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Vibrational spectroscopy of the phosphate mineral lazulite – $(Mg, Fe)Al_2(PO_4)_2{\cdot}(OH)_2$ found in the Minas Gerais, Brazil

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HIGHLIGHTS

- ▶ In this work, we have studied the structure of lazulite.
- ▶ Lazulite is pegmatite phosphate with calculated formula $(Fe_{0.11})Al_{1.86}(PO_4)_{2.08}(OH)_{2.04}$.
- ▶ The structure of lazulite was assessed using a combination of Raman and infrared spectroscopy.

GRAPHICAL ABSTRACT

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ABSTRACT

This research was done on lazulite samples from the Gentil mine, a lithium bearing pegmatite located in the municipality of Mendes Pimentel, Minas Gerais, Brazil. Chemical analysis was carried out by electron microprobe analysis and indicated a magnesium rich phase with partial substitution of iron. Traces of Ca and Mn, (which partially replaced Mg) were found. The calculated chemical formula of the studied sample is: $(Mg_{0.88}, Fe_{0.11})Al_{1.87}(PO_4)_{2.08}(OH)_{2.02}$. The Raman spectrum of lazulite is dominated by an intense sharp band at 1060 cm^{-1} assigned to PO stretching vibrations of of tetrahedral [PO4] clusters presents into the HPO_4^{2-} units. Two Raman bands at 1102 and 1137 cm^{-1} are attributed to both the HOP and PO antisymmetric stretching vibrations. The two infrared bands at 997 and 1007 cm^{-1} are attributed to the ν_1 PO_4^{3-} symmetric stretching modes. The intense bands at 1035, 1054, 1081, 1118 and 1154 cm^{-1} are assigned to the ν_3 PO_4^{3-} antisymmetric stretching modes from both the HOP and tetrahedral [PO4] clusters. A set of Raman bands at 605, 613, 633 and 648 cm^{-1} are assigned to the ν_4 out of plane bending modes of the PO_4, HPO_4 and H_2PO_4 units. Raman bands observed at 414, 425, 460, and 479 cm^{-1} are attributed to the ν_2 tetrahedral PO_4 clusters, HPO_4 and H_2PO_4 bending modes. The intense Raman band at 3402 and the infrared band at 3403 cm^{-1} are assigned to the stretching vibration of the OH units. A combination of Raman and infrared spectroscopy enabled aspects of the molecular structure of the mineral lazulite to be understood.

Introduction

The minerals of lazulite group are basic hydro-phosphates and arsenates with the general composition $M_1^{2} + M_2^{3+}(XO_4)2$ $(OH)_2$, where M_1 can be occupied by Fe^{2+}, Mg, Cu and Zn, and M_2 can be occupied by Al and Fe^{3+}. In the anionic group, X can be occupied by P and As [1]. They crystallize in the monoclinic crystal system, space group $P2_1/c$, and unit cell parameters $a = 7.1526$ Å, $b = 7.278$ Å, $c = 7.2334$ Å, $Z = 2$ and $\beta = 89.233°$ [2]. The name lazulite is used for a solid solution between the end-members lazulite – $MgAl_2(PO_4)_2(OH)_2$ and scorzalite – $FeAl_2(PO_4)_2(OH)_2$ [3]. The mineral is

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known since 18th century, and the name lazulite was first used by Klaproth [4]. The mineral is a bright blue color as shown in the Supplementary information as Fig. S1. The color of the mineral is related to the actual composition of the lazulite sample. Other phosphate members of lazulite group are Barbosalite $Fe^{2+}(Fe^{3+})_2^+(PO_4)2(OH)_2$ [2] and Hentschelite – $Cu^{2+}(Fe^{3+})_2 + (PO_4)_2(OH)_2$ [5]. Wet chemical analysis suggested for natural lazulite–scorzalite samples a complete solid-solution series between the end-members [3]. Contrasting results have exclusively been reported by Duggan et al. [6] who proposed a miscibility gap between 35 and 75 mol% scorzalite [7].

Cationic distribution in the lazulite type minerals according to the ideal formula $M^{2+}M_2^{3+}(PO_4)_2(OH)_2$ of lazulite group members leads to the structure type that can be regarded as to be built up of infinite chains of face – sharing oxygen octahedra which are interconnected via PO^{4-} tetrahedra and common hydroxyl ions. The symmetrically equivalent chains run into the [1 1 0] and [−1 1 0] direction (space group $P2_1/c$). The cations occupy three adjacent octahedra forming a trimer denoted as h-cluster [8,9]. Lazulite and scorzalite occur in many regions throughout the world. The main geological environments are related to metamorphic rocks from green schist to amphibolite facies [10–16] and associated to granitic pegmatites [6,17–19]. The mineral is known from quite a wide variety of locations [6,16,17,19–24].

