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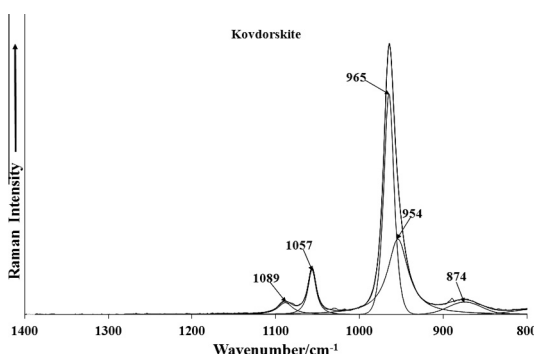
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journal homepage: www.elsevier.com/locate/saaVibrational spectroscopy of the phosphate mineral kovdorskite – $\text{Mg}_2\text{PO}_4(\text{OH})\cdot 3\text{H}_2\text{O}$ Ray L. Frost^{a,*}, Andrés López^a, Yunfei Xi^a, Amanda Granja^b, Ricardo Scholz^b, Rosa Malena Fernandes Lima^c^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 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 the mineral kovdorskite $\text{Mg}_2\text{PO}_4(\text{OH})\cdot 3\text{H}_2\text{O}$.
- A comparison of the vibrational spectroscopy of kovdorskite is made with other magnesium bearing phosphate minerals.
- Electron probe analysis proves the mineral is very pure.
- Vibrational spectroscopy shows that no carbonate bands are present.

GRAPHICAL ABSTRACT



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ABSTRACT

The mineral kovdorskite $\text{Mg}_2\text{PO}_4(\text{OH})\cdot 3\text{H}_2\text{O}$ was studied by electron microscopy, thermal analysis and vibrational spectroscopy. A comparison of the vibrational spectroscopy of kovdorskite is made with other magnesium bearing phosphate minerals and compounds. Electron probe analysis proves the mineral is very pure. The Raman spectrum is characterized by a band at 965 cm^{-1} attributed to the PO_4^{3-} ν_1 symmetric stretching mode. Raman bands at 1057 and 1089 cm^{-1} are attributed to the PO_4^{3-} ν_3 antisymmetric stretching modes. Raman bands at 412 , 454 and 485 cm^{-1} are assigned to the PO_4^{3-} ν_2 bending modes. Raman bands at 536 , 546 and 574 cm^{-1} are assigned to the PO_4^{3-} ν_4 bending modes. The Raman spectrum in the OH stretching region is dominated by a very sharp intense band at 3681 cm^{-1} assigned to the stretching vibration of OH units. Infrared bands observed at 2762 , 2977 , 3204 , 3275 and 3394 cm^{-1} are attributed to water stretching bands. Vibrational spectroscopy shows that no carbonate bands are observed in the spectra; thus confirming the formula of the mineral as $\text{Mg}_2\text{PO}_4(\text{OH})\cdot 3\text{H}_2\text{O}$.

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Introduction

Kovdorskite is a rare magnesium phosphate hydrate with general chemical formula expressed by $\text{Mg}_2\text{PO}_4(\text{OH})\cdot 3(\text{H}_2\text{O})$ [1]. The only known occurrence for kovdorskite in the world is the

Kovdor alkaline massif, Kola Peninsula, Russia [2]. This mineral is found in nests of eruptive breccia carbonate in close association with magnesite and hydrotalcite. Usually the mineral is transparent, ranging from light shades of pink to blue. This mineral was discovered by Kapustin et al. [2] and the crystal structure was refined by Ovchinnikov et al. [3].

