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Raman and infrared spectroscopic study of the molybdate containing uranyl mineral calcurmolite

Ray L. Frost ^{1*}, Jiří Čejka ^{1,2} and Marilla J. Dickfos ¹

Inorganic Materials Research Program, School of Physical and Chemical Sciences, Queensland University of Technology, GPO Box 2434, Brisbane Queensland 4001, Australia.

² National Museum, Václavské náměstí 68, CZ-115 79 Praha 1, Czech Republic.

Abstract

Raman and infrared spectra of calcurmolite were recorded and interpreted from the uranium and molybdenum polyhedra, water molecules and hydroxyls point of view. U-O bond lengths in uranyl and Mo-O bond lengths in MoO₆ octahedra were calculated and O-H...O bond lengths were inferred from the spectra. The mineral calcurmolite is characterised by bands assigned to the vibrations of the UO₂ units. These units provide intense Raman bands at 930, 900 and 868 and 823 cm⁻¹. These bands are attributed to the antisymmetric and symmetric stretching modes of the UO₂ units respectively. Raman bands at 794, 700, 644, 378 and 354 cm⁻¹ are attributed to vibrations of the MoO₄ units. The bands at 693 and 668 cm⁻¹ are attributed to antisymmetric and symmetric A_g modes of terminal MO₂ units. Similar bands are observed at 797 and 773 cm⁻¹ for koechlinite and 798 and 775 cm⁻¹ for lindgrenite. It is probable that some of the bands in the low wavenumber region are attributable to the bending modes of MO₂ units.

Keywords: calcurmolite, mineral, uranyl molybdate, infrared and Raman spectroscopy, U-O (uranyl) bond lengths, Mo-O bond lengths, O-H...O bond lengths

Introduction

Interest in minerals containing molybdate anions has been ongoing for some considerable time ¹⁻⁸. No doubt because these minerals are of commercial value. Interest in the structure and formation of these minerals has also been forthcoming ⁹⁻¹¹. Significant advances have been made over time ¹²⁻¹⁵. This interest has been heightened by the use of the molybdate minerals as catalysts ¹⁶⁻¹⁹. Many of these minerals have layered structures which can lead to high surface active materials ¹²⁻¹⁵. Some papers by the authors on the structure and spectroscopy of molybdate containing minerals have been published ²⁰⁻²⁴. The vibrational spectra of selected molybdate minerals namely lindgrenite (Cu₃(MO₄)₂(OH)₂), iriginite (UO₂Mo₂O₇.3H₂O) and koechlinite (BiMoO₆) has been published ²².

* Author for correspondence Ray L. Frost (r.frost@qut.edu.au)

Uranyl molybdate minerals are formed in uranium-molybdenum deposits containing relatively high concentration of molybdenum minerals which are easily oxidized. They are associated with uranium minerals of the same group, and a set of non-uranium minerals, more rarely with other uranium minerals, such as is the case of tengchongite association with studtite²⁵. According to Finch and Murakami²⁶ uranyl molybdate minerals are locally important as ore minerals and are also common as accessories in roll-front deposits and other deposits where uraninite and molybdenum bearing minerals are being weathered. In these minerals, molybdenum occurs as Mo⁶⁺, while uranium is of mixed valence, U⁴⁺ and U⁶⁺. There are known seven uranyl molybdate minerals: calcurmolite, cousinite, deloryite, iriginite, moluranite, tengchongite and umohoite, however, crystal structures are known only for three of them: deloryite, iriginite and umohoite^{26,27}. Characteristic features of natural and synthetic uranyl molybdates structures are MoO_x polyhedra, where x may be 4, 5 or 6. Crystal chemical studies of uranyl molybdates proved that most of natural and synthetic phases are characterized by MoO₄ tetrahedra, inclusive deloryite and probably also tengchongite, while for such minerals as iriginite and umohoite were found molybdenum octahedra, MoO₆.

Calcurmolite is monoclinic, a 1630(3), b 25.49(5), c 19.50(6) Å²⁸. Chemical formula of the uranyl molybdate mineral calcurmolite should be Ca(UO₂)₃·4(MoO₄)₃(OH)₂₋₅·7-12 H₂O²⁹, Ca(UO₂)₃(MoO₄)₃(OH)₂·11 H₂O³⁰, Ca(UO₂)₄(MoO₄)₃(OH)₄·8 H₂O³¹, and (Ca,Na)₂(UO₂)₃Mo₂(O,OH)₁₁·n H₂O or (Ca_{1.7}Na_{0.3})₂(UO₂)₃Mo₂O_{10.7}·n H₂O or (Ca_{1-x}Na_x)₂(UO₂)₃(MoO₄)₂(OH)_{6-x}·n H₂O³². Infrared spectrum of calcurmolite was published by Sidorenko et al.²⁸.

