A study of the phosphate mineral kapundaite NaCa(Fe$^{3+}$)$_4$(PO$_4$)$_4$(OH)$_3$·5(H$_2$O) using SEM/EDX and vibrational spectroscopic methods

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**HIGHLIGHTS**

- The kapundaite sample originated from the Sapucaia mine a lithium-bearing pegmatite.
- Kapundaite is a hydrated hydroxyl sodium calcium ferric phosphate NaCa(Fe$^{3+}$)$_4$(PO$_4$)$_4$(OH)$_3$·5(H$_2$O).
- The molecular structure of kapundaite was assessed by vibrational spectroscopy.
- Multiple phosphate bands are observed.

**ABSTRACT**

Vibrational spectroscopy enables subtle details of the molecular structure of kapundaite to be determined. Single crystals of a pure phase from a Brazilian pegmatite were used. Kapundaite is the Fe$^{3+}$ member of the wardite group. The infrared and Raman spectroscopy were applied to compare the structure of kapundaite with wardite. The Raman spectrum of kapundaite in the 800–1400 cm$^{-1}$ spectral range shows two intense bands at 1089 and 1114 cm$^{-1}$ assigned to the $m_1$ PO$_4^{3-}$ symmetric stretching vibrations. The observation of two bands provides evidence for the non-equivalence of the phosphate units in the kapundaite structure. The infrared spectrum of kapundaite in the 500–1300 cm$^{-1}$ shows much greater complexity than the Raman spectrum. Strong infrared bands are found at 966, 1003 and 1036 cm$^{-1}$ and are attributed to the $m_3$ PO$_4^{3-}$ antisymmetric stretching mode. Raman bands in the $v_4$ out of plane bending modes of the PO$_4^{3-}$ unit support the concept of non-equivalent phosphate units in the kapundaite structure.

In the 2600–3800 cm$^{-1}$ spectral range, Raman bands for kapundaite are found at 2905, 3151, 3311, 3449 and 3530 cm$^{-1}$. These bands are broad and are assigned to OH stretching vibrations. Broad infrared bands are also found at 2904, 3105, 3307, 3453 and 3523 cm$^{-1}$ and are attributed to water. Raman spectroscopy complimented with infrared spectroscopy has enabled aspects of the structure of kapundaite to be ascertained and compared with that of other phosphate minerals.

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**Introduction**

Kapundaite [1,2] is a hydrated hydroxyl sodium calcium ferric phosphate NaCa(Fe$^{3+}$)$_4$(PO$_4$)$_4$(OH)$_3$·5(H$_2$O). The mineral is structurally related to mélonjosephite [3]. Kapundaite is known from Tom’s phosphate quarry, Kapunda, South Australia, Australia. This locality is a wonderful source of phosphate minerals. Other minerals from this locality are natrodufrenite, meurigite-Na and leucophosphite.

The crystal structures of kapundaite have been solved [1,2]. The mineral crystallize with triclinic symmetry. The cell dimensions...
are Space Group: P-1, $a = 6.317(5)$ Å, $b = 7.698(6)$ Å, $c = 19.04(1)$ Å,
$\alpha = 105.53(1)^\circ$, $\beta = 99.24(2)^\circ$, $\gamma = 90.09(2)^\circ$. $V = 451.2(6)$ Å$^3$ and $Z = 1$. The structure of kapundaite is based on a unique corrugated
octahedral–tetrahedral sheet parallel to [001]. The Na/Ca site be-
tween the sheets is 8-coordinated, with three Na/Ca–O bonds to
one sheet and one Na/Ca–O bond to the other sheet. The remaining
four Na/Ca–O bonds are to H$_2$O molecules. The octahedral–tete-
hedral sheet is composed of two types of chains parallel to the $a$
direction. One chain consists of trans-edge-sharing octahedral
decorated by PO$_4$ linking free vertices of adjacent octahedral in a stag-
gered arrangement [1,2].

