

Vibrational spectroscopic characterization of the phosphate mineral series eosphorite–childrenite–(Mn,Fe)Al(PO₄)(OH)₂·(H₂O)

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ABSTRACT

The phosphate mineral series eosphorite–childrenite–(Mn,Fe)Al(PO₄)(OH)₂·(H₂O) has been studied using a combination of electron probe analysis and vibrational spectroscopy. Eosphorite is the manganese rich mineral with lower iron content in comparison with the childrenite which has higher iron and lower manganese content. The determined formulae of the two studied minerals are: (Mn_{0.72},Fe_{0.13},Ca_{0.01})(Al)_{1.04}(PO₄, OHPO₃)_{1.07}(OH)_{1.89}(F_{0.02})·0.94(H₂O) for SAA-090 and (Fe_{0.49},Mn_{0.35},Mg_{0.06},Ca_{0.04})(Al)_{1.03}(PO₄, OHPO₃)_{1.05}(OH)_{1.90}·0.95(H₂O) for SAA-072. Raman spectroscopy enabled the observation of bands at 970 cm⁻¹ and 1011 cm⁻¹ assigned to monohydrogen phosphate, phosphate and dihydrogen phosphate units. Differences are observed in the area of the peaks between the two eosphorite minerals. Raman bands at 562 cm⁻¹, 595 cm⁻¹, and 608 cm⁻¹ are assigned to the ν₄ bending modes of the PO₄, HPO₄ and H₂PO₄ units; Raman bands at 405 cm⁻¹, 427 cm⁻¹ and 466 cm⁻¹ are attributed to the ν₂ modes of these units. Raman bands of the hydroxyl and water stretching modes are observed. Vibrational spectroscopy enabled details of the molecular structure of the eosphorite mineral series to be determined.

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1. Introduction

Eosphorite is a pink manganese mineral with formula MnAl(PO₄)(OH)₂·(H₂O) and forms prismatic crystals with radiating clusters [1]. The mineral shows pseudo-orthorhombic morphology due to twinning. The mineral occurs worldwide in pegmatites [2–7] and is always associated with other phosphate minerals [8].

Eosphorite forms a solid solution series with the mineral childrenite [9–11]. Childrenite's formula is (Fe,Mn)AlPO₄(OH)₂·H₂O and differs from eosphorite by being rich in iron instead of manganese. The general chemical formula of eosphorite–childrenite series can be written as ABPO₄(OH)₂·H₂O (A – Mn, Fe; B – Al, Fe). The A site can be partially occupied by Ca and Mg [12].

The crystal structure of childrenite and eosphorite were first solved in the orthorhombic crystal system, space groups *Bba*2 and *Bbam* respectively. The Al octahedron contains two oxygen atoms, two OH groups and two water molecules, whereas the more distorted (Mn, Fe) octahedron contains four oxygen atoms and two OH groups. The same authors have redefined the space group of eosphorite as *CmCa*. According to Bermanec et al. [14] on the basis

of optical measurements, childrenite shows monoclinic symmetry as indicated by Hurlbut [11], however with orthorhombic crystal structure. This discrepancy can be related to twins, chemical zonation and strain.

Differences in physical properties of the two minerals are related to the iron/manganese content. Eosphorite is less dense and is generally pinkish to rose-red in colour whereas childrenite's colours tend towards various shades of brown. In terms of crystal habits the two also differ. Eosphorite forms prismatic, slender crystals and rosettes. Childrenite forms tabular or bladed individuals or lamellar aggregates. It has been said that the two different habits belie their solid solution relationship [11].

In this work, samples of the mineral eosphorite from different pegmatites from Minas Gerais were studied. Characterization include chemistry via Electron Probe Microanalysis in the WDS mode (EPMA), thermal analysis and spectroscopic characterization of the structure with mid-infrared and Raman spectroscopy.