Kovdorskite is optically biaxial negative, with $2V = 80\text{--}82^\circ$. The mineral belongs to monoclinic crystal system. The structure was

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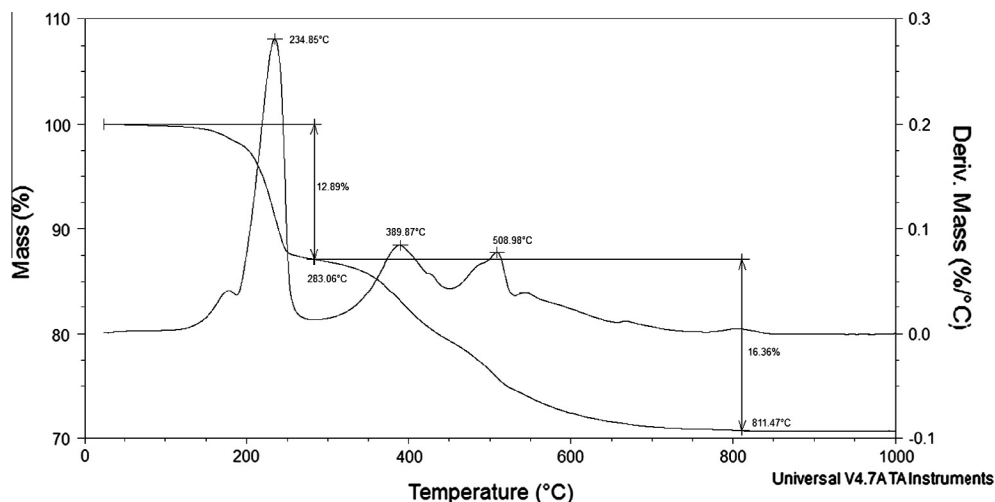


Fig. 1. Thermogravimetric analysis of kovdorskite.

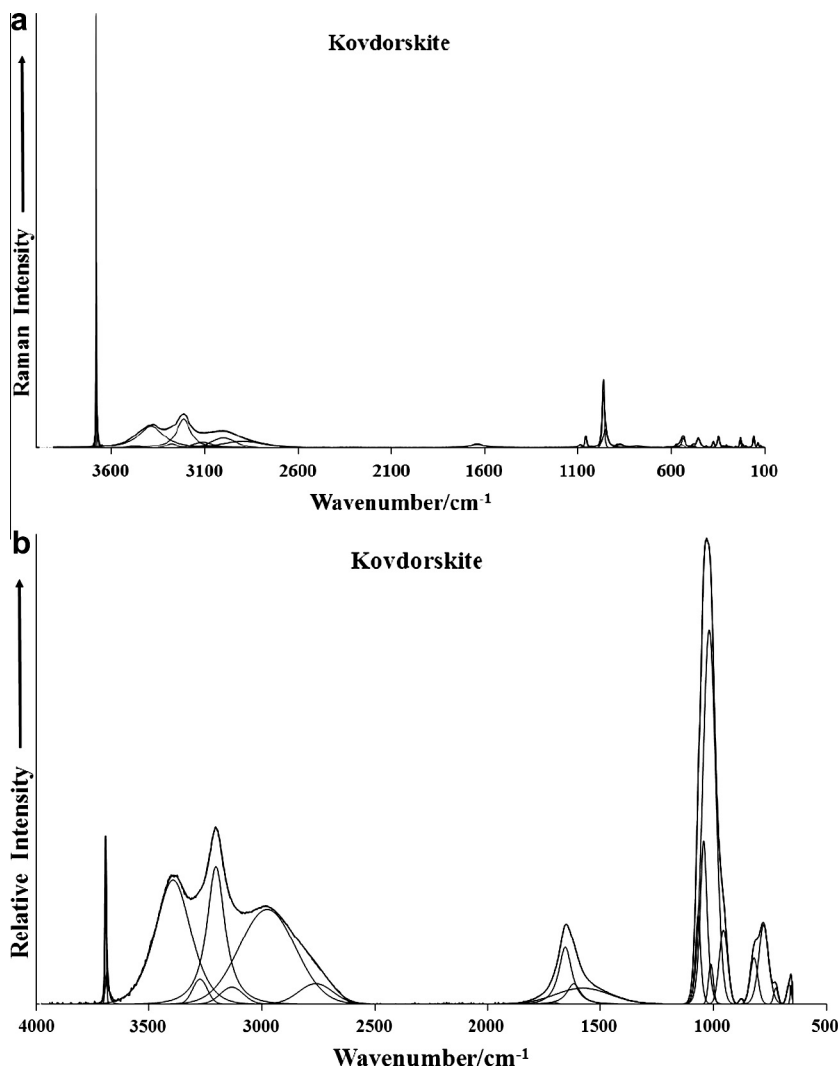


Fig. 2. (a) Raman spectrum of kovdorskite over the 100–4000 cm^{-1} spectral range, and (b) Infrared spectrum of kovdorskite over the 500–4000 cm^{-1} spectral range.

