

# Thermal treatment of moolooite –a high resolution thermogravimetric and hot stage Raman spectroscopic study

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## Abstract

Evidence for the existence of primitive life forms such as lichens and fungi can be based upon the formation of oxalates. These oxalates form as a film like deposit on rocks and other host matrices. Moolooite as the natural copper (II) oxalate mineral is a classic example. High resolution thermogravimetry coupled to evolved gas mass spectrometry shows decomposition takes place at 260 °C. Evolved gas mass spectrometry shows the gas lost at this temperature is carbon dioxide. No water evolution was observed, thus indicating the moolooite is the anhydrous copper (II) oxalate as compared to the synthetic compound which is the dihydrate. The high resolution thermogravimetry was complimented with hot stage Raman spectroscopy. The temperature at which no intensity remains in the bands assigned to the oxalate vibrations is the upper limit of the stability of the moolooite.

*Keywords:* oxalate, moolooite, copper(II) oxalate, Raman spectroscopy, high resolution thermogravimetry, evolved gas mass spectrometry

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## Introduction

The presence of oxalates is widespread in nature. These minerals form as the result of expulsion of heavy metals from fungi, lichens and plants [1-3]. The production of simple organic acids such as oxalic and citric acids has profound implications for metal speciation in biogeochemical cycles [4]. The metal complexing properties of the acids are essential to the nutrition of fungi and lichens and affects the metal stability and mobility in the environment [4]. Lichens and fungi produce the oxalates of heavy metals as a mechanism for the removal of heavy metals from the plant [5]. Thermal analysis has been used for a long time for the analysis of oxalates [6-15]. Many of these analyses were undertaken many years ago [16-21]. The development of technology in thermal analysis has meant that high resolution studies with evolved gas mass spectrometry can now be undertaken to study both synthetic and natural oxalates. A mineral commonly found in the drier parts of Australia is the mineral moolooite which is the anhydrous copper(II) oxalate. The

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mineral has been formed through the expulsion of copper from primitive plant forms. These primitive plant forms have been found on host rocks which contain copper.

Raman spectroscopy however proved useful for the analysis of the calcium oxalate. The presence of these oxalate crystals appears to have an effect similar to that found in cacti [22]. Among the oxalates are the two calcium oxalates known as weddellite (the dihydrate) and whewellite (monohydrate). Ca-oxalate exists in two well-described modifications: as the more stable monoclinic monohydrate whewellite and the less stable tetragonal dihydrate weddellite. Weddellite serves for lichens as a water absorbing and accumulating substrate which transforms to whewellite when humidity drops. Such minerals are important in human physiology as the minerals are found in urinary tracts [23, 24]. Many other divalent oxalates exist in nature. The magnesium based oxalate is known as glushinskite [25, 26]. The copper oxalate is known as moolooite [2, 27] and the iron(II) oxalate as humboldtine [28, 29]. Whilst there have been several studies of synthetic metal oxalates [30-36], few studies of natural oxalates have been forthcoming and few spectroscopic studies of the copper(II) natural oxalate has been undertaken. The objective of this work is to undertake a comparative study of moolooite using a combination of high resolution thermogravimetry coupled to evolved gas mass spectrometry complimented with hot stage Raman spectroscopy [37-40].

## **Experimental**

### *Mineral:*

The moolooite was obtained from the Museum Victoria. The samples were phase analyzed using X-ray diffraction and the compositions checked using EDX measurements.

### *Thermal Analysis*

Thermal decomposition of the natural oxalate was carried out in a TA® Instruments incorporated high-resolution thermogravimetric analyzer (series Q500) in a flowing nitrogen atmosphere (80 cm<sup>3</sup>/min). Approximately 50mg of sample was heated in an open platinum crucible at a rate of 5.0 °C/min up to 500°C. With the quasi-isothermal, quasi-isobaric heating program of the instrument the furnace temperature was regulated precisely to provide a uniform rate of decomposition in the main decomposition stage. The TGA instrument was coupled to a Balzers (Pfeiffer) mass spectrometer for gas analysis. The gases water vapour, oxygen, carbon dioxide and carbon monoxide were measured by MS. Mass numbers 18, 17, 16, 32, 28 and 44 were measured.

