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A Raman spectroscopic study of the uranyl phosphate mineral threadgoldite

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Abstract

Raman spectra of threadgoldite at 298 and 77 K are measured and interpreted for the first time. Bands related to the $(\text{UO}_2)^{2+}$ and $(\text{PO}_4)^{3-}$ stretching and bending vibrations are tentatively attributed together with the bands assigned to the stretching and bending vibrations of water molecules and hydroxyls. Hydrogen bonding network and H_2O and $(\text{OH})^{-1}$ libration modes are mentioned. U-O bond lengths in uranyles are calculated via empirical relations $R_{\text{U-O}} = f[v_1 \text{ and } v_3 (\text{UO}_2)^{2+}] \text{ \AA}$. They are comparable to the values inferred from the single crystal structure analysis of threadgoldite.

Key words: threadgoldite, phosphate, Raman spectroscopy, U-O bond length, uranyl

Introduction

Threadgoldite, $\text{Al}[(\text{UO}_2)_2(\text{PO}_4)_2](\text{OH}) \cdot 8\text{H}_2\text{O}$, is a rare uranyl secondary mineral found in the uraniferous oxide zone of a complex zone granite pegmatite at Kobokobo, Lusungu River District, Kivu Province, Democratic Republic of Congo [1-4]. A similar mineral containing calcium ions and probably also iron ions instead of aluminum ions having comparable X-ray powder pattern was insufficiently described by Threadgold [5] from the South Alligator Valley, Northern Territories, Australia. Recently Threadgoldite has been identified in at least six locations at mine sites in the South Alligator deposits at Rockhole, El Sherana, Palette, Saddle Ridge, Coronation Hill and Sieisbeck [6]. The deposits occur within a north-west trending fault-bounded valley within the Pine Creek Geosyncline. The crystal structure of threadgoldite was studied by Piret et al. [2] and refined by Khosrawan-Sazedj [7].

According to Locock [8, 9] at least twelve aluminum uranyl phosphate minerals have been described, of which only sabugalite, threadgoldite and uranospalthite contain the autunite-type sheet. As mentioned above, only the crystal structure of threadgoldite is known. Althupite, mundite, phuralumite and upalite exhibit the phosphuranylite-type uranyl anion sheet topology. Crystal structures of furongite, kamitugaite, moreauite, ranunculite and triangulite are yet not known.

Infrared spectroscopy and thermal analysis of the uranyl minerals inclusive of uranyl phosphate minerals was reviewed by Čejka [10]. Neither infrared nor Raman spectra of threadgoldite are available. Some Raman studies of uranyl phosphates have been undertaken [11-15]. According to Burns [16-18], the autunite-type uranyl anion sheet contains equal numbers of $[\text{UO}_2\text{O}_4]$ square dipyramids and $[(\text{P,As})\text{O}_4]$

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tetrahedra. The interlayer of the crystal structure of threadgoldite contains Al cations octahedrally coordinated by two (OH)⁻ groups. Symmetrically equivalent AlO₆ octahedra share edges that connect the two (OH)⁻ groups, resulting in dimers Al₂(OH)₂(H₂O)₈. The dimers are connected to the sheets by hydrogen bonds only. Four other symmetrically distinct water molecules are only hydrogen bonded into the interlayer. Some syntheses of phases which may be structurally related to threadgoldite were published by Chernorukov et al. [19]. Short information about the infrared spectra of prepared phases is included.

The paper forms part of the Raman and infrared spectroscopy study of secondary minerals including uranyl minerals [12, 20-25]. This research includes studies of sulphates [20, 23, 26], carbonates [21, 24], phosphates and arsenates [12, 27, 28]. Raman spectroscopy has proven most useful for the study of these minerals. Whilst infrared spectroscopy provides useful information on the study of minerals containing the uranyl unit, the spectra suffer from band overlap making the attribution of the bands difficult. Raman spectroscopy on the other hand provides spectra with spectral regions in which definitive assignments of the bands can be given. In this work we report the Raman spectra of the mineral threadgoldite, a mineral which has been not studied in terms of vibrational spectroscopy, and relate the spectra to the structure of the mineral.

