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Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy

journal homepage: www.elsevier.com/locate/saa

Vibrational spectroscopic characterization of the phosphate mineral kulanite Ba(Fe²⁺,Mn²⁺,Mg)₂(Al,Fe³⁺)₂(PO₄)₃(OH)₃

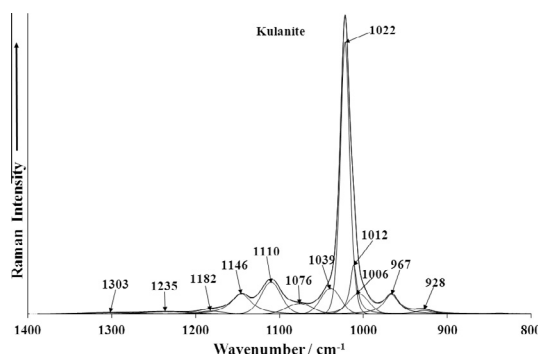Ray L. Frost [a,*], Andrés López [a], Yunfei Xi [a], Amanda Granja [b], Ricardo Scholz [b]

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HIGHLIGHTS

- The mineral kulanite has been studied by using electron microscopy and vibrational spectroscopy.
- SEM with EDX shows the mineral is homogenous with no other phases present.
- The Raman spectrum is dominated by an intense band at 1022 cm⁻¹.
- The infrared spectrum shows a complex spectral profile with overlapping bands.
- Vibrational spectroscopy enables aspects on the molecular structure of kulanite to be assessed.

GRAPHICAL ABSTRACT

ABSTRACT

The mineral kulanite $BaFe_2Al_2(PO_4)_3(OH)_3$, a barium iron aluminum phosphate, has been studied by using a combination of electron microscopy and vibrational spectroscopy. Scanning electron microscopy with EDX shows the mineral is homogenous with no other phases present. The Raman spectrum is dominated by an intense band at 1022 cm⁻¹ assigned to the PO_4^{3-} v_1 symmetric stretching mode. Low intensity Raman bands at 1076, 1110, 1146, 1182 cm⁻¹ are attributed to the PO_4^{3-} v_3 antisymmetric stretching vibrations. The infrared spectrum shows a complex spectral profile with overlapping bands. Multiple phosphate bending vibrations supports the concept of a reduction in symmetry of the phosphate anion. Raman spectrum at 3211, 3513 and 3533 cm⁻¹ are assigned to the stretching vibrations of the OH units. Vibrational spectroscopy enables aspects on the molecular structure of kulanite to be assessed.

Introduction

Kulanite is a barium iron aluminum phosphate, with chemical formula ideally $BaFe_2Al_2(PO_4)_3(OH)_3$ [1]. The color of this mineral is green to blue and occurs as thin tabular plates parallel to (1 0 1). This mineral is triclinic and belongs to the Bjarebyite group. The mineral was first found in the Big Fisher River, at the northeastern part of the Yukon Territory and occurs in association with quartz, siderite and apatite. The species of this group currently known are penikisite – $BaMg_2Al_2(PO_4)_3(OH)_3$ [2]; bjarebyite – $BaMn_2Al_2(PO_4)_3(OH)_3$ [3]; johntomaite – $Ba(Fe^{2+})_2(Fe^{3+})_2(PO_4)_3(OH)_3$ [4] and perloffite – $Ba(Mn^{2+},Fe^{2+})_2(Fe^{3+})_2(PO_4)_3(OH)_3$ [5].

The crystal structure of kulanite was determined by Mandarino and Sturman [1] and latter refined by Cooper and Hawthorne [6]. The unit cell parameters are $a = 9.014(1)$, $b = 12.074(1)$, $c = 4.926(1)$ Å, $\beta = 100.48(1)°$, $V = 527.1(1)$ Å³, space group $P2_1/m$ and $Z = 2$. The crystal structure of this mineral is based upon chains of hydrogen-bonds. One H atom is disordered off its ideal position on the mirror plane, and has a weak hydrogen-bond to another coordinated hydrogen. The H(2) atom occupies the general position, and is strongly bonded to another hydrogen. The hydrogen

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bonds promote cross linkages of the prominent chains of octahedra in this structure type [6]. The kulanite optical study shows unsymmetrical dispersion indicating that kulanite is triclinic (pseudomonoclinic) rather than monoclinic [3]. So, The mineral has an unit cell parameters very similar to bjarebyite.