To the best knowledge of the authors, this work reports the first
vibrational spectroscopic study of kapundaite. Due to similar
composition, the results will be compared with minerals of the wardite
group. Tarte et al. collected the infrared spectra of five samples of
cyrylovite and wardite. Between wardite’s composition, NaAl$_3$
(PO$_4$)$_2$(OH)$_4$2(H$_2$O), and kapundaite’s composition, NaCa(Fe$^{3+}$)$_4$
(PO$_4$)$_4$(OH)$_3$5(H$_2$O), these minerals are able to form end members
of a series of solid solutions. Either of the two minerals can occur in
various proportions in a series of solid solutions in the wardite
mineral group. Kapundaite is a rare accessory mineral in some oxido-
dizing phosphate-bearing granite pegmatites and iron deposits. The
vibrational spectrum is dependent upon the ratio of the Ca/Fe. Tarte
et al. found that the two minerals wardite and cyrylovite
can be distinguished by the spectral patterns of the OH stretching
region in the infrared spectrum [4]. These workers did not inter-
pret the spectra of the phosphate because of complexity and no de-
tailed assignment was given. Breitinger et al. [5] reported the
combined vibrational spectra of a natural wardite. Breitinger and co-
workers used a full array of techniques including inelastic neu-
tron scattering, infrared, Raman and near infrared techniques [5].
These workers used a natural wardite with significant amounts
of ferric iron in the structure. In other words the sample analyzed
was fundamentally a solid solution of wardite and kapundaite, but
at the wardite end. The original papers on the infrared spectrum
of isolated phosphate units was published by Lazarev [6]. Of course,
phosphates structures are different. Usually they have rather low
symmetry: orthorhombic, monoclinic, or even triclinic [7]. Farmer
based upon the work of Petrov et al. [8–10] made a comparison of
the results of the vibrational spectrum of a series of phosphates.

Raman spectroscopy has proven very useful for the study of
minerals [11–15]. Indeed, Raman spectroscopy has proven most
useful for the study of diagnostically related minerals where iso-
morph substitution may occur as with wardite, cyrylovite and
kapundaite, as often occurs with minerals containing phosphate
groups. This paper is a part of systematic studies of vibrational
spectra of minerals of secondary origin in the pegmatite rocks.
The objective of this research is to report the Raman and infrared
spectra of kapundaite and to relate the spectra to the molecular
structure of the mineral.

Experimental

Samples description and preparation

The kapundaite 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 SAC-111.
Kapundaite sample studied in this work is from the Tom’s quarry,
Austrália and can be considered a type material. The sample was
gently crushed and the associated minerals were removed under a
stereomicroscope Leica MZ4. The kapundaite sample was phase
analyzed by X-ray diffraction. Scanning electron microscopy (SEM)
in the EDS mode was applied to support the mineral characterization.

Raman spectroscopy

Crystals of kapundaite were placed on a polished metal surface
on the stage of an Olympus BHS 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 col-
lected at a nominal resolution of 2 cm$^{-1}$ and a precision of ±1 cm$^{-1}$
in the range between 200 and 4000 cm$^{-1}$. Some of these mineral
fluoresced badly at 633 nm; as a consequence other laser excita-
tion wavelengths were used especially the 785 nm laser. Repeated
acquisitions on the crystals using the highest magnification (50×)
were accumulated to improve the signal to noise ratio of the spec-
tra. Spectra were calibrated using the 520.5 cm$^{-1}$ line of a silicon
wafer. Previous studies by the authors provide more details of the
experimental technique. Alignment of all crystals in a similar
orientation has been attempted and achieved. However, differ-
esences in intensity may be observed due to minor differences in
the crystal orientation.

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 Spectracal software
package GRAMS (Galactic Industries Corporation, NH, USA). Band
component analysis was undertaken using the Jandel ‘Peakfit’ soft-
ware 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 under-
taken until reproducible results were obtained with squared corre-
lations of $r^2$ greater than 0.995.

Results and discussion

Chemical characterization

The SEM image of kapundaite sample studied in this work is
shown in the supplementary information as Fig. S1. Kapundaite
crystals show a prismatic to tabular habitus and the crystal forms
a reticular aggregate. Qualitative chemical composition shows a
homogeneous phase, composed by Na, Ca, Fe and P, with minor
amounts of Al (Fig. 1). The sample can be considered a pure phase.

Spectroscopy

The Raman spectrum of kapundaite in the 100–4000 cm$^{-1}$ spec-
tral range is illustrated in Fig. 2a. This spectrum shows the position
of the Raman bands and their relative intensities. It is obvious that
there are large parts of the spectrum where little or no intensity is
observed. Therefore, the spectrum is subdivided into sections
according to the type of vibration being investigated. In this way
the precise position of the bands can be detailed. The infrared spec-
trum of kapundaite in the 500–4000 cm$^{-1}$ spectral range is shown
in Fig. 2b. The reflectance spectrum starts at 500 cm$^{-1}$ because the
ATR cell absorbs all infrared radiation below this wavenumber. As for the Raman spectrum, the infrared spectrum is subdivided into sections depending upon the type of vibration being examined. The complete infrared spectrum displays the position of the infrared bands and their relative intensity.