Experimental

Minerals

Two threadgoldite samples (Registered numbers M22130 and M43442) were obtained from Museum Victoria. The mineral originated from the South Alligator Mine, El Sharana prospect [6]. Photographs of these minerals have been published [6]. The samples were previously analysed by X-ray diffraction and EDX measurements. Chemical composition of the sample M43442 [wt.% Al₂O₃ 5.97, Fe₂O₃ 0.1, UO₃ 61.43, P₂O₅ 15.5, As₂O₅ 0.14, H₂O 16.65, total 99.97] is close to the theoretical values and those found in the type specimen of threadgoldite [2]. Theoretical values for threadgoldite are [wt.% Al₂O₃ 5.55, UO₃ 62.31, P₂O₅ 15.46, H₂O 16.68, total 100.00]

Raman microprobe spectroscopy

The crystals of threadgoldite were placed and orientated 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. In order to ensure that the correct spectra are obtained, the incident excitation radiation was scrambled. Previous studies by the authors provide more details of the experimental technique. The Raman spectra of the oriented single crystals are reported in accordance with the Porto notation.

It should be noted that because of the very small amount of sample supplied on loan from the museum, it was not possible to run the infrared spectrum. This does show a major advantage of Raman spectroscopy in the study of uranium minerals is the ability to study very small amounts of mineral. Spectra at liquid nitrogen temperature were obtained using a Linkam thermal stage (Scientific Instruments Ltd, Waterfield, Surrey, England). Details of the technique have been published elsewhere by the authors [12, 20-22].

Results and discussion

Raman spectroscopy

In the crystal structure of threadgoldite, there are four or two symmetrically distinct U^{6+} in the form of uranyl units, and four or two symmetrically distinct P^{5+} as $(PO_4)^{3-}$ units [2, 7] with eight molecules in the unit cell. The symmetry of free uranyl and phosphate units is lowered. Raman and infrared activation of all vibrations and splitting of the doubly [the $\nu_2(UO_2)^{2+}$ bending vibration and the $\nu_2(PO_4)^{3-}$ bending vibration] and triply [the ν_3 antisymmetric stretching vibration and the $\nu_4(PO_4)^{3-}$ bending vibration] degenerate vibrations is therefore expected depending on site symmetry of individual units. The Raman spectra at 298 and 77 K in the 750 to 1150 cm^{-1} of the two threadgoldite minerals are displayed in Figure 1. The Raman spectra of the low wavenumber region of threadgoldite are shown in Figure 2 and the hydroxyl stretching region are shown in Figure 3. The results of the analyses of the Raman spectra are reported in Table 1.

Uranyl, $(UO_2)^{2+}$, vibrations

Bands at 953 (1.748 Å) cm^{-1} and 952 (1.749 Å) cm^{-1} (298 K), and (913 (1.775 Å) cm^{-1} and 875 (1.803 Å) cm^{-1}) and 912 (1.776 Å) cm^{-1} (77 K) are attributed to the $\nu_3(UO_2)^{2+}$ antisymmetric stretching vibrations. The bands are of very low intensity. Some recent studies have shown that the intensity of phosphate bands may be of a very low intensity in autunites minerals because of a low symmetry [12, 28]. However, some confusion with the $\nu_1(PO_4)^{3-}$ vibrations is possible, especially in the case of the bands at 953 and 952 cm^{-1} , respectively. These bands may be probably in fact be connected with the $\nu_3(UO_2)^{2+}$ vibrations than those of the $\nu_1(PO_4)^{3-}$ vibrations. The intensity of the $\nu_3(UO_2)^{2+}$ antisymmetric stretching bands would be expected to be of a low intensity. Bands at [840 (1.771 Å), 827 (1.784 Å) and 817 (1.794 Å) cm^{-1}] and (845 (1.766 Å), 828 (1.783 Å) and 817 (1.794 Å) cm^{-1}) (298 K), and [853 (1.759 Å), 832 (1.779 Å), 829 (1.782 Å) and 810 (1.801 Å) cm^{-1}] and (832 (1.779 Å), 828 (1.783 Å) and 810 (1.801 Å) cm^{-1}) (77 K) are connected with the $\nu_1(UO_2)^{2+}$ symmetric stretching vibrations (Figure 1). No phosphate or other bands would be expected in this spectral region. The number of the $(UO_2)^{2+}$ vibrations is not in any disagreement with the symmetry of uranyl in the uranyl phosphate sheet, number of molecules in the unit cell of threadgoldite, and FGA. However, some of the observed bands may be attributed to the δ Al-OH bending vibrations.