Studies of the application of vibrational spectroscopy to these molybdate minerals is not often forthcoming³³⁻³⁵. This may be due to the lack of technology at that time or the availability of appropriate specimens. Recently Frost et al. have used vibrational spectroscopic techniques to study groups of related minerals³⁶⁻⁴². Raman spectroscopy has proven a powerful technique for studying closely related minerals, particularly where the minerals can be found associated with each other through paragenesis.

Raman spectroscopy has proven very useful for the study of minerals.⁴³⁻⁵⁸ Indeed Raman spectroscopy has proven most useful for the study of diagenetically related minerals as often occurs with carbonate minerals.^{49,50,52-55,59} Some previous studies have been undertaken by the authors using Raman spectroscopy to study complex secondary minerals formed by crystallisation from concentrated sulphate solutions.⁶⁰ No detailed spectroscopic studies of the uranyl mineral schroeckingerite has been forthcoming. Few Raman studies of any note are available.^{61,62} The paper is a part of systematic studies of vibrational spectra of minerals of secondary origin in the oxide supergene zone and their synthetic analogs. A Raman spectrum of calcurmolite is available on a data base at [http://rruff.info/index.php/r=sample_detail/sample_id=3010/sample_search_id=XfBrFKSjDDXtDykrOYsiKhSib]. The Raman spectrum is of precisely the same mineral which is described in this work. Two spectra of this mineral from two different sources are found.

In this paper we report the Raman and infrared spectra of calcurmolite and to relate the spectra to the molecular structure of the mineral. The paper is a part of the

systematic research of uranyl secondary natural phases realized in our Inorganic Materials Research program.

Experimental

Minerals

The calcurmolite mineral was obtained from the Mineralogical Research Company and originated from Sokh-Karasu area, Kadzharan Molybdenum Deposit, Upper Okhca River, Kafan District, Syunik' Province, Armenia. This sample is a 'type' mineral. The chemical composition of this mineral has been published⁶³ (page 103). The mineral corresponds to the formula above $\text{Ca}(\text{UO}_2)_3(\text{MoO}_4)_3(\text{OH})_2 \cdot 11\text{H}_2\text{O}$.

Raman spectroscopy

The crystals of calcurmolite were placed and oriented on the stage of an Olympus BHSM microscope, equipped with 10x and 50x objectives and part of a Renishaw 1000 Raman microscope system, which also includes a monochromator, a filter system and a Charge Coupled Device (CCD). Raman spectra were excited by a HeNe laser (633 nm) at a resolution of 2 cm^{-1} in the range between 100 and 4000 cm^{-1} . Repeated acquisition using the highest magnification was accumulated to improve the signal to noise ratio. Spectra were calibrated using the 520.5 cm^{-1} line of a silicon wafer. Details of the technique have been published by the authors^{44-50,52-55,59,64,65}.

Mid-IR spectroscopy

Infrared spectra of calcurmolite were obtained using a Nicolet Nexus 870 FTIR spectrometer with a smart endurance single bounce diamond ATR cell. Spectra over the $4000\text{--}525\text{ cm}^{-1}$ range were obtained by the co-addition of 64 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 adjustment, smoothing and normalisation were performed using the Spectracalc software package GRAMS (Galactic Industries Corporation, NH, USA). Band component analysis was undertaken using the Jandel 'Peakfit' software package which 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 Lorentz-Gauss cross-product function with the minimum number of component bands used for the fitting process. The Lorentz-Gauss 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

Spectroscopy of uranyl cation

Characteristic vibrations of the uranyl, $(\text{UO}_2)^{2+}$, ion are: the ν_1 symmetric stretch (approximately $900\text{--}750\text{ cm}^{-1}$ – Raman active), ν_3 antisymmetric stretch (approximately $1000\text{--}850\text{ cm}^{-1}$ – infrared active), and ν_2 (δ) doubly degenerate bend

(approximately 300-200 cm^{-1} – infrared active) may be observed in the studied Raman and infrared spectra. The $D_{\infty h}$ symmetry of the free uranyl, $(\text{UO}_2)^{2+}$, lowering may cause infrared and Raman activation of all vibrations and splitting of doubly degenerate bending vibration. The tentative assignment of the observed bands is therefore made with regard to these assumptions.