Nowadays Ca–Al and Mg–Al-phosphate minerals have gained recently growing interest in experimental mineralogy because of their stability properties and their potential as index minerals [25]. In this investigation members of the lazulite–scorzalite solid-solution series are synthesized in compositional steps of 12.5 mol% at $T = 485$ °C and $P = 0.3$ GPa under standard hydrothermal conditions and controlled oxygen fugacities of the Ni/NiO-bufer [11]. However, in this work, samples of a lazulite mineral from the Minas Gerais, Brazil has been structurally characterized. Studies include chemistry via electron microprobe analysis in the wavelength dispersive X-ray spectroscopy (WDXS) elemental characterization and structural by means of infrared and Raman, spectroscopic characterization.

Geological setting, occurrence and samples description

The lazulite sample studied in this work was collected from the Gentil mine, a lithium bearing pegmatite located in the municipality of Mendes Pimentel, Minas Gerais, Brazil. The pegmatite is located in the Conselheiro Pena pegmatite district, one of the subdivisions of the Eastern Brazilian Pegmatite province (EBP). The pegmatite district is inserted in the central domain of the Araçuaí mobile belt [26], formed during the Brasiliano orogeny (630–490 Ma) by accretion to the eastern margin of the São Francisco craton. The Gentil pegmatite is mined out and in the past was mined for industrial feldspar and with minor importance of gemstones and samples for the collectors market. The pegmatite is heterogeneous with mineralogical and textural zoning well developed. It has asymmetric lens shape with the longer axis trending to NNE–SSW and body dips about 70° to SSE. The maximum extension is of about 40 m and 12 m thickness. Detailed geology of the pegmatite was described by Chaves [13]. The primary mineral association is represented by quartz, muscovite, microcline, beryl, schorl, almandine–spessartite, triplite and triphylite. The secondary association is mainly composed by albite, Ta and Nb oxides, siderite, elbaite, cassiterite, arsenopyrite, pharmacosiderite and a complex paragenesis of phosphates formed in the result of alteration of triphylite [13,18]. In addition to lazulite, others secondary phosphates, namely autunite, barbosalite, brazilianite, eosphorite, fluorapatite, frondelite, gormanite, heterosite, hureaulite, lithiophillite, matioliite, montebrasite, phosphosiderite, purpurite, roscherite group minerals, scorzalite, souzalite and vivianite are common minerals in miarolitic cavities and in massive blocks formed after the aggregates of primary triphylite up to 0.5 m length [13]. Lazulite nodules up to 3.0 cm long occur in miarolitic cavities, in association with muscovite, triphylite–lithiophilite, gormanite, brazilianite and albite.

Experimental

Samples and preparation

Deep blue and transparent fragments of lazulite were collected from the Gentil mine. The sample was incorporated in 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 Gentil mine, a lithium bearing pegmatite with triphylite and spodumene. The mine is located in Mendes Pimentel, east of Minas Gerais. To remove contaminate phases, with the support of a Stereomicroscope Leica Model EZ4, lazulite fragments were handily selected from a sample in association with quartz and muscovite. Lazulite was phase analyzed by X-ray powder diffraction and Scanning electron microscopy in the EDS mode (SEM/EDS). An image of the lazulite sample used in this work is displayed in the Supplementary information and is shown in Fig. S1.

Electron micro probe analysis (EMP)

A quantitative chemical analysis was carried via EMP. Lazulite fragment selected for this study was analyzed with the performance of eight 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, Mn–rodhonite, P and Ca–$Ca_2P_2O_7$, Al–Al_2O_3 and Mg–MgO. The epoxy embedded lazulite sample was polished in the sequence of 9 μm, 6 μm and 1 μm 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 lazulite was coated with a thin layer of evaporated carbon. The electron probe microanalysis in the WDS (wavelength dispersive spectrometer) mode was obtained at 15 kV accelerating voltage and beam current of 10 nA. Chemical formula was calculated on the basis of ten oxygen atoms (O, OH).

Raman microprobe spectroscopy

Crystals of lazulite 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 polarised 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.

A Raman spectrum of lazulite is given in the RRUFF data base (http://rruff.info/Lazulite/R050110). The spectra are given in the Supplementary information. This lazulite mineral sample originated from Rapid Creek, Yukon Territory, Canada. The spectra are shown in Figs. S2–S4. The issue with the spectra as published in