### *Raman microprobe spectroscopy*

The crystals glushinskite 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<sup>-1</sup> in the range between 100 and 4000

cm<sup>-1</sup>. Repeated acquisition using the highest magnification was accumulated to improve the signal to noise ratio. Spectra were calibrated using the 520.5 cm<sup>-1</sup> 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 elevated temperatures were obtained using a Linkam thermal stage (Scientific Instruments Ltd, Waterfield, Surrey, England).

### *Infrared emission spectroscopy*

Details of infrared emission spectroscopy has been previously published [41-43]. Spectroscopic 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 Gauss-Lorentz cross-product function with the minimum number of component bands used for the fitting process. The Gauss-Lorentz ratio was maintained at values greater than 0.7 and fitting was undertaken until reproducible results were obtained with squared correlations of R<sup>2</sup> greater than 0.995.

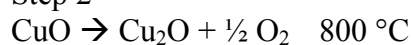
## **Results and discussion**

The high resolution thermogravimetric analysis of moolooite is shown in Figure 1. Clearly only one weight loss step is involved at 240 °C. A higher temperature weight loss (not shown) is observed at around 800 °C. The theoretical mass loss for the reaction shown in step 1 is 29.04 %. The experimental mass loss was determined as 45.0 %. This value is much closer to the value of the loss of water and carbon dioxide from the copper oxalate dihydrate where a theoretical % mass loss of 42.6 % is observed. No water vapour was gained in the evolved gas mass spectrum. It is unrealistic to compare the results of a natural copper oxalate mineral with a pur synthesised sample as the natural sample will contain impurities. The theoretical mass for step 2 is 10.56 % and may be compared with an experimental result of 8.7 %. The evolved gas mass spectra for selected gases are shown together with the DTG curve in Figure 2. The mass gain is in terms of mass 44 attributed to carbon dioxide evolution. No intensity in the water vapour mass spectrum was observed. This proves that the naturally occurring copper(II) oxalate moolooite is the anhydrous copper oxalate. This may be contrasted to the synthetic copper (II) oxalate which occurs as the dihydrate. The following mechanism is proposed for the thermal decomposition of moolooite.

Step 1



Step 2



### *Hot stage Raman spectroscopy*

Phases changes associated with the thermal treatment of moolooite can be followed by the use of a Raman microscope in combination with a thermal stage. Such a suite of spectra are shown in Figure 3. The spectra clearly show changes in the Raman spectrum between 50 and 100 °C. The greatest change in intensity occurs over this temperature range. Further decreases are observed up to 250 °C. The CO symmetric stretching vibration is observed for oxalate in aqueous solution at 1496  $\text{cm}^{-1}$  and for solid potassium oxalate at 1449  $\text{cm}^{-1}$ . The band position is cation dependent. A single band is observed at 1475  $\text{cm}^{-1}$  for weddellite, showing that the two CO bonds are equivalent. Two Raman bands are observed for moolooite at 1514 and 1486  $\text{cm}^{-1}$  in the 25 °C spectrum. The observation of two bands in the 25 °C Raman spectrum suggests the non-equivalence of the CO stretching vibrations. Thus at 25 °C, the structure is not centrosymmetric. The bands are observed at 1513 and 1482  $\text{cm}^{-1}$  at 100 °C. No intensity remains in the spectra above 250 °C; thus showing that the results of the hot stage Raman spectroscopy agrees with the results of the HRTG and MS results. For the copper (II) dihydrate two Raman bands are observed at 1495 and 1526  $\text{cm}^{-1}$  [44]. These bands are in reasonable agreement with the data for the hot stage Raman spectra. It would be expected that there would be a shift in the position of the bands in the spectra of the synthetic copper (II) oxalate dihydrate and the natural mineral, the anhydrous copper (II) oxalate.