determined by Ovchinnikov et al. [3] and latter refined by Morrison et al. [4]. The refined unit cell parameters are: $a = 10.4785(1) \text{ \AA}$; $b = 12.9336(2) \text{ \AA}$; $c = 4.7308(1) \text{ \AA}$ and $\beta = 105.054(1)^\circ$. Space group

is $P2_1/a$ with $Z = 4$. The genesis of kovdorskite is related to temperature not exceeding 300° due to the stability of the structure at or below this temperature. In the microscope, the mineral is

transparent and colorless. The variation of the iron content gives rise to greenish blue while traces of manganese cause a pink color [5].

According to Morrison et al. [4], the crystal structure of kovdorskite is characterized by clusters of four-sharing MgO_6 octahedra that are interconnected by PO_4 tetrahedra and hydrogen bonds, forming columns and channels parallel to [001]. Within each cluster there are two special corners where three octahedral are joined. These corners are occupied by hydroxyl ions. The hydrogen-bonding system is mainly formed by the H atoms of H_2O units, which are all directed toward the channels.

To the best knowledge of the authors, data about vibrational spectroscopic characterization of kovdorskite are restricted to the database of the University of Arizona (ruff.info); however no interpretation is given, however, in recent years, the application of spectroscopic techniques to understand the structure of phosphates has been increasing.

Farmer [6] 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} . The value for the ν_1 symmetric stretching vibration of PO_4 units as determined by infrared spectroscopy was also described. 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 was also described by Frost et al. [11].

In this work, a sample of the rare mineral kovdorskite 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. Thermogravimetric analysis was also applied to determine the mass loss and the thermal stability of the mineral.