The Raman spectra of calcurmolite in the 100 to 1000 cm^{-1} region are shown in Figure 1 and the infrared spectra in the 550 to 1150 cm^{-1} region in Figure 2. The Raman spectrum as shown in the data base given above differs significantly from the Raman spectrum as presented in Figure 1. No assignment or labeling of the bands is given on this web site. Further no bands in the OH stretching region were forthcoming which would be expected for a mineral containing H_2O and OH units. It is interesting that the spectrum of the second calcurmolite sample from Kyzulsai Mo-U deposit, South Kazakhstan is even of lesser quality than the Raman spectrum of calcurmolite from Gornoe, Transbaikal region, Russia, given in this data base. Further the spectra in this data base are different even though the spectra are from the same mineral. The spectra may be observed at web site:

[http://truff.info/index.php/r=sample_search/sample_search_id=TzuZNCzKpZbUYIJKFtsEqHMjR].

A summary of the results of the Raman spectra of calcurmolite are reported in Table 1. Bands are observed in the Raman spectra at 868, 900 and 930 cm^{-1} and are assigned to the $\nu_3 (\text{UO}_2)^{2+}$ antisymmetric stretching vibrations. Previous studies by the authors have shown that bands in these positions are characteristic of the uranyl ion.^{44,45,49,50,52-55,59} Bands which may be attributed to the molybdate anion would not occur in this spectral region.²¹ Infrared bands are observed at 866, 918 and 945 cm^{-1} (Figure 2). These three infrared bands are the bands which correspond to the Raman bands above. Raman band at 823 cm^{-1} and infrared band at 839 cm^{-1} were assigned to the $\nu_1 (\text{UO}_2)^{2+}$ symmetric stretching vibrations. A comparison may be made with the Raman spectra of iriginite. Iriginite is the uranyl molybdate mineral $(\text{UO}_2)(\text{Mo}_2\text{O}_7)3\text{H}_2\text{O}$. In the Raman spectrum of iriginite two closely overlapping bands are observed at 826 and 818 cm^{-1} and are attributed to these two UO stretching vibrations. This doubling of the UO symmetric stretching vibrations is also reflected in the UO_2 antisymmetric stretching region where two bands are observed at 965 and 950 cm^{-1} .⁶⁶ Two comparatively intense bands are observed at 246 and 198 cm^{-1} and are assigned to the bending modes of the UO_2 units⁶⁶.

Previous studies have shown that the two UO bonds in the UO_2 units are not equivalent⁶⁶⁻⁶⁸. This gives rise to two UO stretching bands. By using an empirical relationship as published by Bartlett and Cooney⁶⁹ the wavenumber of the Raman and infrared bands may be used to estimate UO bond lengths. Raman bands at 930/1.763, 900/1.785 and 868/1.809 $\text{cm}^{-1}/\text{\AA}$ and infrared bands at 918/1.772 and 866/1.810 $\text{cm}^{-1}/\text{\AA}$ are attributed to the $\nu_3 (\text{UO}_2)^{2+}$ antisymmetric stretching vibrations. Raman band at 823/1.788 and infrared band at 839/1.772 $\text{cm}^{-1}/\text{\AA}$ were assigned to the $\nu_1 (\text{UO}_2)^{2+}$ symmetric stretching vibrations. U-O bond lengths in uranyl were calculated with two empirical relations by Bartlett and Cooney⁶⁹. They are in good agreement with U-O bond lengths in uranyls as inferred by Burns²⁷ for uranyl pentagonal dipyramidal coordination polyhedra. Raman band at 271 cm^{-1} was related to the $\nu_2 (\delta) (\text{UO}_2)^{2+}$ bending vibration. It is assumed from the number bands assigned to the uranyl

stretching that symmetrically distinct $(\text{UO}_2)^{2+}$ units may be present in the crystal structure of calcurnolite.