The Raman data obtained by using a thermal stage is complimented by the infrared emission spectroscopy. Here in situ infrared spectra are obtained by using the hot moolooite as the emission source. The infrared emission spectra of moolooite are shown in Figure 4. A broad band centred upon 1685  $\text{cm}^{-1}$  is observed in the IE spectrum of moolooite at 200 °C. The intensity of this band decreases significantly with temperature increase; such that after 300 °C, almost no intensity remains. Edwards et al. noted that the band at around 1670  $\text{cm}^{-1}$  assigned to the CO antisymmetric stretching vibration was the only band coincident between potassium oxalate, copper(II) oxalate dihydrate and dipotassium bis-oxalato copper (II) tetrahydrate. It is probable that this coincidence may be attributed to the width of the bands. There are two possibilities for the structure of moolooite; namely a square planar centrosymmetric structure in which case there would be a non-coincidence of the Raman and infrared spectra or alternatively a staggered see-saw  $\text{CuO}_4$  system. The non-coincidence of the Raman and infrared spectra confirm the square planar arrangement for moolooite.

The 25 °C and 50 °C Raman spectra show a single low intensity band for moolooite at 1617  $\text{cm}^{-1}$ . This band is attributed to the antisymmetric stretching vibration which for a planar structure should not be observed in the Raman spectrum. However the structure is probably a distorted square antiprism brought about through the thermal treatment [45]. This distortion results in the observation of the forbidden Raman bands. For aqueous oxalate the antisymmetric stretching ( $B_{2u}$ ) mode is observed in the infrared spectrum at 1600  $\text{cm}^{-1}$ . This band is observed at 1617  $\text{cm}^{-1}$  in the 50 °C spectrum and at 1618  $\text{cm}^{-1}$  for the 150 °C spectrum. This band corresponds to the CO antisymmetric stretching mode of the copper (II) oxalate. This band was reported to be at 1632  $\text{cm}^{-1}$  which agrees well with the data reported in this work [46]. The observation of the antisymmetric stretching vibration suggests that the thermal treatment of the moolooite causes non-planarity in the structure.

Further evidence for significant changes in the structure of moolooite may be obtained by a study of the C-C stretching region. The hot stage Raman spectra of the 750 to 1250  $\text{cm}^{-1}$  region of moolooite is shown in Figure 5. Two bands are observed at 922 and 832  $\text{cm}^{-1}$ , the intensity of which decreases to zero by 200 °C. This suggests the oxalate is already decomposing by this temperature. It is noted that the position of the C-C stretching vibration is 902  $\text{cm}^{-1}$  for the free oxalate ion. Previous studies showed that the C-C stretching mode was observed at 896 and 904  $\text{cm}^{-1}$  for calcium oxalate monohydrate and anhydrous calcium oxalate respectively [32]. These bands are not observed in the infrared spectra.

The Raman spectra of the 500-700  $\text{cm}^{-1}$  region are shown in Figure 6. Three Raman bands are observed at 610, 585 and 558  $\text{cm}^{-1}$ . These bands are assigned to C-C-O and also the MO ring and MO stretching modes. The Raman spectrum of weddellite shows an intense band at 505  $\text{cm}^{-1}$  with a broad band at 596  $\text{cm}^{-1}$ . Previous studies have assigned the band at around 500  $\text{cm}^{-1}$  to the bending mode of C-C-O and the MO ring and MO stretching modes. [30, 44] The band at around 596  $\text{cm}^{-1}$  is also associated with MO stretching modes. [30, 44] Importantly two bands are observed at 523 and 505  $\text{cm}^{-1}$  with different intensities. The intensity of the band at 610  $\text{cm}^{-1}$  reaches zero at 100 °C. The band at 558  $\text{cm}^{-1}$  loses all intensity by 200 °C. The intensity of the 558  $\text{cm}^{-1}$  band is lost after 250 °C. This study suggested that the two bands at 610, 585 and 558  $\text{cm}^{-1}$  were due to Breit-Wigner coupling. This work shows there is an intensity relationship between these two bands which is temperature dependent. A number of intense bands are observed between 200 and 300  $\text{cm}^{-1}$  for the natural oxalate moolooite (Figure 7). Two intense bands are observed at 300 and 209  $\text{cm}^{-1}$ . These bands are attributed to CuO and OCuO bending modes. Raman spectroscopy does have the advantage that bands below 400  $\text{cm}^{-1}$  are readily obtained. This is important to the study of oxalates as the MO stretching and OMO ring bending modes may be determined. In comparison the Raman spectrum of weddellite, shows bands at 259 and 220  $\text{cm}^{-1}$  in the 25 °C spectrum. These bands are probably attributable to CaO ring stretching or bending modes. In some ways the behaviour of moolooite (the anhydrous copper (II) oxalate) resembles that of weddellite (the anhydrous calcium oxalate).

