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A Raman spectroscopic study of synthetic giniite

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Abstract

The mineral giniite has been synthesised and characterised by XRD, SEM and Raman and infrared spectroscopy. SEM images of the olive green giniite display a very unusual image of pseudo-spheres with roughened surfaces of around 1 to 10 microns in size. The face to face contact of the spheres suggests that the spheres are colloidal and carry a surface charge. Raman spectroscopy proves the $(\text{PO}_4)^{3-}$ units are reduced in symmetry and in all probability more than one type of phosphate unit is found in the structure. Raman bands at 77 K are observed at 3380 and 3186 cm^{-1} with an additional sharp band at 3100 cm^{-1} . The first two bands are assigned to water stretching vibrations and the latter to an OH stretching band. Intense Raman bands observed at 396, 346 and 234 cm^{-1} are attributed to the FeO stretching vibrations. The giniite phosphate units are characterised by two Raman bands at 1023 and 948 cm^{-1} assigned to symmetric stretching mode of the $(\text{PO}_4)^{3-}$ units. A complex band is observed at 460.5 cm^{-1} with additional components at 486.8 and 445.7 cm^{-1} attributed to the ν_2 bending modes suggesting a reduction of symmetry of the $(\text{PO}_4)^{3-}$ units.

Keywords: giniite, synthesis, phosphate, kintoreite, segnitite, scanning electron microscopy, Raman spectroscopy

Introduction

The mineral giniite was discovered in 1980 at the Sandamap pegmatite, west of Usakos, Namibia [1]. Giniite is the mineral of formula $\text{Fe}^{2+}(\text{Fe}^{3+})_4(\text{PO}_4)_4(\text{OH})_2 \cdot 2\text{H}_2\text{O}$ and is an olive-green to dark greenish black in appearance and is related to the minerals schoonerite $(\text{Fe}^{2+})_2\text{ZnMn}^{2+}(\text{Fe}^{3+})(\text{PO}_4)_3(\text{OH})_2 \cdot 9\text{H}_2\text{O}$, landsite $(\text{Mn}^{2+}, \text{Mg})_9(\text{Fe}^{3+})_3(\text{PO}_4)_8(\text{OH})_3 \cdot 9\text{H}_2\text{O}$ and kalunginite $(\text{Mn}^{2+}, \text{Ca}, \text{Mg})(\text{Fe}^{3+})_3(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$. The mineral is monoclinic and of point group $2/m$.

The amount of published data on the Raman spectra of mineral phosphates is limited [2-6]. The Raman spectra of the hydrated hydroxy phosphate minerals have not been reported. Giniite and related minerals form part of this group. 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} [4, 5, 7]. S.D. Ross in Farmer (1974) (page 404) listed some well-known minerals containing phosphate which were either hydrated or hydroxylated or both [8]. The value for the ν_1

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symmetric stretching vibration of PO₄ units as determined by infrared spectroscopy was given as 930 cm⁻¹ (augelite), 940 cm⁻¹ (wavellite), 970 cm⁻¹ (rockbridgeite), 995 cm⁻¹ (dufrenite) 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 PO₄ units. Some studies have been undertaken on MgHPO₄·3H₂O [9, 10]. It is not known whether a mineral was studied or whether a synthetic chemical was used. Infrared bands were found at 1162, 1057 and 1017 cm⁻¹ and were assigned to the ν₃ antisymmetric stretching modes.

The value for the ν₂ symmetric bending vibration of PO₄ 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 PO₄ units. This symmetry reduction is also observed through the ν₃ antisymmetric stretching vibrations. Augelite shows infrared bands at 1205, 1155, 1079 and 1015 cm⁻¹; wavellite at 1145, 1102, 1062 and 1025 cm⁻¹; rockbridgeite at 1145, 1060 and 1030 cm⁻¹; dufrenite at 1135, 1070 and 1032 cm⁻¹; beraunite at 1150, 1100, 1076 and 1035 cm⁻¹. Some Raman spectra have been published [11, 12]. The studies of the synthetic newberyite showed bands at 398 cm⁻¹ assigned to the ν₂ bending mode and at 554 and 509 cm⁻¹ corresponding to the ν₄ bending modes [10, 13].

In this work we report the synthesis and characterisation of the compound equivalent to giniite including SEM images of a synthetic giniite and the spectroscopy of the compound.

Experimental

Mineral Synthesis of Giniite

The methodology used in the preparation of giniite was originally intended for the synthesis of kintoreite. However giniite was synthesised instead. 1g PbCl₂ and 1.85g FePO₄ were combined in 15mL water. 5mL of 1.23M FeCl₃ and 12mL of 9.83M LiCl were added to this solution. The solution was then placed in a 100mL autoclave and water added until the autoclave was ³/₄ full. The autoclave was heated at 120°C for 2 days. The final product was collected and washed by vacuum filtration. It was dried in an oven at ~100°C for ½ hr. The main product, (0.185g), was a olive-green powder containing brown and black flakes of material. A white powder was also collected from the filtrate. XRD analysis identified the main material as Fe-rich giniite and the filtrate product as PbCl₂. The synthesised mineral was olive green to greenish black in appearance.