U-O bond lengths were calculated with the empirical relations $R_{U-O} = f[\nu_1$ and $\nu_3(UO_2)^{2+}$ [29]. Obtained values are close to and comparable with the data from the single crystal structure analyses of threadgoldite: average values for individual

uranyls U(1)-O 1.77 Å, U(2)-O 1.76 Å, U(3)-O 1.75 Å and U(4)-O 1.92 Å, in summary U-O 1.8 Å [2] and U(1)-O 1.84 Å and U(2)-O 1.705 Å, in summary U-O = 1.772₅ Å [7]. Bands observed at lower wavenumbers than 331 cm⁻¹ are assigned to the ν_2 (δ) (UO₂)²⁺ and ν (U-O_{ligand}) and δ (U-O_{ligand}) vibrations without any detailed attribution [30-33] (Figure 2).

Phosphate, (PO₄)³⁻, vibrations

Bands at (953 (?) and 974) and (952 (?) and 975 cm⁻¹) (298 K), and (913 (?) and 976 cm⁻¹) and (912 (?) and 976 cm⁻¹) (77 K) are connected with the ν_1 (PO₄)³⁻ symmetric stretching vibrations. Coincidence with the ν_3 (UO₂)²⁺ antisymmetric stretching vibrations is very probable, as mentioned above. Bands at (999, 1019, 1026, 1057 and 1107 cm⁻¹) and (998, 1016, 1025, 1061 and 1114 cm⁻¹) (298 K), and (983, 998, 1016, 1021, 1031, 1041, 1076, 1122 cm⁻¹) and (983, 998, 1015, 1021, 1031, 1032, 1089 and 1121 cm⁻¹) (77 K) are attributed to the split triply degenerate ν_3 (PO₄)³⁻ antisymmetric stretching vibrations (Figure 1).

Wavenumbers of the bands of the (PO₄)³⁻ bending vibrations are located in the region 391-615 cm⁻¹. Bands at (391, 398, 419, 451 cm⁻¹) and (399, 414 and 455 cm⁻¹) (298 K), and (399, 416, 449 and 490 cm⁻¹) and (399, 417 and 448 cm⁻¹) (77 K) are assigned to the split doubly degenerate ν_2 (PO₄)³⁻ in-plane bending vibrations, while those at (533 and 612 cm⁻¹) and (542, 611 and 614 cm⁻¹) (298 K), and (514, 536, 565 and 615 cm⁻¹) and (516 and 615 cm⁻¹) (77 K) to the split triply degenerate ν_4 (PO₄)³⁻ out-of-plane bending vibrations (Figure 2).

Some difficulties with the band assignments in the region of the (PO₄)³⁻ stretching vibrations and also in the region of the (PO₄)³⁻ bending vibrations cannot be excluded. Some bands are in all probability related to the δ Al-OH bending vibrations.

Water molecules, H₂O, and hydroxyls, (OH)⁻, vibrations

Bands at (3576, 3411 and 3158 cm⁻¹) and (3580, 3499, 3404, 3210 and 3039 cm⁻¹) (298 K), and (3576, 3562, 377, 3338, 3250, 3197, 3090 and 3009 cm⁻¹) and (3574, 3561, 3478, 3379, 3326, 3251, 3193, 3083 and 3030 cm⁻¹) (77 K) are attributed to the ν OH stretching vibrations of water molecules and hydroxyls (Figure 3). Because of hydrogen bonding in the crystal structure of threadgoldite, the resolution of the ν_1 and ν_3 of H₂O is difficult. Only in the 77 K spectrum is resolution obtained. Bands at 3576 and 3580 cm⁻¹ (298 K) and (3576 and 3562 cm⁻¹) and (3574 and 3561 cm⁻¹) are related to the ν OH of the (OH)⁻ ions, free or only very weakly hydrogen-bonded in the crystal structure. All other bands in this region prove the presence of a hydrogen-bonding network in which water molecules are very strongly to weakly hydrogen-bonded [Libowitzky 1999]. This supports the conclusions from the crystal structure analysis that symmetrically distinct and therefore structurally nonequivalent water molecules are present in the crystal structure. Some of them are coordinated in the Al₂O₁₀ [Al₂(OH)₂O₈] dimers as [Al₂(OH)₂(OH₂)₈], while the remaining water

molecules are hydrogen bonded only. The resolution is better at 77 K because the broad bands are more split.