It should be noted that there are differences in the results as determined by TG-MS and hot stage Raman spectroscopy (HSRS). The TG experiment is a dynamic experiment with a constant heating rate. TG shows the oxalate decomposition is completed by 260 °C. HSRS seems to show that the oxalate is lost by 200 °C. The experiment here is not a dynamic experiment. The sample is heated to a selected temperature, with a time delay to establish an equilibrium then the Raman data is collected. This experiment is a step or batch process. Thus whilst a comparison can be made between the TG-DTG and the HSRS results, it must be understood that the two heating treatments of the moolooite sample are different.

## Conclusions

High resolution thermogravimetric analysis has been used to determine the upper stability limits of the mineral moolooite. A mass loss step of 260 °C was found. Evolved gas mass spectrometry shows that during the mass loss step no water was evolved, thus proving the moolooite is the anhydrous mineral. The results of the HRTG were complimented with those found using hot stage Raman spectroscopy.

The temperature at which no intensity remains in bands attributable to the oxalate is the upper limit of the stability of the moolooite. This temperature was determined to be 250 °C although the intensity of some of the bands decreases before this temperature.

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**Figure 4** Infrared emission spectra of moolooite at 200 to 375 °C at 25 °C intervals in the 650 to 1850  $\text{cm}^{-1}$  range.

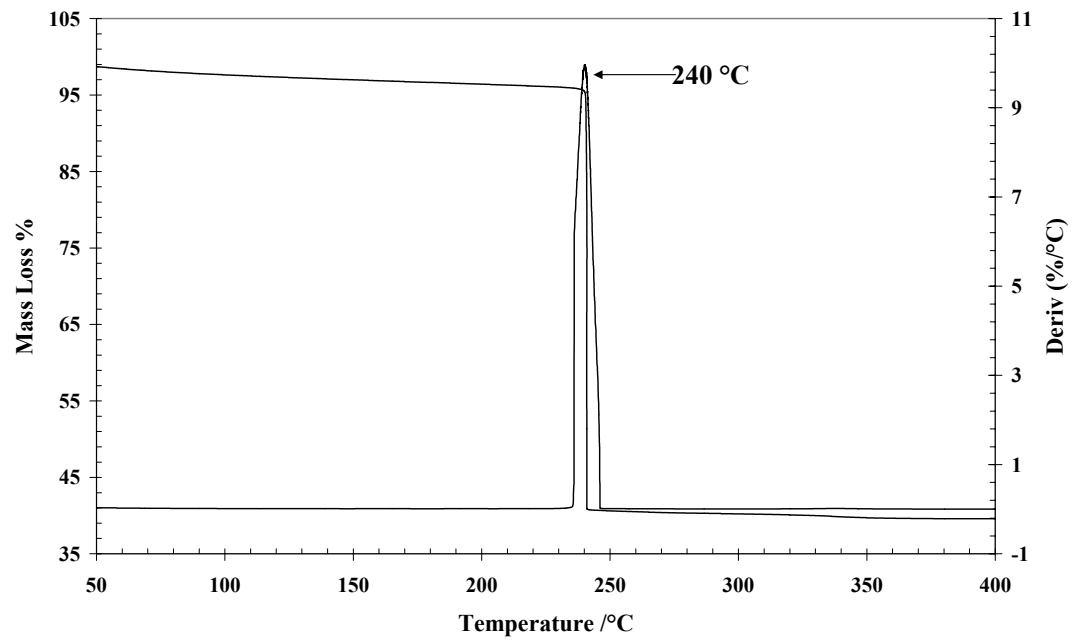
**Figure 5** Raman spectra of moolooite at 50, 100, 150, 200, 250 °C in the 750 to 1300  $\text{cm}^{-1}$  range.