X-ray diffraction

X-Ray diffraction patterns were collected using a Philips X'pert wide angle X-Ray diffractometer, operating in step scan mode, with Cu K_α radiation (1.54052 Å). Patterns were collected in the range 3 to 90° 2θ with a step size of 0.02° and a rate of

30s per step. Samples were prepared as a finely pressed powder into aluminium sample holders.

SEM

Giniite sample was coated with a thin layer of evaporated carbon and secondary electron images were obtained using an FEI Quanta 200 scanning electron microscope (SEM). For X-ray microanalysis (EDX), three samples were embedded in Araldite resin and polished with diamond paste on Lamplan 450 polishing cloth using water as a lubricant. The samples were coated with a thin layer of evaporated carbon for conduction and examined in a JEOL 840A analytical SEM at 25kV accelerating voltage. Preliminary analyses of the giniite sample was carried out on the FEI Quanta SEM using an EDAX microanalyser, and microanalysis of the clusters of fine crystals was carried out using a full standards quantitative procedure on the JEOL 840 SEM using a Moran Scientific microanalysis system. The giniite was analysed from many spots on the mineral surface and an average value obtained.

Raman spectroscopy

The crystals of giniite were placed 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. 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 by the authors [14-17].

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 $4000\text{--}525\text{ cm}^{-1}$ 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 . Spectral manipulation such as baseline adjustment, smoothing and normalisation was performed using the GRAMS® software package (Galactic Industries Corporation, Salem, NH, USA).

Results and Discussion

X-ray diffraction

The X-ray diffraction pattern of synthetic giniite is shown in Figure 1.

SEM and EDX analysis

The EDAX analysis of the compound equivalent to giniite is shown in Figure 2. The analysis shows that only P, Fe with a trace of Al is present in the compound. The analysis shows that 49.5 % Fe and 40.0 % P is present in the mineral. It is considered that the impurity of Al originated as an impurity in the Fe starting compounds.

The SEM images of the giniite (Figures 3 a, b, c) show that the compound consists spherical crystals of around 10 microns in size. Whilst some variation in size is observed the spheres are surprisingly uniform in size. Close examination of the spheres shows that the surface is not smooth but has a rough undulating surface. The particles seem to agglomerate suggesting the surface is carrying a surface charge. Some holes in the spheres are observed (Figure 3 b and c).

Raman spectroscopy

The mineral giniite has several vibrational groups (a) the $(\text{PO}_4)^{3-}$ units (b) the OH units (c) water molecules and (d) FeO units. Each of these vibrating units will have a characteristic spectrum which may overlap with the spectrum of other units. The Raman spectrum at 298 and 77 K and the infrared spectrum at room temperature in the 750 to 1350 cm^{-1} , 100 to 700 cm^{-1} and 2500 to 3700 cm^{-1} are shown in Figures 4, 5 and 6 respectively. The results of the spectral analyses are reported in Table 1.

The Raman spectrum of the giniite compound at 298 K gives an intense band at 1023 cm^{-1} which shifts to 1026.3 cm^{-1} at 77K. This band is assigned to the symmetric stretching mode of the $(\text{PO}_4)^{3-}$ units. The infrared band for the $(\text{PO}_4)^{3-}$ units should be inactive but because of symmetry reduction a band is observed at 984.7 cm^{-1} which is attributed to this vibration. A second Raman band is observed at 948 cm^{-1} in the 298 K spectrum and at 949 cm^{-1} in the 77 K spectrum. An intense band is observed in the infrared spectrum at 931 cm^{-1} . These bands may be ascribed to a second $(\text{PO}_4)^{3-}$ unit. This suggests that the phosphate units are not equivalent in the giniite structure. A number of bands are observed at 1183.6 , 1147.9 , 1127.7 cm^{-1} in the 298 K spectrum and at 1187.3 , 1150.6 , 1086.4 and 1065.4 cm^{-1} in the 77 K spectrum. These bands may be attributed to the antisymmetric stretching vibrations of the $(\text{PO}_4)^{3-}$ units. In the infrared spectrum strong bands are observed at 1155 and 1072 cm^{-1} which may be assigned to this vibration.

A complex band is observed at 460.5 cm^{-1} (298 K) and 464.7 cm^{-1} (77K) with additional components at 486.8 and 445.7 cm^{-1} (298 K). These bands are attributed to the ν_2 bending mode. Bands are not observed in our infrared spectrum as the position of the bands is below the detection limits of the ATR DRIFT technique. The observation of a complex Raman profile in this spectral region suggests that there is a reduction of symmetry of the $(\text{PO}_4)^{3-}$ units. In the Raman spectrum of augelite Raman bands at 298 K bands are observed at 467 , 439 , 419 and 407 cm^{-1} (298 K) and 465 , 442 , 426 and 403 cm^{-1} (77 K). These bands are attributed to the ν_2 bending modes of the PO_4 units.