2. Experimental

2.1. Samples description and preparation

The eosphorite samples studied in this work were obtained from the collection of the Geology Department of the Federal University

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Table 1Chemical composition of eosphorite from pegmatites from Minas Gerais; H₂O calculated by thermogravimetric analysis and values given in mass fraction %.

Sample	P ₂ O ₅	Al ₂ O ₃	MnO	FeO	CaO	MgO	H ₂ O	F	Total	
SAA-072	34.13	24.05	11.25	16.15	0.89	1.11	15.65	0.02	103.26	
SAA-090	34.06	23.68	22.70	4.30	0.13	0.07	15.22	0.13	100.67	
Eosphorite	31.00	22.27	30.99	0.00	0.00	0.00	15.74	0.00	100.00	
Childrenite	30.88	22.18	0.00	31.26	0.00	0.00	15.68	0.00	100.00	
	P	Al	Mn	Fe	Ca	Mg	H	F	Mn/(Mn + Fe)	
SAA-072	1.05	1.03	0.35	0.49	0.04	0.06	3.80	0.00	0.42	6.81
SAA-090	1.07	1.04	0.72	0.13	0.01	0.00	3.78	0.02	0.85	6.77
Eosphorite	1.00	1.00	1.00	0.00	0.00	0.00	4.00	0.00	1.00	7.0
Childrenite	1.00	1.00	0.00	1.00	0.00	0.00	4.00	0.00	0.00	7.0

of Ouro Preto, Minas Gerais, Brazil, with sample code SAA-090 and SAA-072 respectively. The samples are from two different granitic pegmatites from Minas Gerais, Brazil.

Sample SAA-072 was collected from the Ponte do Piauí mine, located in the Piauí valley, municipality of Itinga. The region is well-known as an important source of rare phosphates and gemological minerals. The pegmatite is located in the Araçuaí pegmatite district, one of the subdivisions of the Eastern Brazilian Pegmatite province [13]. The pegmatite is mined for gemstones and samples for the collectors market. It is heterogeneous with well-developed mineralogical and textural zoning. The primary mineral association is represented by quartz, muscovite, microcline, schorl and almandine–spessartine. The secondary association is mainly composed by albite, Li bearing micas, cassiterite, elbaite and hydrothermal rose quartz. In the Ponte do Piauí pegmatite, secondary phosphates, namely childrenite, eosphorite, fluorapatite, zanzaziite, occur in miarolitic cavities in association with albite, quartz and muscovite. Childrenite grows usually along the surface of quartz crystals and in albite aggregates.

Sample SAA-090 was collected from Roberto mine, a granitic pegmatite located in Divino das Laranjeiras east of Minas Gerais. The region is situated 65 km ENE of Governador Valadares. The pegmatite is located in the Conselheiro Pena pegmatite district, also one of the subdivisions of the Eastern Brazilian Pegmatite province (EBP). The primary mineral association is represented by quartz, muscovite, microcline, schorl, almandine–spessartine and triphylite. The secondary association is mainly composed by albite, quartz crystals and a number of secondary phosphates, namely eosphorite, fluorapatite, zanzaziite and brazilianite. The phosphates occur in miarolitic cavities.

The samples were gently crushed and the associated minerals were removed under a stereomicroscope Leica MZ4. The eosphorite and childrenite samples were phase analyzed by X-ray diffraction (not shown). Scanning electron microscopy (SEM) was applied to support the mineral characterization.