**Figure 6** Raman spectra of moolooite at 50, 100, 150, 200, 250 °C in the 500 to 700  $\text{cm}^{-1}$  range.

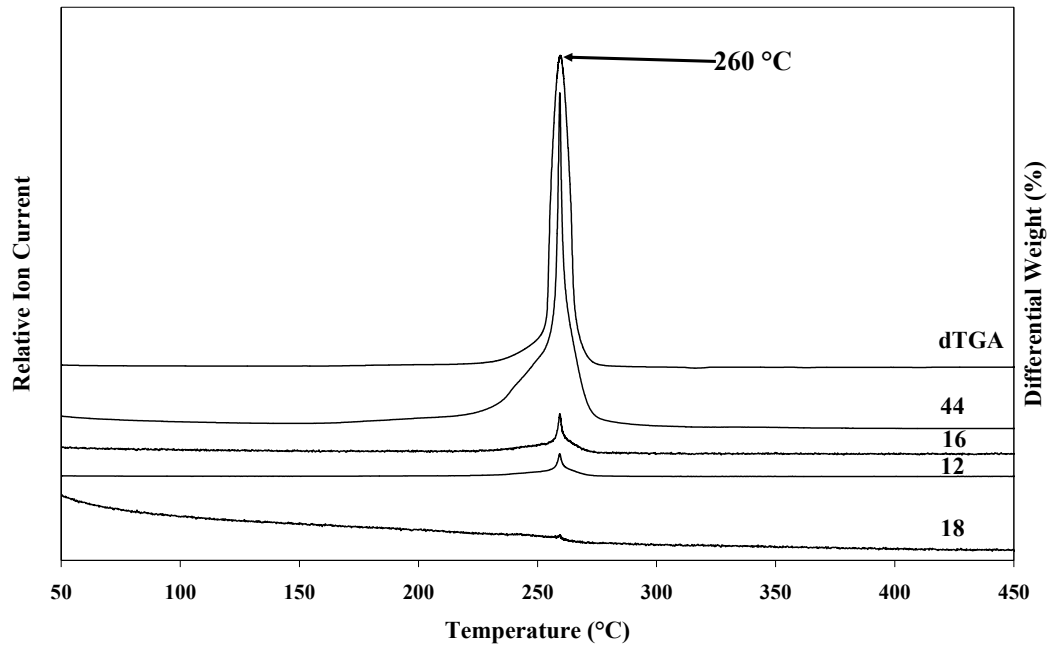
**Figure 7** Raman spectra of moolooite at 50, 100, 150, 200, 250 °C in the 100 to 450  $\text{cm}^{-1}$  range.