A number of bands are observed in the $\sim 600\text{ cm}^{-1}$ region at 627.3 , 617.8 and 584.2 cm^{-1} (298 K) and 624.9 and 587.4 cm^{-1} (77 K). These bands may be assigned to the ν_2 bending vibration of $(\text{PO}_4)^{3-}$ units. In the infrared spectrum three bands are observed

at 598.4, 569.0 and 539.3 cm^{-1} . These bands are assigned to the ν_2 bending vibration of the $(\text{PO}_4)^{3-}$ units. For the Raman spectrum of kintoreite two bands are found at 573.2 and 550.9 cm^{-1} (298 K) and 583.7 and 558.1 cm^{-1} in the 77 K spectrum. These bands are assigned to the ν_4 $(\text{PO}_4)^{3-}$ bending modes. For the mineral augelite in the Raman spectrum at 298 K an intense band is observed at 635 cm^{-1} with component bands at 643 and 615 cm^{-1} . These bands are in similar positions to that of giniite. The observation of multiple ν_4 $(\text{PO}_4)^{3-}$ bands for giniite shows the symmetry lowering of the phosphate unit in line with the structure.

A number of intense bands are observed in the Raman spectrum at 396, 346 and 234 cm^{-1} . These bands may be ascribed to the FeO stretching vibrations. In the spectra of the low wavenumber region of the K and Na jarosites two bands are found at around 366 and 299 cm^{-1} . One probable assignment of the bands is to FeO stretching vibrations. An intense band is also found for jarosites at around 230 cm^{-1} . It is also attributed to FeO vibration. These bands for jarosite correspond quite closely to the bands for giniite

In the Raman spectrum at 298 K of the OH stretching region two bands are observed at 3387 and 3206 cm^{-1} with a low intensity band at 2918 cm^{-1} . these bands are very broad with band widths of 219, 364 and 124 cm^{-1} . In the 77 K spectrum a band is found at 3380 and 3186 cm^{-1} with an additional sharp band at 3100 cm^{-1} with a band width of 55.0 cm^{-1} . There is such a significant change in the spectrum, it is suggested that a change in the structure of the giniite occurs upon cooling to liquid nitrogen temperature. In the infrared spectrum three broad bands are found at 3349, 3182 and 2960 cm^{-1} .

Conclusions

The mineral giniite $\text{Fe}^{2+}(\text{Fe}^{3+})_4(\text{PO}_4)_4(\text{OH})_2 \cdot 2\text{H}_2\text{O}$ has been synthesised and characterised by XRD, SEM with EDAX and vibrational spectroscopic techniques. XRD confirms the compound synthesised is giniite. The SEM pictures of the giniite show a very unusual image of pseudo-spheres with roughened surfaces of around 10 microns in size. The face to face contact of the spheres suggests that the spheres carry a surface charge.

The vibrational spectroscopy of the giniite compound shows the $(\text{PO}_4)^{3-}$ units are reduced in symmetry and in all probability more than one type of phosphate unit is found in the structure. The observation of multiple bending modes confirms reduction in symmetry of the $(\text{PO}_4)^{3-}$ units.

Acknowledgements

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References

- [1]. P. Keller, Neues Jahrbuch fuer Mineralogie, Monatshefte (1980) 49.
- [2]. R. L. Frost, L. Duong and W. Martens, Neues Jahrb. Mineral., Monatsh. (2003) 223.
- [3]. R. L. Frost, W. Martens, P. A. Williams and J. T. Kloprogge, J. Raman Spectrosc. 34 (2003) 751.
- [4]. R. L. Frost, W. Martens, P. A. Williams and J. T. Kloprogge, Mineral. Mag. 66 (2002) 1063.
- [5]. R. L. Frost, P. A. Williams, W. Martens, J. T. Kloprogge and P. Leverett, J. Raman Spectrosc. 33 (2002) 260.
- [6]. R. L. Frost, P. A. Williams, W. Martens and J. T. Kloprogge, J. Raman Spectrosc. 33 (2002) 752.
- [7]. R. L. Frost, W. N. Martens, T. Kloprogge and P. A. Williams, Neues Jahrb. Mineral., Monatsh. (2002) 481.
- [8]. V. C. Farmer, *Mineralogical Society Monograph 4: The Infrared Spectra of Minerals*, 1974.
- [9]. F. A. Miller, G. L. Carlson, F. F. Bentley and W. H. Jones, Spectrochimica Acta 16 (1960) 135.
- [10]. F. A. Miller and C. H. Wilkins, Anal. Chem. 24 (1952) 1253.
- [11]. B. Soptrajanov, I. Kuzmanovski, V. Stefov and G. Jovanovski, Spectroscopy Letters 32 (1999) 703.
- [12]. B. Soptrajanov, G. Jovanovski, I. Kuzmanovski and V. Stefov, Spectroscopy Letters 31 (1998) 1191.
- [13]. J. R. Lehr, E. H. Brown, A. W. Frazier, J. P. Smith and R. D. Thrasher, Tennessee Valley Authority, Chemical Engineering Bulletin No. 6 (1967) 166 pp.
- [14]. R. L. Frost and M. L. Weier, Thermochem. Acta 406 (2003) 221.
- [15]. R. L. Frost, M. L. Weier and J. T. Kloprogge, J. Raman Spectrosc. 34 (2003) 760.
- [16]. R. L. Frost and M. L. Weier, J. Raman Spectrosc. 34 (2003) 776.
- [17]. R. L. Frost and M. L. Weier, Thermochem. Acta 409 (2004) 79.