The Raman spectrum of kapundaite in the 900–1300 cm\(^{-1}\) spectral range is reported in Fig. 3a. The Raman spectrum is dominated by two intense bands at 1089 and 1114 cm\(^{-1}\). These two bands are assigned to the \(\nu_1\) PO\(_{4}\) symmetric stretching vibrations. Two intense bands are observed reflecting two non-equivalent phosphate units in the kapundaite structure. A comparison may be made with the spectrum of wardite. The Raman spectrum of wardite is dominated by two intense bands at around 995 and 1051 cm\(^{-1}\). The spectra appear to differ considerably from that obtained by Breitinger et al. [5]. Breitinger et al. used FT-Raman to obtain their spectrum and found overlapping Raman bands at 999 and 1033 cm\(^{-1}\) and assigned these bands to the \(\nu_1\) PO\(_{4}\) symmetric stretching and \(\nu_3\) PO\(_{4}\) antisymmetric stretching modes. The difference in the spectra between our work and that of Breitinger et al., may be attributed to the improved technology of the Raman spectrometer with greater resolution. The Raman spectrum (Fig. 3a) shows a resolved component band at 1024 cm\(^{-1}\). There is also a band at 972 cm\(^{-1}\). Breitinger et al. [5] also assigned the band at 999 cm\(^{-1}\) to AlOH deformation modes. In this work the band at 972 cm\(^{-1}\) is very sharp and well resolved.

A series of low intensity bands are noted at 1128, 1159 and 1203 cm\(^{-1}\). These bands are assigned to the \(\nu_3\) PO\(_{4}\) antisymmetric stretching modes. The Raman spectrum of wardite shows a group of low intensity bands are observed at 1084, 1108, 1120, 1140 and 1186 cm\(^{-1}\). Breitinger et al. [5] did not report any bands in these positions in the Raman spectrum of synthetic wardite. These researchers reported infrared bands at 1058 (strong) with shoulders at 1129 and 1168 cm\(^{-1}\) and assigned these bands to \(\delta\)Al\(_2\)OH deformation modes. A low intensity broad band at 884 cm\(^{-1}\) (a), 902 cm\(^{-1}\) (b) and 893 cm\(^{-1}\) (c) are assigned to a water librational mode. In the work of Breitinger et al. [5] a broad low intensity band was found at around 800 cm\(^{-1}\) and was attributed to water librational modes. In the Raman spectrum of kapundaite two component bands are observed at 811 and 852 cm\(^{-1}\). These bands may be attributed to the water librational modes. Normally the intensity of water librational modes are of a quite low intensity in the Raman spectrum but may show significantly greater intensity in the infrared spectrum.

The infrared spectrum of kapundaite in the 650–1300 cm\(^{-1}\) spectral range is shown in Fig. 3b. The infrared spectrum of kapundaite shows much greater complexity than the Raman spectrum. It is

![Fig. 1. EDS spectra of kapundaite.](image1)

![Fig. 2. (a) Raman spectrum of kapundaite over the 100–4000 cm\(^{-1}\) spectral range and (b) infrared spectra of kapundaite over the 500–4000 cm\(^{-1}\) spectral range.](image2)

![Fig. 3. (a) Raman spectrum of kapundaite over the 800–1400 cm\(^{-1}\) range and (b) Infrared spectrum of kapundaite over the 500–1300 cm\(^{-1}\) range.](image3)
noted that the two infrared bands at 844 and 913 cm\(^{-1}\) attributed to the water librational modes show much greater intensity. Strong infrared bands are found at 935, 966, 1003, 1036, 1059, 1091 and 1199 cm\(^{-1}\) and are attributed to the \(v_3\) \(\text{PO}_4^{3-}\) symmetric and antisymmetric stretching modes. The observation of these bands supports the concept that the phosphate units in the kapundaite structure are not equivalent. The series of infrared bands between 1036 and 1199 cm\(^{-1}\) are assigned to the \(v_4\) \(\text{PO}_4^{3-}\) antisymmetric stretching modes. In the infrared spectrum of wardite, bands are observed at 1039, 1056, 1069, 1084, 1102, 1135 and 1165 cm\(^{-1}\).

Some of these infrared bands may also be due to the \(\delta\text{Al}_2\text{OH}\) deformation modes, in harmony with the assignment of Breitinger et al. He and his co-workers stated that the deceptively simple strong IR bands for wardite are attributed to the \(\delta\text{Al}_2\text{OH}\) involving the two pairs of the non-equivalent OH groups. In this work we have obtained much greater resolution and these components are resolved into the component bands.