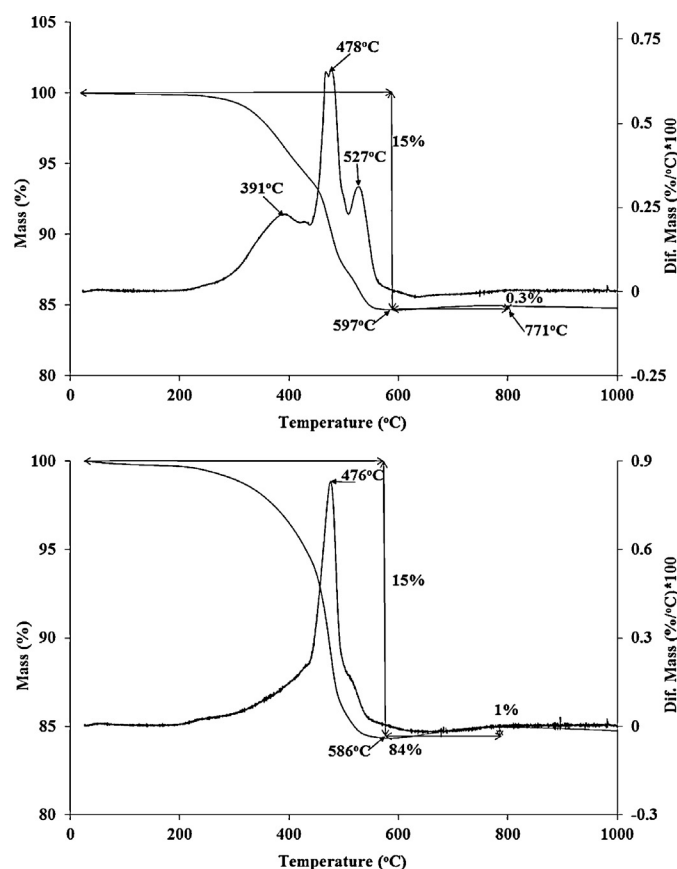


Fig. 1. Thermogravimetric analysis of eosphorite (upper curves sample SAA-090, lower curves sample SAA-072).

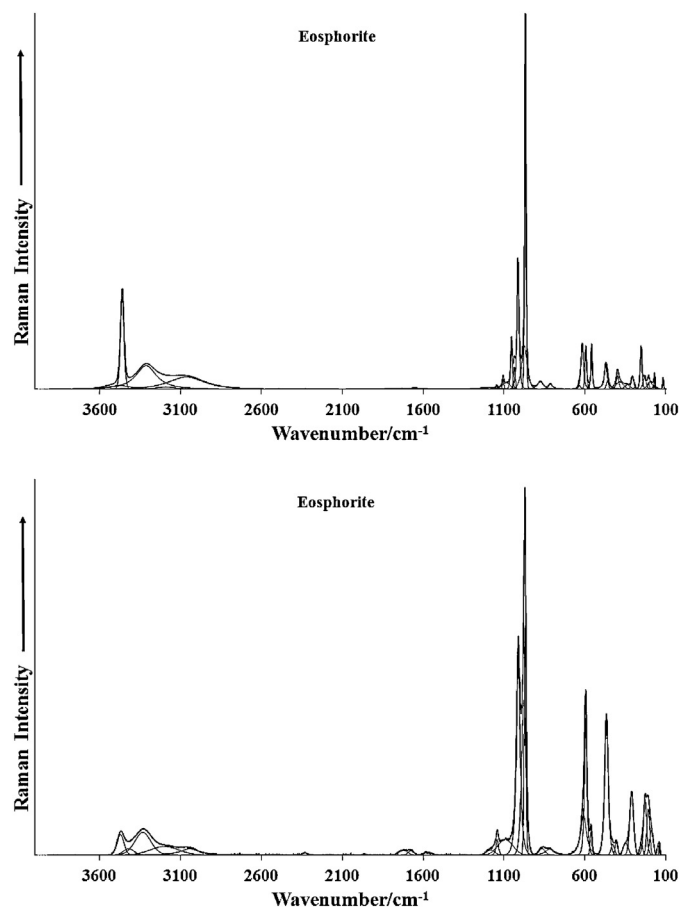


Fig. 2. Raman spectrum of eosphorite over the 4000–100 cm⁻¹ spectral range (upper spectrum sample SAA-090, lower spectrum sample SAA-072).

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