Infrared			Raman at 298K			Raman at 77K		
Centre	FWHM	% Area	Centre	FWHM	% Area	Centre	FWHM	% Area
3349.4	193.4	9.1	3387.1	219.2	6.5	3380.2	205.4	6.7
3182.3	270.7	16.4	3206.0	346.4	5.6	3186.2	279.1	8.5
2960.4	258.1	9.2				3100.3	55.0	0.8
			2918.4	124.3	0.4	2942.4	160.5	0.7
2788.2	163.7	1.6						
1628.9	64.9	0.7						
1549.5	95.4	0.8						
1155.4	66.4	2.0	1183.6	40.8	1.2	1187.3	41.1	1.5
			1147.9	28.0	0.9	1150.6	40.7	3.9
			1127.7	110.7	9.5			
1071.7	111.9	21.2				1086.4	112.6	12.1
			1040.0	66.4	25.0	1065.4	33.9	1.3
			1022.5	30.5	3.4	1026.3	66.2	28.8
			999.3	38.9	6.6			
984.7	89.1	17.1	947.9	43.5	5.5	948.8	37.7	4.4
931.2	32.0	1.1						
910.9	62.5	6.5						
873.1	142.5	8.4						
758.6	80.9	2.2	766.1	51.6	0.2			
700.2	39.6	0.4						
622.4	22.0	0.5	627.3	28.6	1.2	624.9	29.9	1.6
			617.8	30.0	0.9			
598.4	38.1	1.1	584.2	84.7	6.7	587.4	87.6	6.7
569.0	23.3	0.6						
539.3	76.5	1.1						
			486.8	25.8	0.4	489.6	26.6	0.5
			460.5	77.2	6.4	464.7	65.6	5.3
			445.7	15.4	0.1	445.4	22.6	0.7
						419.2	29.4	0.7
			396.2	23.9	1.1	396.3	25.5	2.4
			346.0	42.0	1.2	347.2	87.3	5.7
			326.6	167.9	11.5			
						267.2	90.1	3.7
			233.7	81.0	5.0			
			201.8	49.7	0.8	218.3	82.0	4.0

Table 1 Results of the Raman and Infrared Spectroscopic analysis of giniite

List of Figures

Figure 1 EDX analysis of giniite

Figure 2 EDX analysis of giniite

Figure 3a,b,c SEM images of giniite

Figure 4 Raman at 298 and 77 K and infrared spectroscopy of giniite in the 750 to 1350 cm^{-1} region

Figure 5 Raman at 298 and 77 K and infrared spectroscopy of giniite in the 100 to 700 cm^{-1} region

Figure 6 Raman at 298 and 77 K and infrared spectroscopy of giniite in the 2500 to 3700 cm^{-1} region