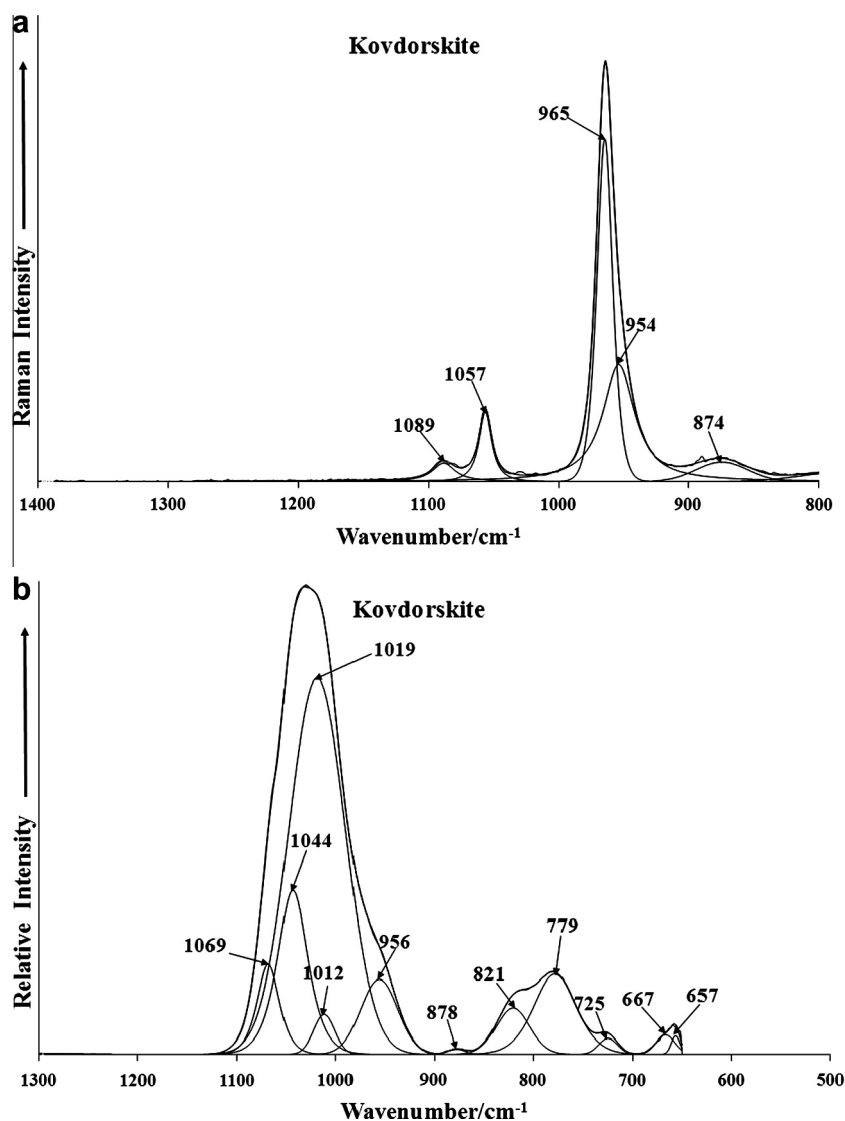


Fig. 3. (a) Raman spectrum of kovdorskite over the $800\text{--}1400\text{ cm}^{-1}$ spectral range, and (b) Infrared spectrum of kovdorskite over the $500\text{--}1300\text{ cm}^{-1}$ spectral range.

Experimental

Occurrence, samples description and preparation

The kovdorskite 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 SAA-129. The sample is from the Kola Peninsula, Russia, and can be considered a reference material or type mineral.

The Kola Peninsula, the northeastern segment of the Precambrian Baltic Shield, is characterized by complicated block structures, which were reactivated during several tectono-magmatic episodes. During the Devonian, numerous ultramafic, alkaline and carbonatitic intrusions were emplaced over an area of more than 100,000 km² which extends from eastern Finland to the eastern Kola Peninsula, and comprise the Kola Alkaline Province (KAP). These various ultramafic and alkaline silicate rocks found in Kovdor are considered to have been formed from several batches of a carbonated olivine melanephelinite parental magma by a mechanism involving fractional crystallization, magma mixing and/or contamination [7].

The Kovdor massif is a typical ultrabasic–alkaline complex bearing a wide compositional range of magmatic and metasomatic

rocks, including olivinite, pyroxenite, ijolite-melteigite, turjaite, melilitolite and various phoscorites and carbonatites. The Kovdor massif is an important source of industrial minerals such as magnetite, apatite, baddeleyite, phlogopite and vermiculite [8]. The massif is also the type locality of a number of rare minerals.

The sample was gently crushed and prepared to be analyzed by different methods. The kovdorskite sample was phase analyzed by X-ray diffraction. Scanning electron microscopy (SEM) was applied to support the mineralogical chemical.

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 kovdorskite 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 were applied to support the mineral characterization.