To the best of the authors' knowledge, data about vibrational spectroscopic characterization of kulanite are restricted to the database of the University of Arizona (rruff.info); however no interpretation is given. In recent years, the application of spectroscopic techniques to understand the structure of phosphates has been increasing. In this work, a sample of the rare mineral kulanite from the type locality was studied. Characterization includes chemistry via scanning electron microscopy (SEM) in the EDS mode and spectroscopic characterization of the structure with infrared and Raman spectroscopy.

Experimental

Occurrence, samples description and preparation

The kulanite sample 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 SAB-100.

The Rapid Creek sedimentary phosphatic iron formation comprises the upper and youngest portion of an Aptian–Albian flyschoid sequence which reaches a maximum thickness of 4 km in the Blow Trough. The phosphate association is composed mainly of rare minerals such as the satterlyite, arrojadite group minerals, augelite, lazulite and gormanite, which reflect an original calcium-deficient composition. The deposition of iron and magnesium phosphates as well as apatite is strongly indicated, and this condition is unique for marine phosphorites.

The sample was gently crushed and prepared to be analyzed by different methods. Scanning electron microscopy (SEM) was applied to support the mineralogical composition.

Scanning electron microscopy (SEM)

Experiments and analyses involving electron microscopy were performed in the Center of Microscopy of the Universidade Federal de Minas Gerais, Belo Horizonte, Minas Gerais, Brazil (http://www.microscopia.ufmg.br).

A fragment of a kulanite single crystal was prepared in a carbon tape. Due to the low vacuum conditions the sample was not metalized. 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 was applied to support the mineral characterization.

Raman microprobe spectroscopy

A kulanite single crystal was 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 polarized 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.

Infrared spectroscopy

Infrared spectra were obtained 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.

Spectral manipulation such as baseline correction/adjustment and smoothing were performed using the Spectracalc software package GRAMS (Galactic Industries Corporation, Salem, NH, USA). Band component analysis was undertaken using the Jandel 'Peakfit' software package that enabled the type of fitting function to be selected and allows specific parameters to be fixed or varied accordingly. Band fitting was done using a Lorentzian–Gaussian cross-product function with the minimum number of component bands used for the fitting process. The Gaussian–Lorentzian ratio was maintained at values greater than 0.7 and fitting was undertaken until reproducible results were obtained with squared correlations of r^2 greater than 0.995.

Results and discussion

Chemical characterization

The SEM image of kulanite sample studied in this work is shown in Fig. S1. Qualitative chemical analysis shows a homogeneous
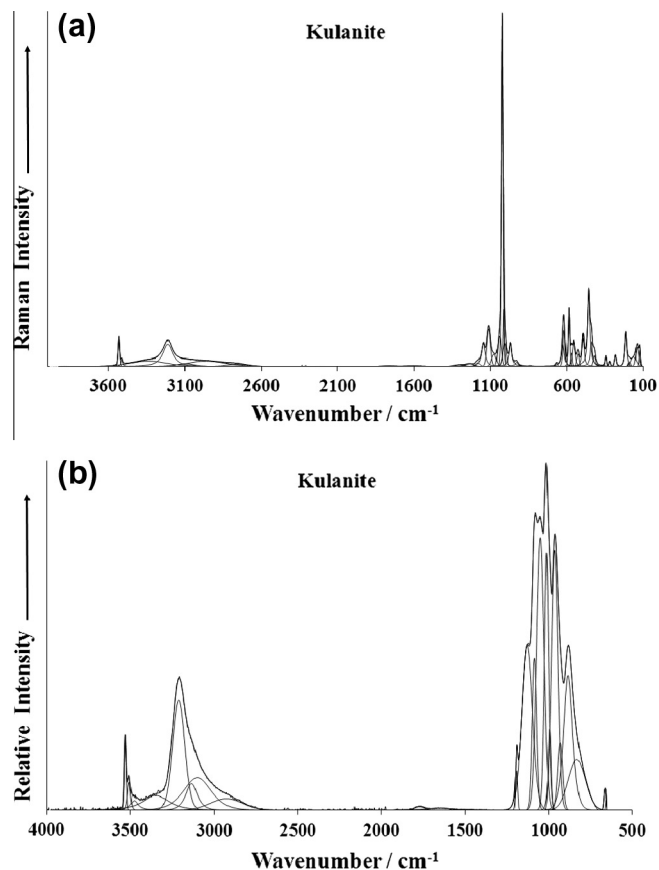

Fig. 1. (a) Raman spectrum of kulanite over the 100–4000 cm^{-1} spectral range and (b) infrared spectrum of kulanite over the 500–4000 cm^{-1} spectral range.