List of Tables

Table 1 Results of the Raman and Infrared Spectroscopic analysis of giniite

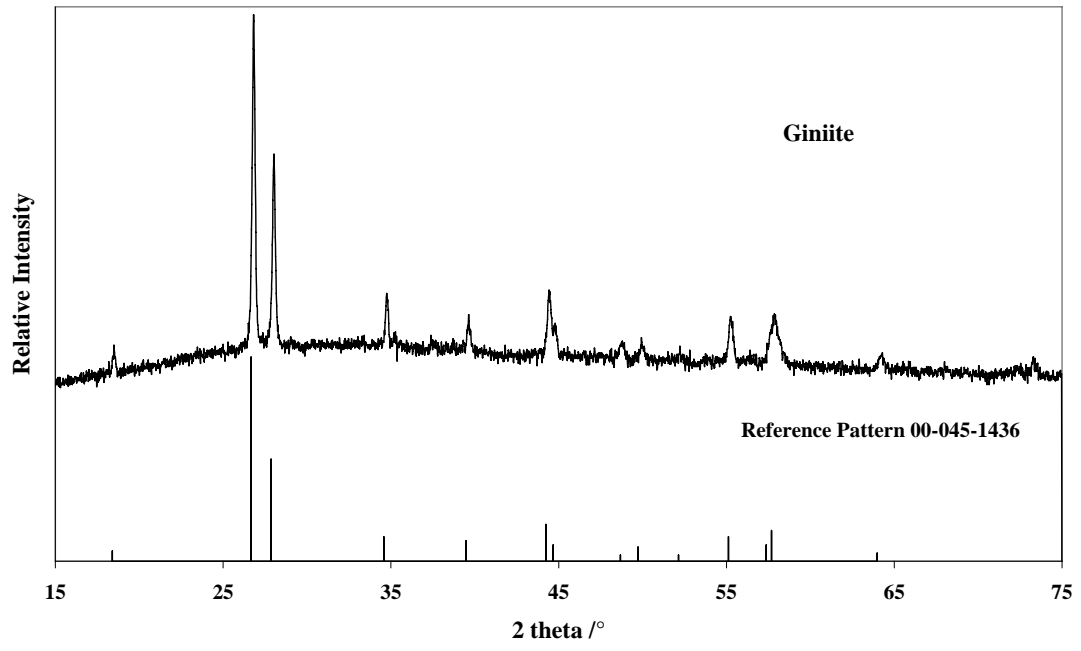


Figure 1

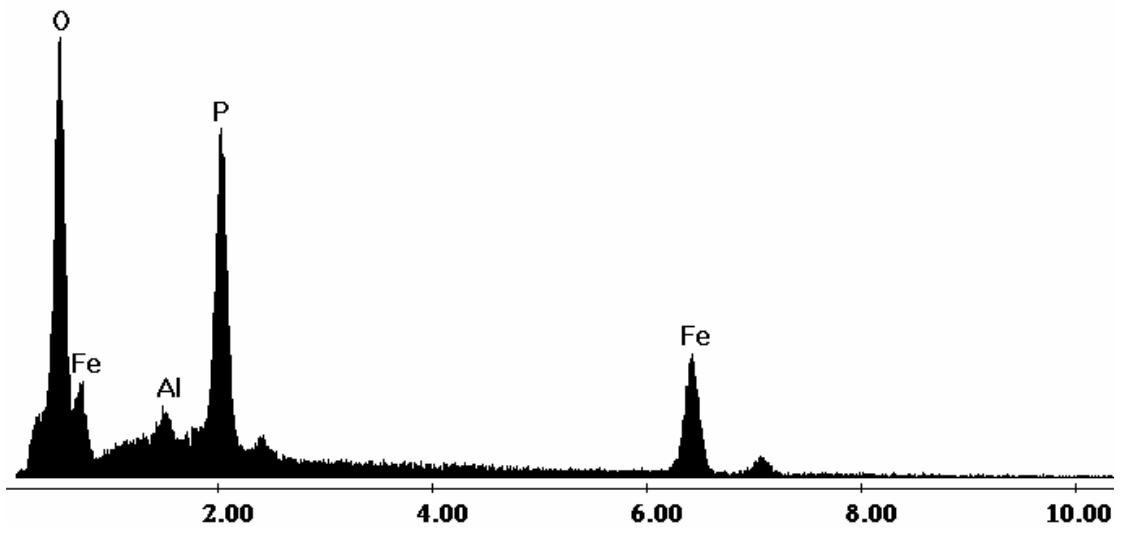