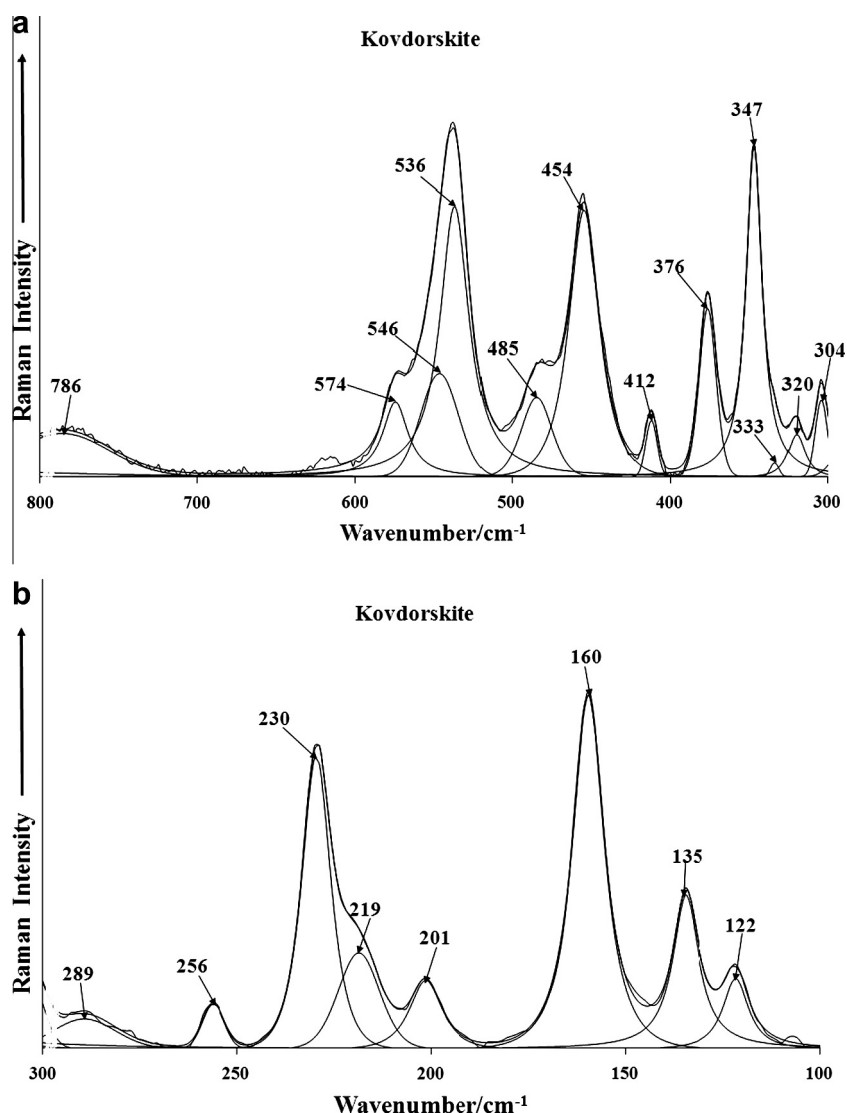


Fig. 4. (a) Raman spectrum of kovdorskite over the 300–800 cm⁻¹ spectral range, and (b) Raman spectrum of kovdorskite over the 100–300 cm⁻¹ spectral range.

Thermogravimetric analysis – TG/DTG

Thermogravimetric analysis of kovdorskite was obtained by using TA Instruments Inc. Q50 high-resolution TGA operating at a 10 °C/min ramp with data sample interval of 0.50 s/pt from room temperature to 1000 °C in a high-purity flowing nitrogen atmosphere (100 cm³/min). A total mass of 24.62 mg of finely ground samples were heated in an open platinum crucible.

Raman microprobe spectroscopy

A kovdorskite 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, 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.