Spectroscopy of the molybdate anion

The Raman spectra of some molybdate minerals have been published. However very few Raman spectra of uranyl molybdate minerals have been published. Minerals with a scheelite structure like wulfenite have site group S_4 and space group C_{4h}^6 . The crystal structure resembles that of zircon and therefore the WO_4 and MoO_4 groups should show four bands only in the Raman spectra, two components each of ν_3 and ν_4 . The scheelite structure has been shown to be one of the few for which the correlation splitting of the internal modes has been observed. This results in $\nu_1: A_g(\text{R}) + B_u(\text{inactive})$, $\nu_2: A_g + B_g(\text{R}) + A_u(\text{ir}) + B_u$, $\nu_3, \nu_4: B_g + E_g(\text{R}) + A_u(\text{ir}) + E_u(\text{ir})$ ²¹. Raman and infrared spectra of calcurnolite are interpreted from the MoO_6 octahedra point of view, in which the vibrations are as follows: $\nu_1 (A_{1g}, \nu(\text{XY}))$, $\nu_2 (E_g, \nu(\text{YXY}))$, $\nu_3 (F_{1u}, \delta(\text{YXY}))$, $\nu_4 (F_{1u}, \nu(\text{XY}))$, $\nu_5 (F_{2g}, \delta(\text{YXY}))$, $\nu_6 (F_{2u}, \delta(\text{YXY}))$ ⁷⁰. Calculations for the wulfenite-type structure indicates the following Raman bands $\nu_1: A_g + B_u(\text{inactive, but activated due to strain})$, $\nu_2: A_g + B_g + B_u$, $\nu_3, \nu_4: B_g + E_g$, most of which are easily observed for wulfenite (and scheelite). The $\nu_1(A_g)$ band is observed at 871 cm^{-1} and although the corresponding $\nu_1(B_u)$ vibration should be inactive a minor band is observed around 858 cm^{-1} . It may be possible that this band is visible as a weak band due to strain in the crystal causing activation of this band. This band for synthetic powellite is observed in the infrared spectrum at 819 cm^{-1} ⁷¹. For powellite the bands are observed at 879 and 847 cm^{-1} . Interestingly Farmer reported the $\nu_1(A_g)$ band in the Raman spectrum for synthetic powellite at 880 cm^{-1} and for wulfenite at 872 cm^{-1} ⁷².

The Raman spectra attributable to MoO_4 units may be observed in Figure 1 and in the infrared spectra of Figure 2. Raman bands at $644, 700$ and 794 cm^{-1} are assigned to stretching vibrations of the MoO_4 units. Infrared bands are observed at $621, 721, 799$ and 945 cm^{-1} . The band at 888 cm^{-1} is therefore assigned to the ν_1 symmetric stretching vibration of the MO_4 units. In the Raman spectra of calcurnolite Raman bands are observed at 378 and 354 cm^{-1} . These bands are assigned to the ν_2 bending modes of the MO_4 units. For iriginite, bands are observed at 337 and 301 cm^{-1} . Raman bands for calcurnolite are found at 644 and 495 cm^{-1} . The first band is assigned to the $\nu_3(B_g)$ vibrational mode and the second to the $\nu_4(E_g)$ modes. For iriginite the $\nu_3(B_g)$ vibration is located around 693 cm^{-1} , whereas the $\nu_3(E_g)$ of iriginite is found at 668 cm^{-1} . The bands of iriginite observed at $487, 457$ and 413 cm^{-1} are attributed to $\nu_4(E_g)$ modes.

Mo-O bond lengths were calculated using wavenumbers of the Mo-O antisymmetric stretching with the empirical formula by Hardcastle and Wachs ⁷³. Observed Mo-O stretching vibrations are: infrared $945/1.753, 799/1.793, 721/1.841$ and $621/1.915 \text{ cm}^{-1}/\text{\AA}$ and Raman $794/1.796, 700/1.857, 644/1.897, 495/2.021, 378/2.154$ and $354/2.186 \text{ cm}^{-1}/\text{\AA}$. Calculated Mo-O bond lengths prove the distortion of Mo-O octahedra. Mo-O bonds longer than 2 \AA are related to

water molecules (Mo-OH₂) and hydroxyl ions (Mo-OH). Recorded infrared spectrum of calcurmolite is comparable with that published by Sidorenko et al. ³².

Spectroscopy of water molecules and hydroxyls

The infrared spectra of calcurmolite in the HOH bending and OH stretching region are shown in Figures 3 and 4 respectively. In the spectra of Figure 3 a number of low intensity bands are found at 1545, 1491, 1468 and 1429 cm⁻¹. These bands are assigned to the δUO₂-OH bending vibrations. A band at 3694 cm⁻¹ is assigned to the relatively free hydroxyl unit, while those bands at 3539 (2.98), 3425 (2.82), 3223 (2.73) and 2914(2.64) cm⁻¹ are attributed to the hydrogen bonded water molecules and hydroxyls. H-bond lengths (Å) are given in parentheses. Correlation of OH stretching frequencies and OH...O hydrogen bond lengths was calculated according to Libowitzky ⁷⁴. The Infrared bands at 1624 cm⁻¹ are ascribed to the δ H₂O bending vibrations. The presence of symmetrically distinct hydroxyls in the crystal structure of calcurmolite is supported by a number of bands in the range 1000-1491 cm⁻¹ assigned to the δM-OH bending vibrations, where M may be U⁶⁺ and/or Mo⁶⁺. It may be also inferred from the spectrum that symmetrically different water molecules may be present in the crystal structure of calcurmolite.