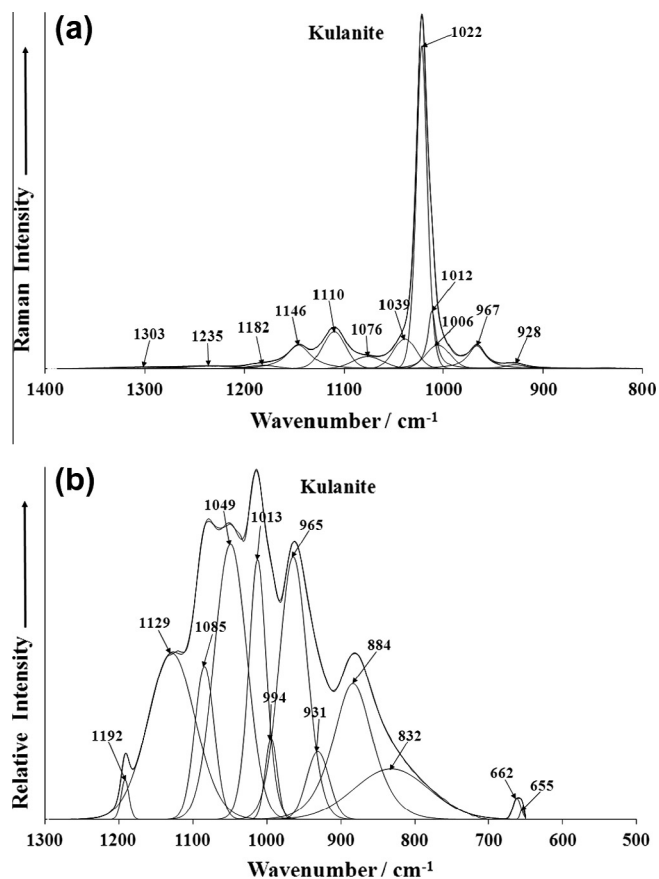**Fig. 2.** (a) Raman spectrum of kulanite over the 800–1400 cm^{-1} spectral range and (b) infrared spectrum of kulanite over the 500–1300 cm^{-1} spectral range.

phase, composed by P and Mg. No other cations were observed (Fig. S2).

Vibrational spectroscopy

Background spectroscopy of phosphate

Farmer [7] divided the vibrational spectra of phosphates according to the presence, or absence of water and/or hydroxyl units in the minerals. In aqueous systems, Raman spectra of phosphate oxyanions show a symmetric stretching mode (v_1) at 938 cm^{-1}, the antisymmetric stretching mode (v_3) at 1017 cm^{-1}, the symmetric bending mode (v_2) at 420 cm^{-1} and the v_4 mode at 567 cm^{-1}. The value for the v_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} (dufrénite) 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 v_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} (dufrénite) 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 v_3 antisymmetric stretching vibrations. Augelite shows infrared bands at 1205, 1155, 1079 and 1015 cm^{-1} [8,9]; wavellite at 1145, 1102, 1062 and 1025 cm^{-1}; rockbridgeite at 1145, 1060 and 1030 cm^{-1}; dufrénite at 1135,

1070 and 1032 cm^{-1}; and beraunite at 1150, 1100, 1076 and 1035 cm^{-1}.

Vibrational spectroscopy

The Raman spectrum of kulanite over the complete wavenumber range from 100 to 4000 cm^{-1} spectral range is displayed in Fig. 1a. This spectrum shows the position of the peaks and the relative intensities of the bands. It is apparent that there are large parts of the spectrum where no intensity is observed. Therefore the spectrum is subdivided into sections depending upon the type of vibration being studied. The infrared spectrum over the 500–4000 cm^{-1} spectral range is reported in Fig. 1b. This spectrum of kulanite shows the relative intensity of the infrared bands and their position. There are also large parts of the infrared spectrum where no intensity is observed. Hence, the spectrum is subdivided into sections as a function of the type of vibration being examined.