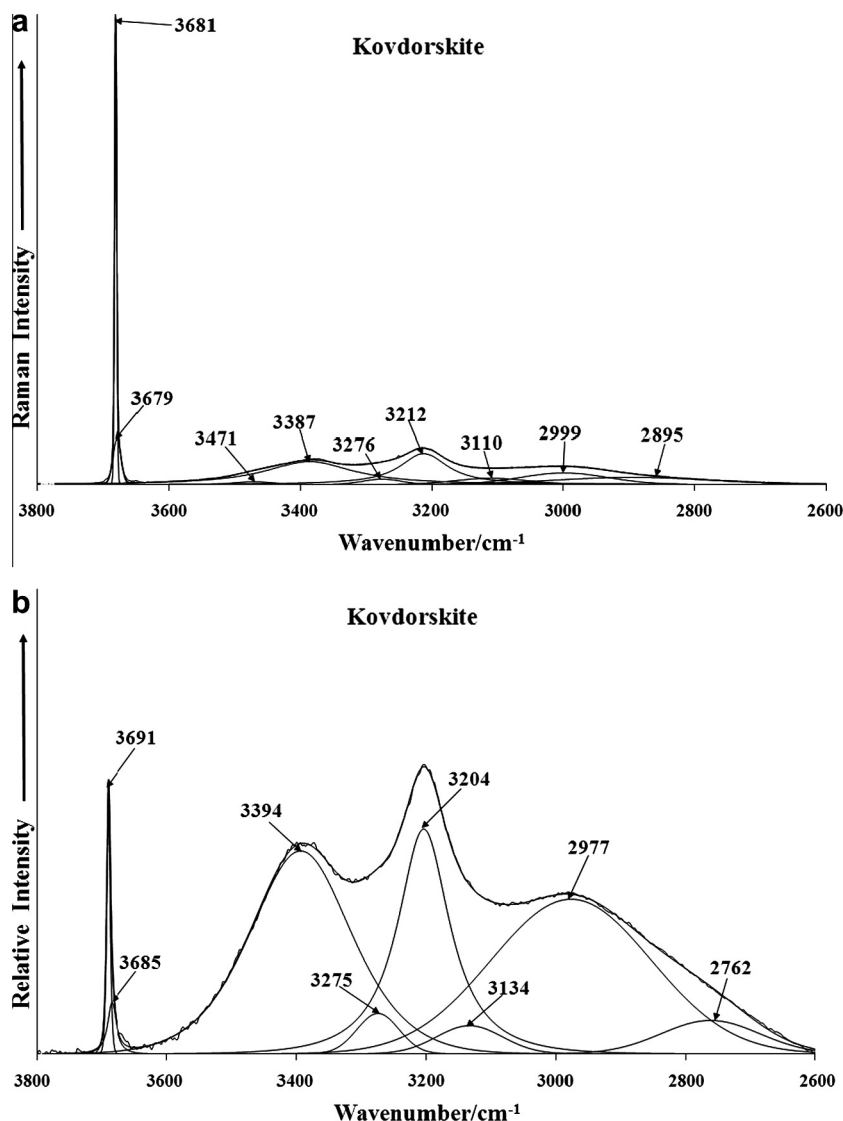


Fig. 5. (a) Raman spectrum of kovdorskite over the 2600–3800 cm^{−1} spectral range, and (b) Infrared spectrum of kovdorskite over the 2600–3800 cm^{−1} spectral range.

Results and discussion

Chemical characterization

The SEM image of kovdorskite sample studied in this work is presented as supplementary information in Fig. S1. Qualitative chemical analysis shows a homogeneous phase, composed by P and Mg. No other cations were observed (please see Fig. S2). The mineral can be considered as a standard sample of kovdorskite.

Thermogravimetric (TG) analyses were carried out to give support in the chemical characterization. The TG curve is shown in Fig. 1. Kovdorskite shows a total mass loss up of 29.25%. This result is in agreement with chemical data published by Morrison et al. [4]. The derivative thermogravimetric analysis (DTG) shows three exothermic reactions at 234.85 °C, 389.87 °C and 508.98 °C.

Spectroscopy

The Raman spectrum of kovdorskite over the complete spectral range from 100 to 4000 cm^{-1} is illustrated in Fig. 2a. This figure shows the position of the bands and the relative intensities of these Raman bands. It is obvious 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 observed. In comparison, the infrared spectrum of kovdorskite over the 500–4000 cm^{-1} spectral region is reported in Fig. 2b. This figure shows the position of the infrared peaks and the relative intensities. Parts of the spectrum show no intensity and therefore, the spectrum is subdivided into sections according to the type of vibration being observed.