Figure 2

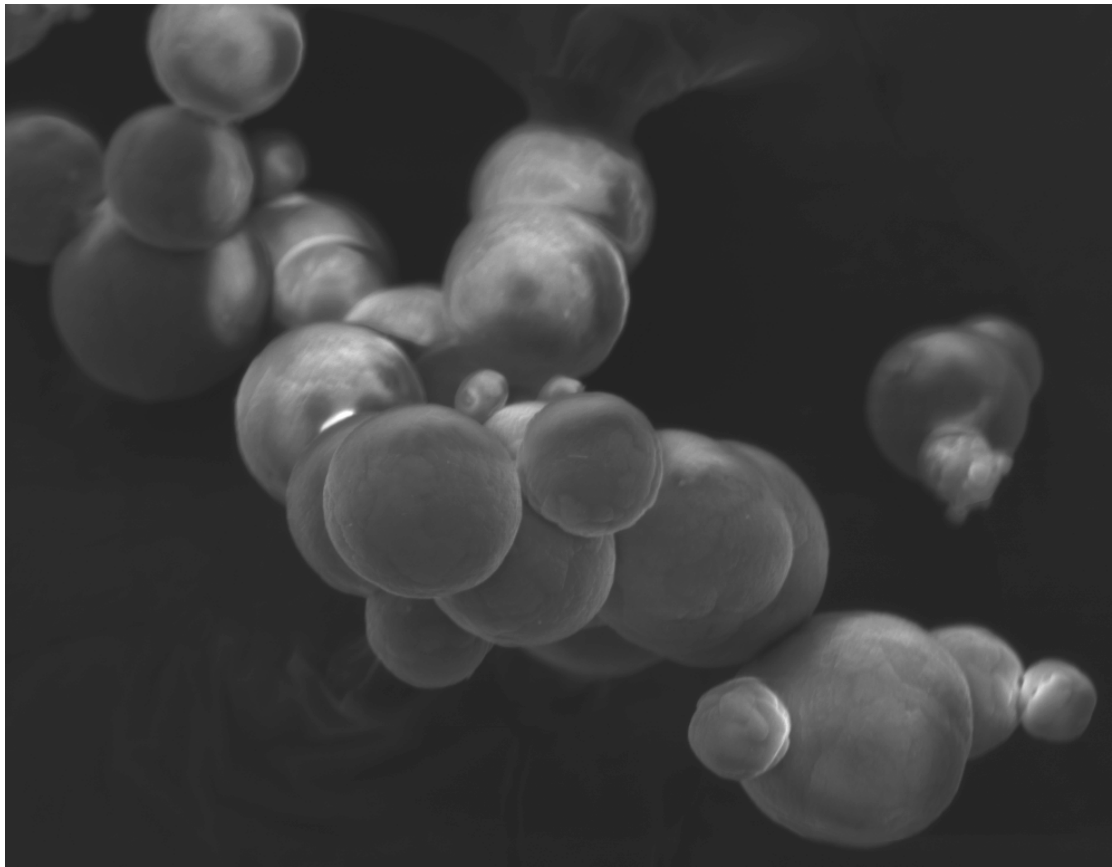


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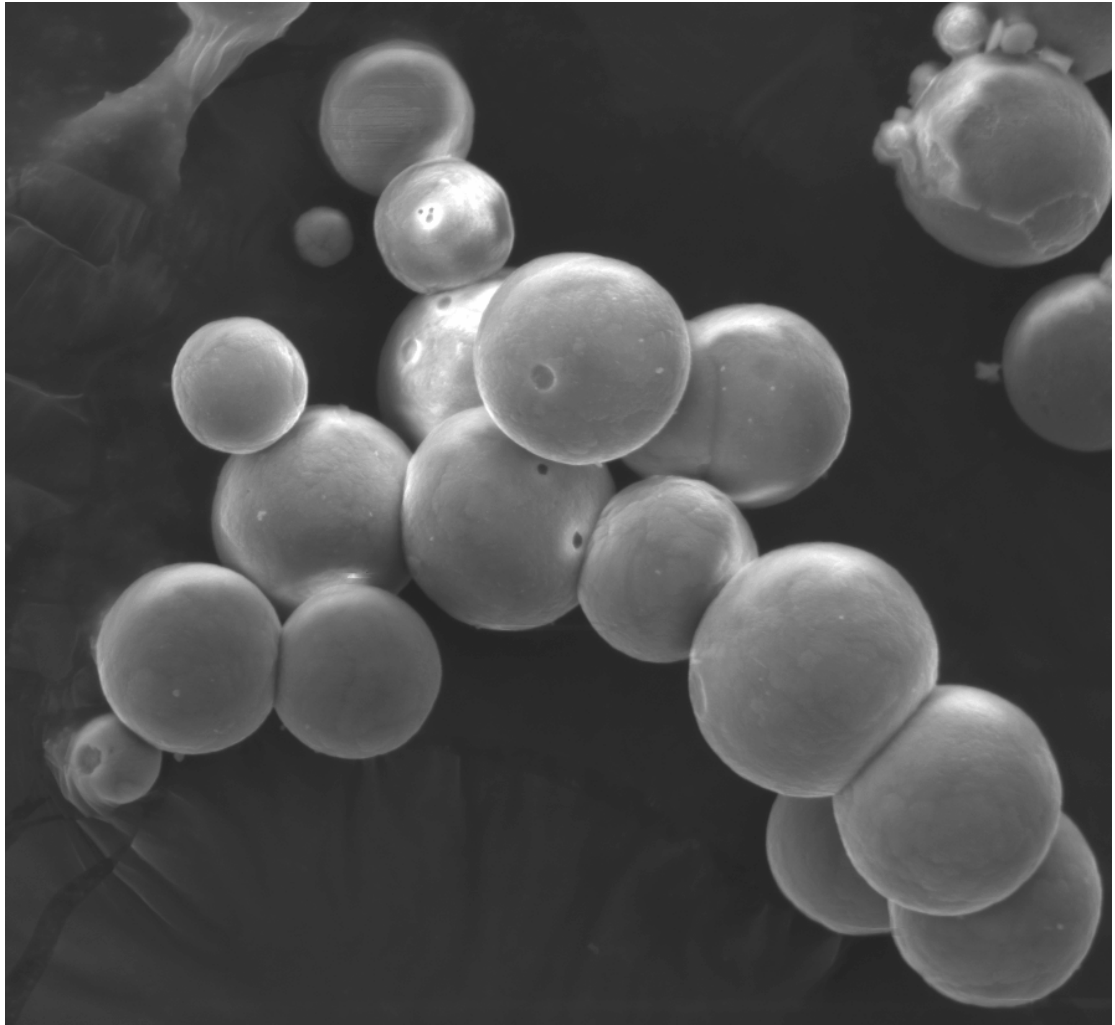