The Raman spectrum of kulanite over the 800–1400 cm^{-1} spectral range is illustrated in Fig. 2a. The spectrum is dominated by an intense band at 1022 cm^{-1} with shoulders at 1012 and 1039 cm^{-1}. This band is assigned to the PO$_4^{3-}$ v_1 symmetric stretching mode. Low intensity Raman bands are found at 1076, 1110, 1146, 1182 cm^{-1} and are attributed to the PO$_4^{3-}$ v_3 antisymmetric stretching vibrations. The formula of kulanite is Ba(Fe^{2+},Mn^{2+},Mg)$_2$ (Al,Fe^{3+})$_2$(PO$_4$)$_3$(OH)$_3$ and it could be expected that Raman bands associated with the hydroxyl units would be found. The Raman bands at 928 and 967 cm^{-1} may be ascribed to the OH deformation modes. An alternative explanation is that the bands are due to hydrogen phosphate units. The infrared spectrum of kulanite over the 500–1300 cm^{-1} spectral range is illustrated in Fig. 2b. Multiple overlapping bands are observed, which may be resolved into
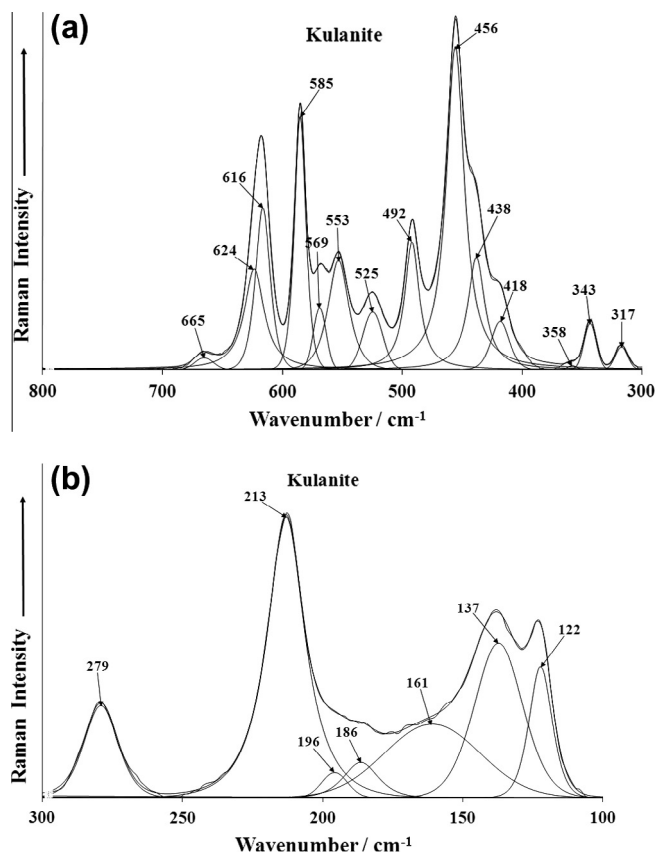

Fig. 3. (a) Raman spectrum of kulanite over the 300–800 cm^{-1} spectral range and (b) Raman spectrum of kulanite over the 100–300 cm^{-1} spectral range.
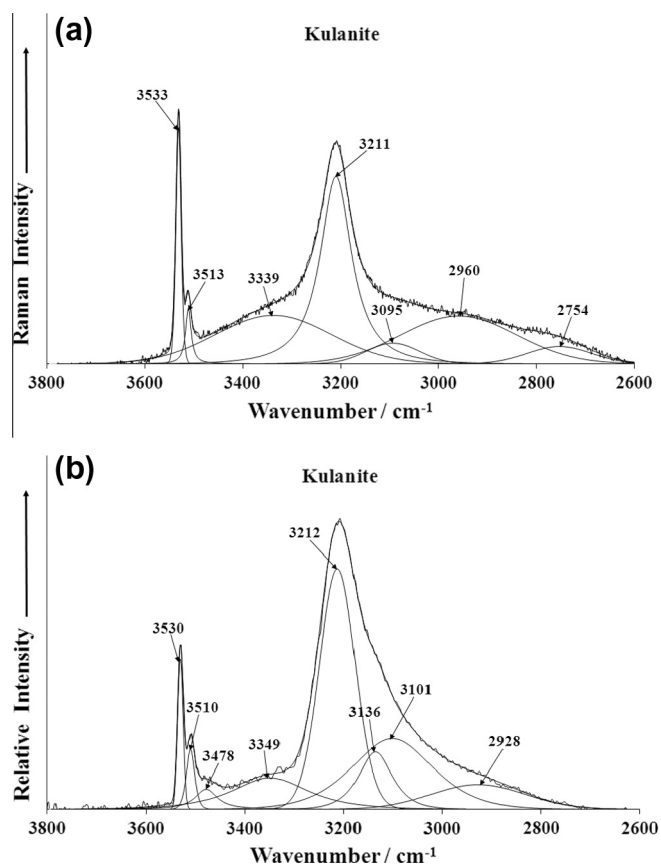
Fig. 4. (a) Raman spectrum of kulanite over the 2600–4000 cm^{-1} spectral range and (b) infrared spectrum of kulanite over the 2600–4000 cm^{-1} spectral range.