The Raman spectrum of kovdorskite in the 800–1400 cm^{-1} spectral range is shown in Fig. 3a. This spectral region is where the phosphate stretching modes are found. The infrared spectrum over the 500–1300 cm^{-1} spectral region is reported in Fig. 3b. The infrared spectrum displays the infrared active stretching vibrations together with some bending modes. The Raman spectrum displays an intense Raman band at 965 cm^{-1} . The band shows some strong asymmetry on the low wavenumber side and a second band is resolved at 954 cm^{-1} . These bands are assigned to the PO_4^{3-} ν_1 symmetric stretching modes. In the infrared spectrum a shoulder band at 956 cm^{-1} is observed and may correspond to this vibrational mode. This fact supports the concept that the symmetry of the phosphate anion symmetry is not reduced. Two Raman bands at 1057 and 1089 cm^{-1} are attributed to the PO_4^{3-} ν_3 antisymmetric stretching modes. These vibrational modes show much greater intensity in the infrared spectrum where strong bands are found at 1019, 1044 and 1069 cm^{-1} . A comparison may be made with the spectra of other magnesium containing phosphates. For the compound $\text{Mg}_3(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$, PO_4^{3-} ν_1 symmetric stretching mode was found at 938 cm^{-1} and the PO_4^{3-} ν_3 antisymmetric stretching modes were observed at 1010, 1040, 1135 and 1155 cm^{-1} [6]. For the compound $\text{Mg}_3(\text{PO}_4)_2 \cdot 22\text{H}_2\text{O}$ [6], PO_4^{3-} ν_1 symmetric stretching modes were found at 930 and 971 cm^{-1} and the PO_4^{3-} ν_3 antisymmetric stretching modes were observed at 1000, 1046 and 1130 cm^{-1} . Another magnesium phosphate is newberyite $\text{Mg}(\text{PO}_3\text{OH}) \cdot 3\text{H}_2\text{O}$ [9,10]. For newberyite, an intense sharp band at 982 cm^{-1} is assigned to the PO_4^{3-} ν_1 symmetric stretching mode and the low intensity Raman bands at 1152, 1263 and 1277 cm^{-1} are assigned to the PO_4^{3-} ν_3 antisymmetric stretching vibrations.

The Raman band at 874 cm^{-1} and the corresponding infrared band at 878 cm^{-1} are ascribed to water librational modes. For the compound $\text{Mg}_3(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$, this band was observed at 780 cm^{-1} .

The Raman spectra of kovdorskite in the 300–800 cm^{-1} spectral range and in the 100–300 cm^{-1} spectral range are shown in Fig. 4a

and b. The first spectrum shows the bending modes of the phosphate anions and the second region is described as showing the lattice vibrations. A number of Raman bands are found in the 300–400 cm^{-1} spectral range, Raman bands are observed at 304, 320, 347 and 376 cm^{-1} . These bands are attributed to metal–oxygen stretching vibrations. Raman bands are found at 412, 454 and 485 cm^{-1} . These bands are assigned to the PO_4^{3-} ν_2 bending modes. Raman bands at 536, 546 and 574 cm^{-1} are assigned to the PO_4^{3-} ν_4 bending modes. For the compound $\text{Mg}_3(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$, PO_4^{3-} ν_2 bending mode was found at 430 cm^{-1} and the ν_2 bending mode at 489, 570 and 603 cm^{-1} . For this compound, a band was tabled at 341 cm^{-1} and is described as a MgO stretching vibration [6]. For newberyite, Raman bands at 497 and 552 cm^{-1} are attributed to the PO_4^{3-} ν_4 bending modes. An intense Raman band for newberyite at 398 cm^{-1} with a shoulder band at 413 cm^{-1} is assigned to the PO_4^{3-} ν_2 bending modes [9,10].

The Raman and infrared spectra of kovdorskite in the 2600–3800 cm^{-1} spectral range are reported in Fig. 5. The Raman spectrum is dominated by a very sharp intense band at 3681 cm^{-1} . This band is attributed to the stretching vibration of OH units. This band confirms the presence of the OH units in the formula $\text{Mg}_2\text{PO}_4(\text{OH}) \cdot 3\text{H}_2\text{O}$. A lower intensity band is observed as a shoulder at 3679 cm^{-1} . The vibrational mode is also observed in the infrared spectrum at 3691 cm^{-1} with a shoulder at 3685 cm^{-1} . The Raman spectrum shows a series of low intensity bands at 2895, 2999, 3110, 3212 and 3387 cm^{-1} . These bands are assigned to water stretching vibrations. These vibrational modes show much greater intensity in the infrared spectrum with infrared bands observed at 2762, 2977, 3204, 3275 and 3394 cm^{-1} .

For the compound $\text{Mg}_3(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$ [6], OH stretching bands were found at 3260 and 3460 cm^{-1} .