However, only one band is surprisingly observed in all cases close to 1650 cm^{-1} . This band is connected with the ν_2 (δ) H_2O bending vibrations. Water is a very poor scatterer in Raman spectroscopy and thus it is not unexpected that the water bending modes are of a low intensity. Some bands especially close to the region from 650 to 700 cm^{-1} observed at 77 K are attributed to the libration modes of water molecules and hydroxyls as expected from the existence of the hydrogen-bonding network in the crystal structure of threadgoldite. According to Hawthorne [34, 35], this hydrogen-bonding network stabilizes the crystal structure of threadgoldite.

Conclusions

Raman spectra of two samples of threadgoldite were studied and assigned. Observed bands were attributed to the $(\text{UO}_2)^{2+}$ and $(\text{PO}_4)^{3-}$ stretching and bending vibrations and to the H_2O and $(\text{OH})^-$ stretching, bending and also libration modes. U-O bond lengths were calculated with two empirical relations $R_{\text{U-O}} = f[\nu_1 \text{ and } \nu_3 (\text{UO}_2)^{2+}]$. Their values are good comparable with those inferred from the published single crystal structure analysis of threadgoldite. Hydrogen bonding network, important for the stability of threadgoldite structure, was shortly mentioned.

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Threadgoldite								
M22130				M43442				Proposed assignment
298K		77K		298K		77K		
Centre (cm ⁻¹)	FWHM (cm ⁻¹)	Centre (cm ⁻¹)	FWHM (cm ⁻¹)	Centre (cm ⁻¹)	FWHM (cm ⁻¹)	Centre (cm ⁻¹)	FWHM (cm ⁻¹)	
3576	61	3576	7	3580	64	3574	8	v OH stretching vibrations of hydroxyls
		3562	7			3561	8	„
				3499	73	3478	44	„
3411	215			3404	152			„
								v OH stretching vibrations of water molecules
		3377	29			3379	58	
		3338	154			3326	49	„
		3250	43			3251	80	„
		3197	54	3210	331	3193	45	„
3158	375							„
		3090	49			3083	37	„
		3009	84	3039	183	3030	161	„
								v ₂ (δ) H ₂ O bending vibrations
1655	105	1651	126	1639	93	1645	56	v ₃ (PO ₄) ³⁻ antisymmetric stretching vibrations
								v ₃ (PO ₄) ³⁻ antisymmetric stretching vibrations
1107	26	1122	14	1114	33	1121	16	v ₃ (PO ₄) ³⁻ antisymmetric stretching vibrations
		1076	77			1089	40	v ₃ (PO ₄) ³⁻ antisymmetric stretching vibrations
1057	86			1061	147			
		1041	5			1032	23	
		1031	7			1031	7	
1026	12	1021	10	1025	11	1021	11	
1019	14	1016	7	1016	16	1015	8	
999	19	998	8	998	14	998	9	
		983	7			983	8	
								v ₁ (PO ₄) ³⁻ symmetric stretching vibrations
974	15	976	7	975	15	976	8	
953 (?)	17			952 (?)	17			v ₃ (UO ₂) ²⁺ antisymmetric stretching vibrations
		913	13			912	26	
		875	7					
		853 (?)	16					
840	20			845	12			
		832	6			832	7	
827	12	829	11	828	12	828	14	v ₁ (UO ₂) ²⁺

								symmetric stretching vibrations
817	28	810	25	817	29	810	23	
		700	32			697	23	L H ₂ O vibration modes
						650	26	
612	36	615	20	614	76	615	15	
				611	24			ν_4 (PO ₄) ³⁻ bending vibrations
		565	6					
533	26	536	19	542	30			
		514	10			516	59	
		490	26					
451	18	449	17	455	15	448	16	
								ν_2 (PO ₄) ³⁻ bending vibrations
419	8	416	13	414	52	417	8	
398	13	399	7	399	9	399	7	
391	7							
329	28	331	21	327	24	331	15	
292	11	287	18	290	23	300	5	
						285	11	ν_2 (δ) (UO ₂) ²⁺ or ν (U-O _{ligand}) or δ (U-O _{ligand})
		252	7			270	4	
		237	6			251	10	
		214	4					
201	12	201	9	199	21	202	8	
188	16	189	9	184	10	197	16	
		177	8			178	6	
		167	9	164	30			
146	13	134	7	146	19	149	18	
		122	10					
114	15	110	11	112	14	111	12	

Table 1 Results of the Raman spectra at 298 and 77 K of threadgoldite mineral samples M22130 and M43442

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Figure 1 Raman spectra of threadgoldite at 298 and 77 K in the 750 to 1150 cm^{-1} region.