component bands. The strong infrared band at 965 cm^{-1} may be assigned to the PO_4^{3-} v_1 symmetric stretching vibration. The infrared bands at 1013, 1049, 1085, 1129 and 1192 cm^{-1} are ascribed to the PO_4^{3-} v_3 antisymmetric stretching vibrations. The infrared band at 884 cm^{-1} with a broad feature at 832 cm^{-1} may be attributed to the OH deformation mode.

The Raman spectrum of kulanite over the 300–800 cm^{-1} spectral range is illustrated in Fig. 3a and the Raman spectrum of kulanite over the 100–300 cm^{-1} spectral range is illustrated in Fig. 3b. The first spectrum displays a series of overlapping Raman bands. This spectrum may be subdivided into sections. The first section is the 600–800 cm^{-1} spectral region, the second section is the bands around 500 cm^{-1} and the third section is the bands between 300 and 400 cm^{-1}. Raman bands at 553, 569, 585, 616 and 624 cm^{-1} are assigned to the $v_4 PO_4^{3-}$ bending modes. The Raman bands at 418, 438, 456 and 492 cm^{-1} are due to the $v_2 PO_4^{3-}$ bending modes. The observation of multiple bending vibrations supports the concept of a reduction in symmetry of the phosphate anion. The band at 665 cm^{-1} may be ascribed to water librational modes. The low intensity Raman bands at 317 and 343 cm^{-1} are ascribed to metal–oxygen stretching vibrations (Ba(Fe^{2+},Mn^{2+},

Mg)$_2$(Al,Fe^{3+})$_2$(PO$_4$)$_3$(OH)$_3$. Low intensity Raman bands are observed in the far low wavenumber region at 122, 137, 161, 186, 196, 213 and 279 cm^{-1}.

The Raman and infrared spectra of kulanite in the 2600–3800 cm^{-1} spectral range are reported in Fig. 4 a and 4b. The Raman spectrum consists of three bands at 3211, 3513 and 3533 cm^{-1} superimposed upon a broad spectral background. These bands are assigned to the stretching vibrations of the OH units. The infrared spectrum displays a similar spectral profile with bands observed at 3101, 3136, 3478, 3510 and 3530 cm^{-1}. The first two bands are observed as shoulders on the 3212 cm^{-1} band. These bands are assigned to the OH stretching vibrations.

Conclusions

Kulanite with ideal chemical formula BaFe$_2$Al$_2$(PO$_4$)$_3$(OH)$_3$ belongs to the bjarebyite mineral group which includes penikisite – BaMg$_2$Al$_2$(PO$_4$)$_3$(OH)$_3$; bjarebyite – BaMn$_2$Al$_2$(PO$_4$)$_3$(OH)$_3$; johntomaite – Ba(Fe^{2+})$_2$(Fe^{3+})$_2$(PO$_4$)$_3$(OH)$_3$ and perloffite – Ba(Mn^{2+}, Fe^{2+})$_2$(Fe^{3+})$_2$(PO$_4$)$_3$(OH)$_3$. Assessment of the molecular structure of these bjarebyite minerals is very limited. Vibrational spectroscopy enables an assessment of the molecular structure of kulanite to be made.

Acknowledgements

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.saa.2013.06.016.

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