffness, light weight and dimensional stability over a wide temperature range. Despite the importance for industry, the major field of use of beryllium minerals is in the gemstones and jewelry market, mainly, emerald and aquamarine [1].

Be phosphates are relatively rare in nature and are related to a range of temperature and pressure during the pegmatite evolution [2], occurring from the magmatic process [3,4] to the hydrothermal and supergene [5,6]. Černý [7] and Černá et al. [8] describes beryllium phosphates as secondary product of late alteration of beryl. The most common Be phosphates are hydroxylherderite, moraesite, beryllonite and the members of the roscherite group [7–10]. Herderite and hydroxylherderite are two rare gemstones and also shows importance in the mineral collectors market [11–13]. Herderite was first described from samples associated with the Sn-bearing pegmatites at Ehrenfriedersdorf in the Erzgebirge of Germany [14], and hydroxylherderite was first described from the mineral District of Paris, Maine, USA by Penfield [15] as hydro-herderite. Later, Palache et al. [16] were responsible to establish the herderite–hydroxylherderite series. Byrappa and Pushcharovsky [17] have observed the structural similarity between hydroxylherderite and datolite. Chrystallographic studies were carried out by Lager and Gibbs [18] in hydroxylherderite from Golconda pegmatite, in Brazil and Harlow and Hawthorn [19] have solved the crystal structure of herderite from Mogok, Myanmar.

According to Lager and Gibbs [18], hydroxylherderite crystallizes in the monoclinic system, $P2_1/a$ space group, with $a = 9.789(2)$ Å, $b = 7.661(1)$ Å, $c = 4.804(1)$ Å and $\beta = 90.02(1)°$. Hydroxylherderite consists of sheets of corner-sharing PO_4 and BeO_3OH tetrahedra linked along the c axis by sheets of edge-sharing Ca-containing polyhedral. Each tetrahedral sheet contains alternating PO_4 and BeO_3OH polyhedral which form a network of four- and eight-membered centro-symetric rings extending parallel to (0 0 1). Herderite, as described by Harlow and Hawthorn [19] crystallizes in monoclinic crystal system, space group $P2_1/a$, with $a = 9.7446(4)$ Å, $b = 7.6769(3)$ Å, $c = 4.7633(2)$ Å, $\beta = 90.667(1)°$, $V = 356.31(4)$ Å^3, and $Z = 4$. The authors cited that as effect of increasing of herderite content, generally occurs a contraction of the structure, with a decrease in a, c, and V and the increase in b. The relation F—OH in herderite and hydroxylherderite were also studied in different ways. In a systematic optical and chemical characterization, Leavens et al. [20] have described the dependence of the refractive index with the F/OH ratios and have established the increase of refractive index to the decrease of F content.

In the infrared spectroscopic characterization of the amblygonite–montebrasite mineral series, Fransolet and Tarte [21] established a correlation between OH wavenumbers (ν_{OH} in the region between 3400–3350 cm^{-1} and δ_{OH} in the 840–800 cm^{-1} region) and the fluorine content. With the application of Raman spectroscopy, Rondeau et al. [22] have observed correlation between the F content with the position of 3 characteristic Raman peaks and the full width at medium height (FWMH) of the peak around 3370 cm^{-1}.

Farmer [23] 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} [24–28]. 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 [28]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}.

Published data concerning the spectroscopic characterization of beryllium phosphates are very rare in the literature. In the characterization of fluid inclusions in quartz from granitic pegmatites, Rickers et al. [29] describes Raman bands in herderite at 584, 595, 983, 1005 cm^{-1}; however, the authors gave no assignment of the bands. In recent studies, in reference to the datas published by Rickers et al. [29], Frezzoti et al. [30] described Raman vibrations related to $(PO_4)^{3-}$ anion in herderite at 584 cm^{-1} (ν_4), 983 cm^{-1} (ν_1) and 1005 (ν_3) cm^{-1}.

The objectives of this work are to understand the structure of herderite–hydroxylherderite minerals with the application of the vibrational spectroscopic methods infrared and Raman spectroscopy and to establish a relation between the F/OH ratios and the position of the vibrations bands of OH^- anion.

Experimental

Occurrence, sample description and preparation

For the development of this work, three natural single crystal specimens of the hydroxylherderite series were chosen. The samples were collected from different pegmatites and incorporated into the collection of the Geology Department of the Federal University of Ouro Preto, Minas Gerais, Brazil.

Sample SAA-073 was collected from the Morro Redondo mine, which belongs to the Araçuai pegmatite district, located near Coronel Murta, north of Minas Gerais. It corresponds to a bluish 3.0 cm single crystal and was found in association with muscovite and albite in a miarolitic cavity. Sample SAA-074 was collected from Jove Lauriano mine, located in the Conselheiro Pena pegmatite district, municipality of Divino das Laranjeiras, east of Minas Gerais. It corresponds to a single crystal up to 2 cm with yellowish color. The crystal was found in association with muscovite and albite in a miarolitic cavity. Samples SAA-075 and SAA-076 were also collected from pegmatites in the municipality of Divino das Laranjeiras. SAA-075 corresponds to an aggregate of 0.4 cm colorless single crystals and was found in association with muscovite, albite and fluorapatite in a miarolitic cavity. SAA-076 was collected from the Almerindo mine [31]. It corresponds to a yellowish single crystal, up to 2 cm in length and was found in association with muscovite, albite, fluorapatite and brazilianite in a miarolitic cavity. Sample SAA-093 was collected from a muscovite and topaz pegmatite in Medina, north from Minas Gerais. The single crystal shows bluish color, and occurs in association with muscovite.

The calcium and beryllium phosphates herderite and hydroxylherderite are the end member of a solid solution between fluorine and hydroxyl anions. The minerals occur in miarolitic