Figure 2 Raman spectra of threadgoldite at 298 and 77 K in the 100 to 750 cm^{-1} region.

Figure 3 Raman spectra of threadgoldite at 298 and 77 K in the 2600 to 3800 cm^{-1} region.

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Table 1 Results of the Raman spectra at 298 and 77 K of threadgoldite mineral samples M22130 and M43442

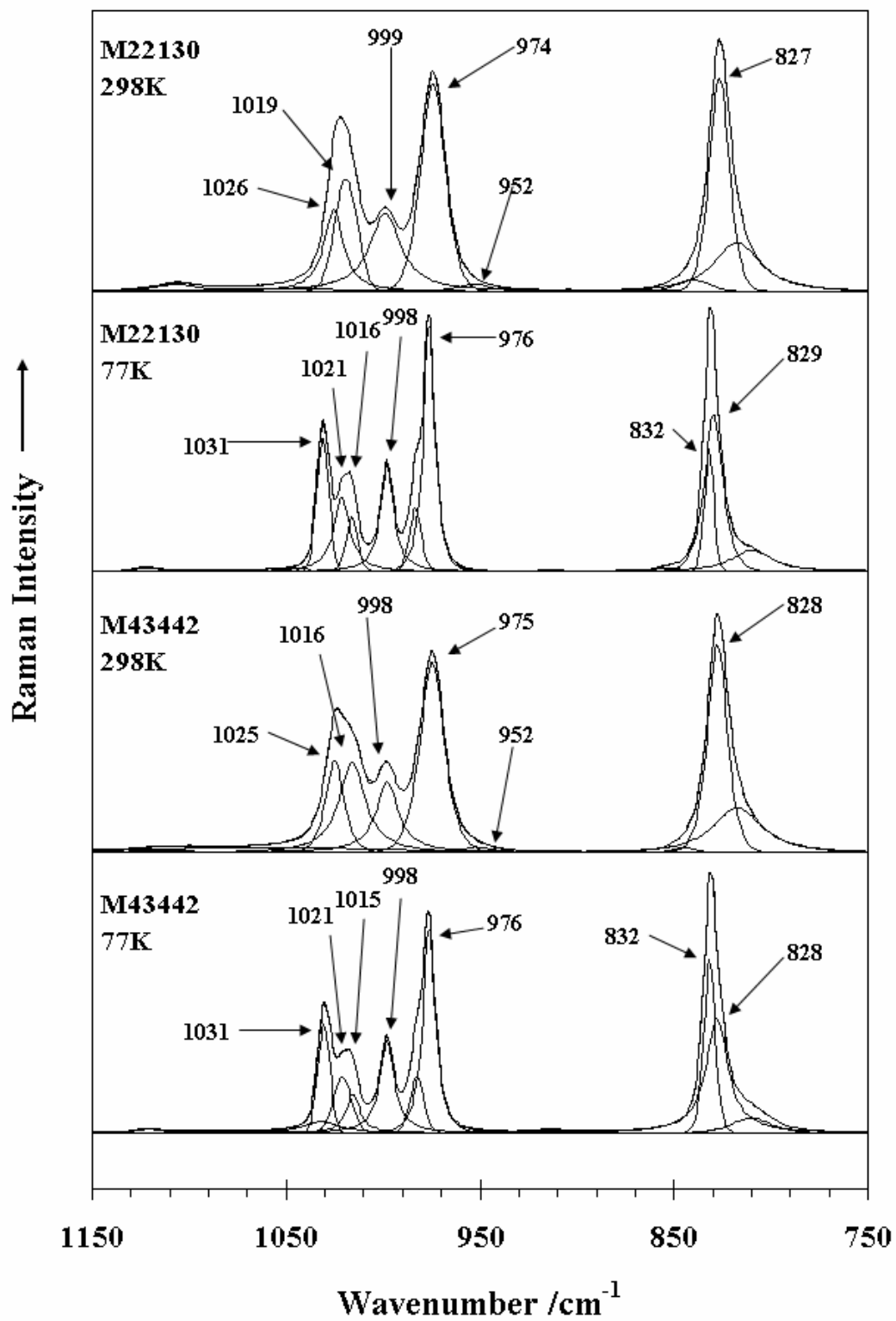


Figure 1

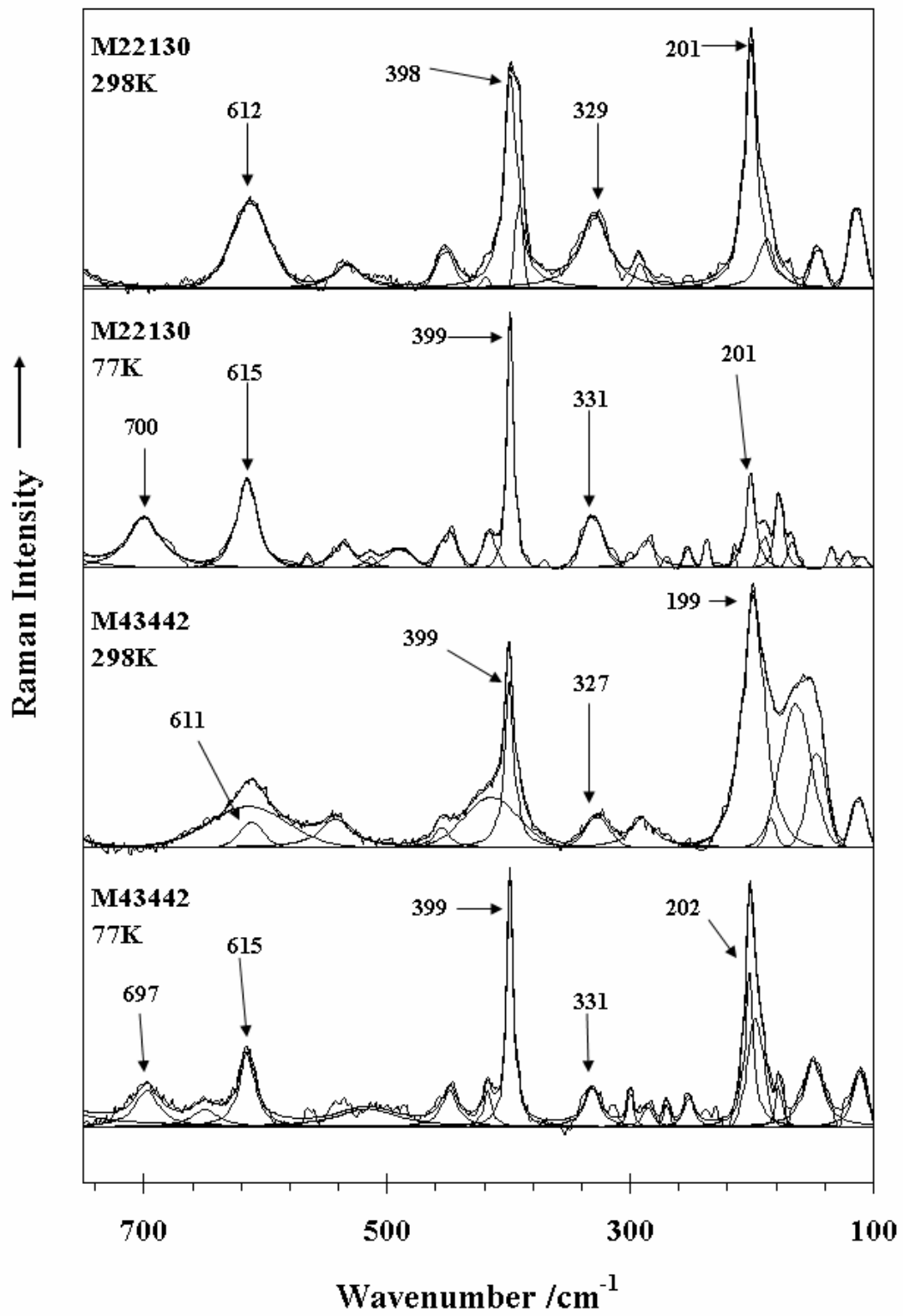


Figure 2