Figure 3b

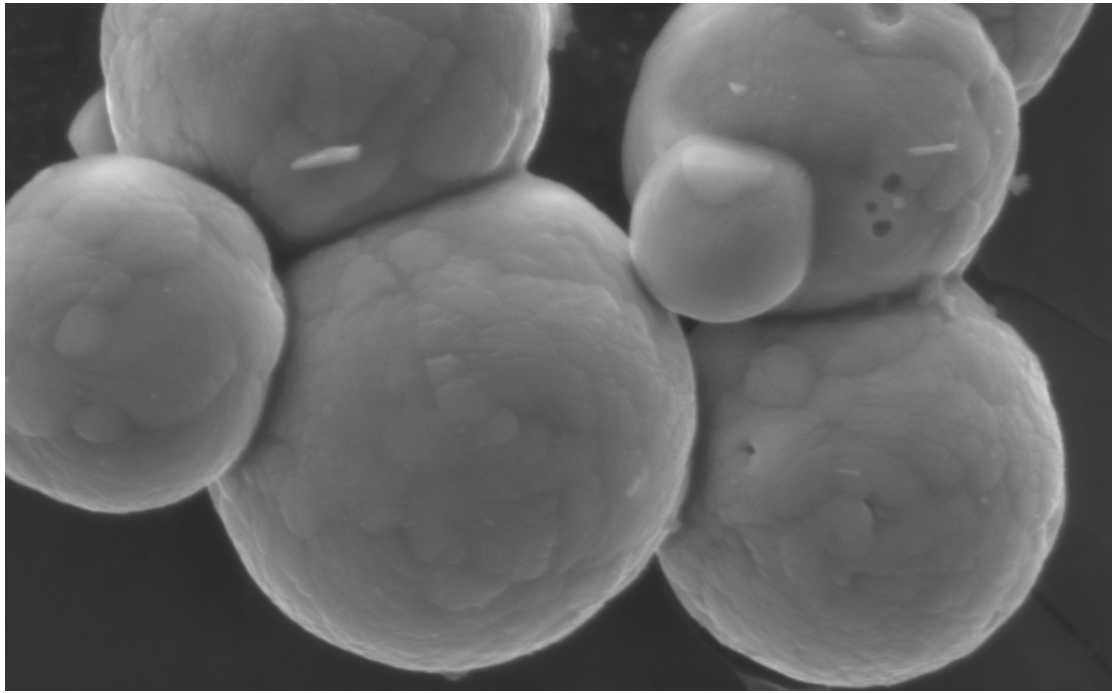


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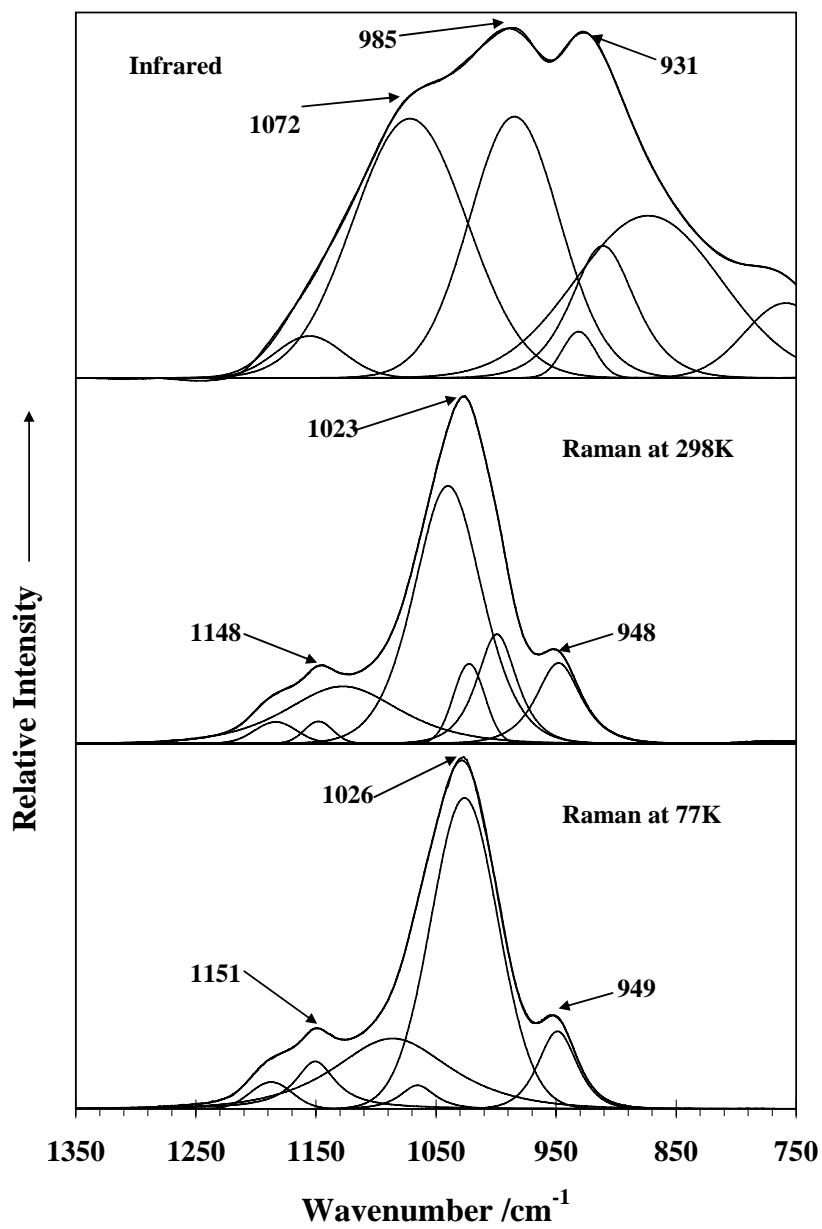