Conclusions

- (a) Raman and infrared spectra of the secondary uranyl mineral calcurmolite were measured and interpreted with regard to (UO₂)²⁺ (uranyl), MoO₆ octahedra, water molecules and hydroxyl ions.
- (b) U-O bond lengths in uranyls and Mo-O bond lengths in were calculated with corresponding empirical relations.
- (c) O-H...O hydrogen bond lengths in the crystal structure of calcurmolite were correlated on the basis of Libowitzky's relation ⁷⁴.

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Figure 2 Infrared spectra of calcurmolite in the 550 to 1150 cm^{-1} region

Figure 3 Infrared spectra of calcurmolite in the 1200 to 1800 cm^{-1} region

Figure 4 Infrared spectra of calcurmolite in the 2500 to 4000 cm^{-1} region

Infrared	Raman	Siderenko IR	IR	Assignment	UO bond distance	MoO
3694						
3539						
3425		3450	3395	OH stretch		
3223		3250	3230	OH stretch		
2914						
		1655				
1624		1623	1625	HOH bending		
1545			1570			
1491						
1468				MOH bend		
1429		1400	1396			
		1352	1360			
1119						
1079				MOH bend		
1030		1020	1020			
1000						
945		946	945		1.753	
	930	930	930	Nu3 UO22+	1.763	
918	900	898	897		1.772, 1.785, 1.786, 1.787	
866	868				1.810, 1.809	
			855			
839	823	848	846	Nu1 UO22+	1.772, 1.788, 1.764, 1.766	
799	794	806	805	Nu MoO	1.793, 1.796, 1.789, 1.79	
721	700	723	721		1.843, 1.857, 1.841, 1.843	
621	644	632	630		1.915, 1.897, 1.907, 1.908	
		520	515		2.001, 2.005	
	495	479	475		2.021, 2.040	
			410		2.115	
	378				2.154	
	354				2.186	
	271			$\nu_2 (\delta OY)_2^{+2}$		