The Raman spectrum of kapundaite in the 350–700 cm\(^{-1}\) spectral range and in the 100–350 cm\(^{-1}\) spectral range are displayed in Fig. 4a and b. Raman bands are observed at 609 and 646 cm\(^{-1}\) and are assigned to the \(v_4\) out of plane bending modes of the \(\text{PO}_4^{3-}\) units. In the Raman spectrum of wardite, bands are observed at 605 and 618 cm\(^{-1}\) with shoulders at 578 and 589 cm\(^{-1}\). Breitinger et al. assigned these bands to \(v(\text{AlO}_6\text{OH})\) stretching vibrations. No phosphate bending modes in the work of Breitinger et al. were reported. The Raman spectrum of crystalline NaH\(_2\)PO\(_4\) shows Raman bands at 526, 546 and 618 cm\(^{-1}\) (data obtained by the authors). A series of Raman bands for kapundaite at 395, 412, 435, 460 and 491 cm\(^{-1}\) are observed. These bands are attributed to the \(v_2\) \(\text{PO}_4^{3-}\) and H\(_2\)PO\(_4\) bending modes. A comparison may again be made with the Raman spectrum of wardite. The series of Raman bands at 388, 400, 455, 478 and 502 cm\(^{-1}\) for wardite are attributed to the \(v_2\) \(\text{PO}_4^{3-}\) bending modes. Raman bands at 317, 446 and 515 cm\(^{-1}\) for wardite reported by Breitinger et al. [5] were assigned to vibrational modes of the Al\(_2\text{O}_3\)/Al\(_2\text{OH}_6\) units. However, this assignment differs from that reported in this work. An intense Raman band is observed at 361 cm\(^{-1}\) and is denoted as a CaO stretching vibration (Fig. 4a). Strong Raman bands are observed at 257, 275 and 295 cm\(^{-1}\). Intense Raman bands for wardite observed at 258 cm\(^{-1}\) are thought to be related to the O–Al–O skeletal stretching vibrations. Other Raman bands for kapundaite are observed at 113, 137, 162 and 186 cm\(^{-1}\). These bands are simply described as external vibrations.

The Raman spectrum of kapundaite in the 2700–3700 cm\(^{-1}\) spectral range is displayed in Fig. 5a. The infrared spectrum of kapundaite in the 2500–3800 cm\(^{-1}\) is reported in Fig. 5b. Strong Raman bands for kapundaite are found at 2905, 3449 and 3530 cm\(^{-1}\) with a broad bands at 3151 and 3311 cm\(^{-1}\). These bands are assigned to OH stretching vibrations. In the infrared spectrum (Fig. 5b), strong infrared bands are observed at 3105, 3307, 3453 and 3523 cm\(^{-1}\). The infrared spectrum shows broad bands. Tarte et al. reported the infrared spectrum of wardite and cyrilovite. They found that O–H stretching wavenumbers are distributed into 2 spectra regions: 2 very broad bands near 2950 and 3300 cm\(^{-1}\), which are due to H\(_2\)O molecules engaged in short H bonds; and 2 very sharp and strong peaks (3550 and 3495 cm\(^{-1}\) for pure cyrilovite, 3621 and 3555 cm\(^{-1}\) for pure wardite) due to the stretch of hydroxyl group. Sharp infrared bands for wardite are observed at 3544 and 3611 cm\(^{-1}\) and are attributed to the OH stretching vibrations of the hydroxyl units. A sharp band in the infrared spectrum is observed at 3480 cm\(^{-1}\) for the sample.
wardite are observed at 1549, 1670 and 1748 cm\(^{-1}\). The bands in this region result from correlation splitting as a result of the short distance and orientation of the \(\text{H}_{2}\text{O}\) molecules. Additional bands for wardite are observed at 1417 and 1476 cm\(^{-1}\). The assignment of these bands is due to OH deformation modes. The presence or absence of these bands depends upon the Fe/Al ration in the kapundaite/wardite mineral samples.

**Conclusions**

Kapundaite [1,2] is a hydrated hydroxyl sodium calcium ferric phosphate \(\text{NaCa(Fe}^{3+})_2(\text{PO}_4)_3(\text{OH})_2(\text{H}_2\text{O})_5\). The mineral is structurally related to mélonjosephite [3].

Raman spectroscopy complimented with infrared spectroscopy has been used to study aspects of the molecular structure of the mineral kapundaite. The structure of kapundaite is triclinic. As a consequence multiple phosphate vibrational modes are observed. Raman and infrared bands are observed and attributed to phosphate, hydroxyl and water vibrational stretching and bending modes.

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**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.2013.11.020](http://dx.doi.org/10.1016/j.saa.2013.11.020).

**References**