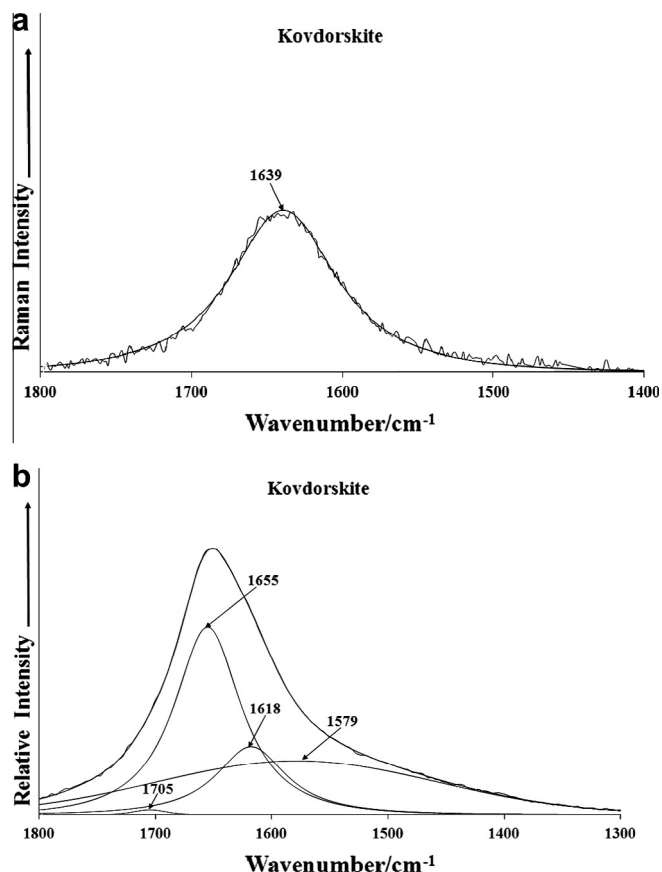


Fig. 6. (a) Raman spectrum of kovdorskite over the 1400–1800 cm^{-1} spectral range, and (b) Infrared spectrum of kovdorskite over the 1300–1800 cm^{-1} spectral range.

The Raman spectrum of kovdorskite in the 1400–1800 cm^{-1} spectral range is shown in Fig. 6a. This spectral region is where the water bending modes are found as is evidenced by the low intensity Raman band at 1639 cm^{-1} . The position of this band gives an indication that the water in the kovdorskite structure is strongly hydrogen bonded. The infrared spectrum of kovdorskite in the 1300–1800 cm^{-1} spectral range is reported in Fig. 6b. The spectrum shows overlapping bands at 1618 and 1655 cm^{-1} with broad bands at 1579 and 1705 cm^{-1} . The infrared band at 1655 cm^{-1} is assigned to the bending mode of water involved in strong hydrogen bonding. The position and assignation of the band is in harmony with the Raman band at 1639 cm^{-1} .

The mineral has been written with the formula $\text{Mg}_5(\text{PO}_4)_2(\text{CO}_3)(\text{OH})_2 \cdot 4.5(\text{H}_2\text{O})$. [see for example <http://webmineral.com/data/Kovdorskite.shtml>] However, no evidence of any carbonate bands was found in this research. Our research, based upon our results of vibrational spectroscopy confirms the formula as $\text{Mg}_2\text{PO}_4(\text{OH}) \cdot 3\text{H}_2\text{O}$.

Conclusions

We have studied the phosphate mineral kovdorskite $\text{Mg}_2\text{PO}_4(\text{OH}) \cdot 3\text{H}_2\text{O}$. The SEM/EDS analysis shows that the studied sample is composed by a single phase. The molecular structure of the mineral has been assessed by vibrational spectroscopy. Raman spectroscopy shows that the phosphate units are characterized by Raman bands at 965, 1057 and 1089 cm^{-1} which are typical of the phosphate anion. No bands attributable to hydrogen phosphate or even dihydrogen phosphate units were found. No bands which could be attributed to carbonate vibrations were found. Thus, the formula of the mineral is confirmed as $\text{Mg}_2\text{PO}_4(\text{OH}) \cdot 3\text{H}_2\text{O}$.

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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.2013.05.033>.

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