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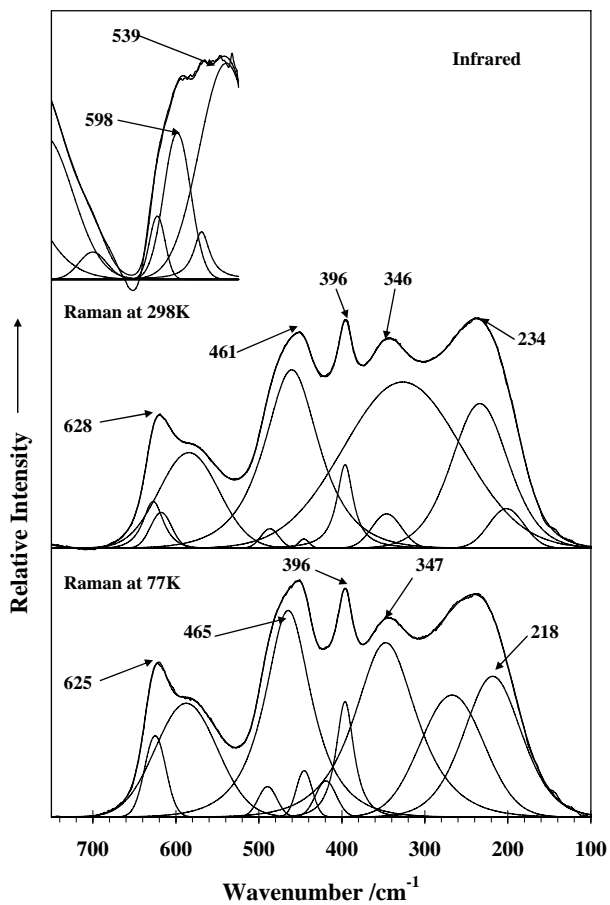


Figure 5

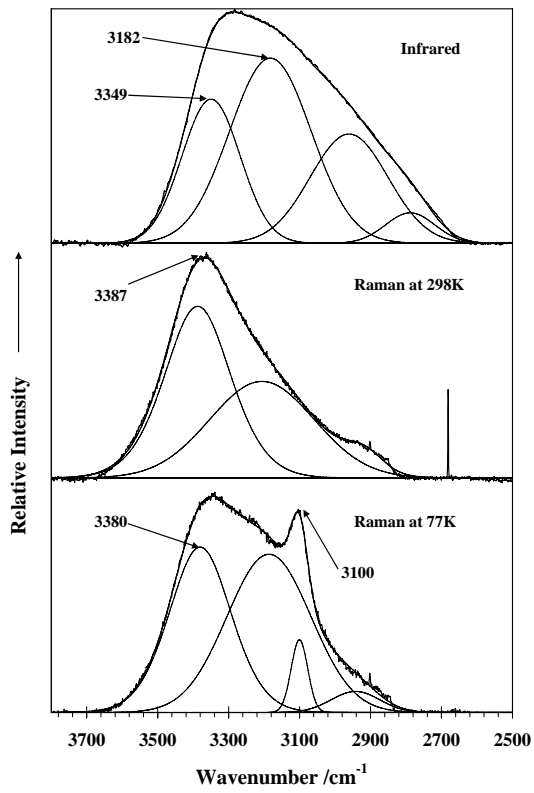


Figure 6