Table 1 Results of the Infrared and Raman spectra of calcurmolite

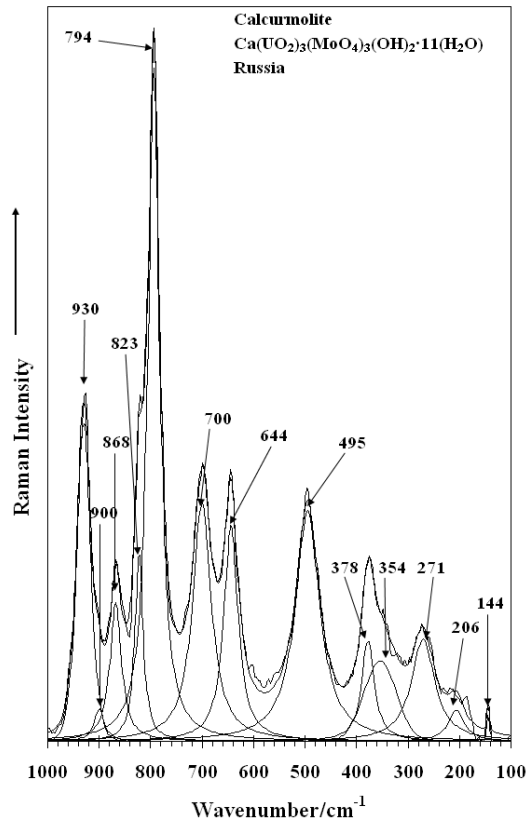


Figure 1

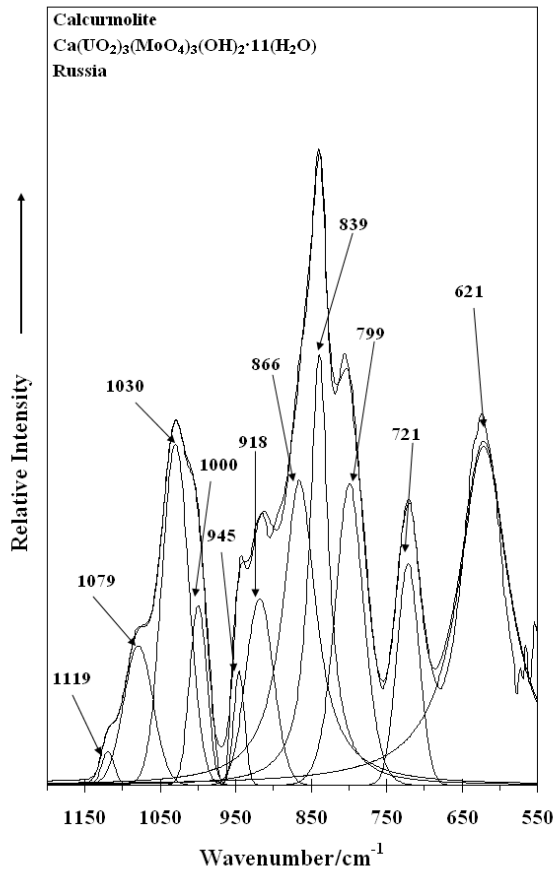


Figure 2

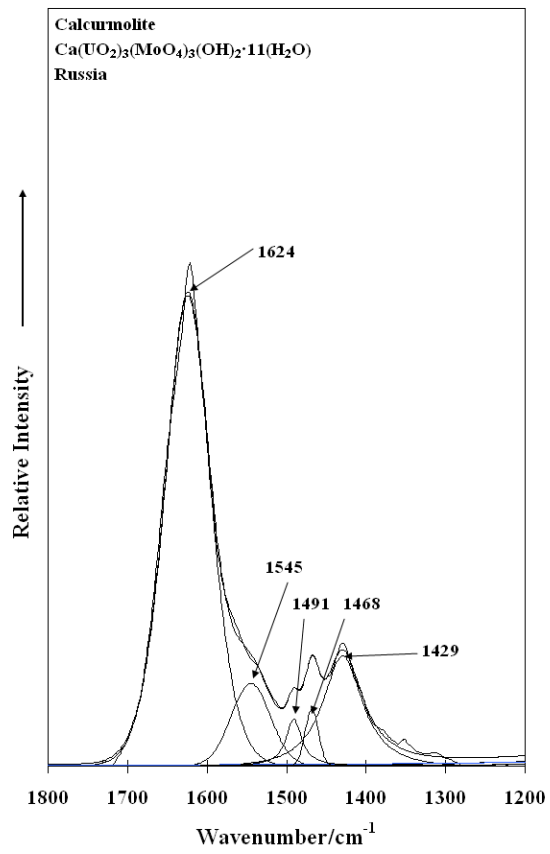


Figure 3

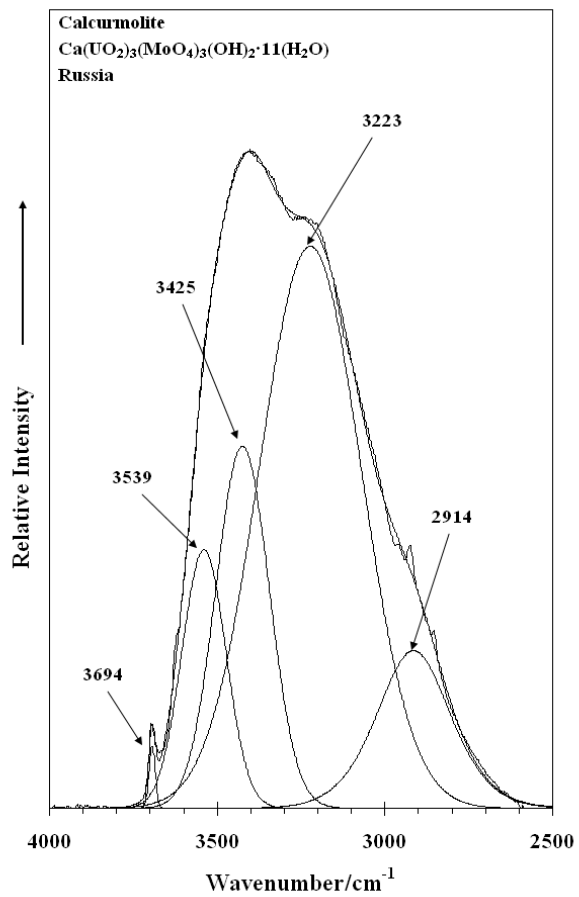


Figure 4