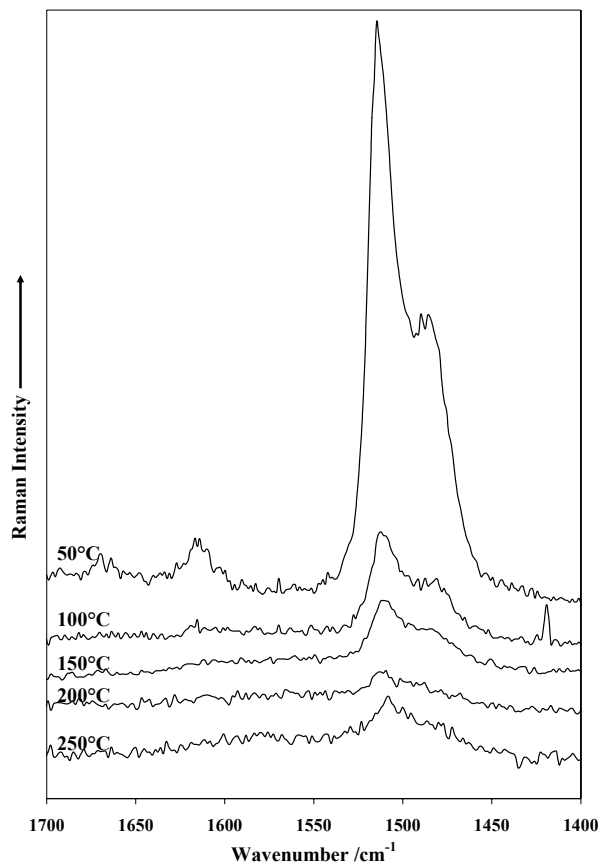


**Figure 1**      **Results of the high resolution thermal analysis of moolooite**

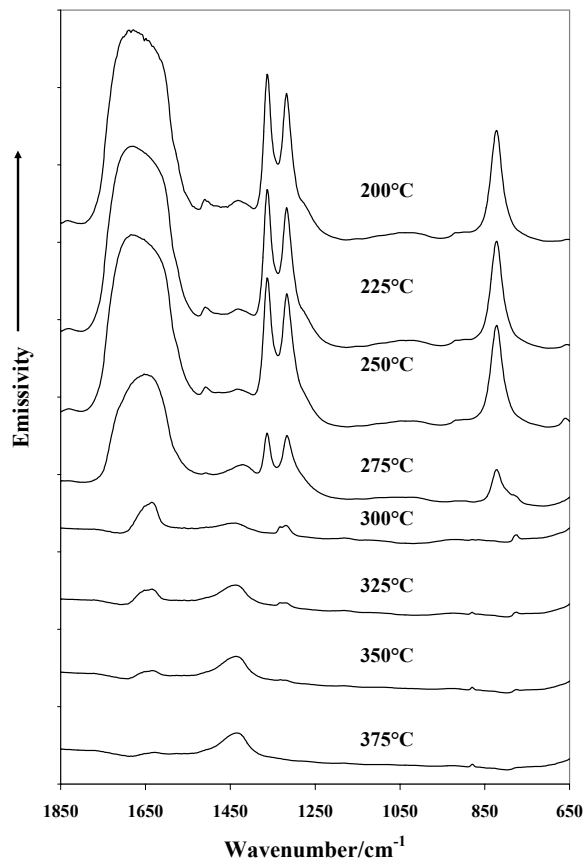


**Figure 2** Results of the Mass spectrometric analysis of moolooite

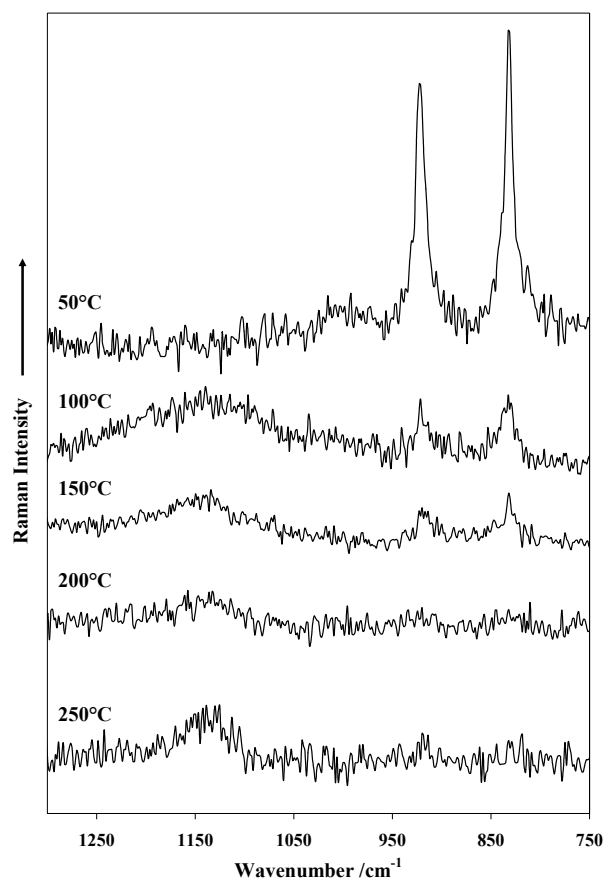




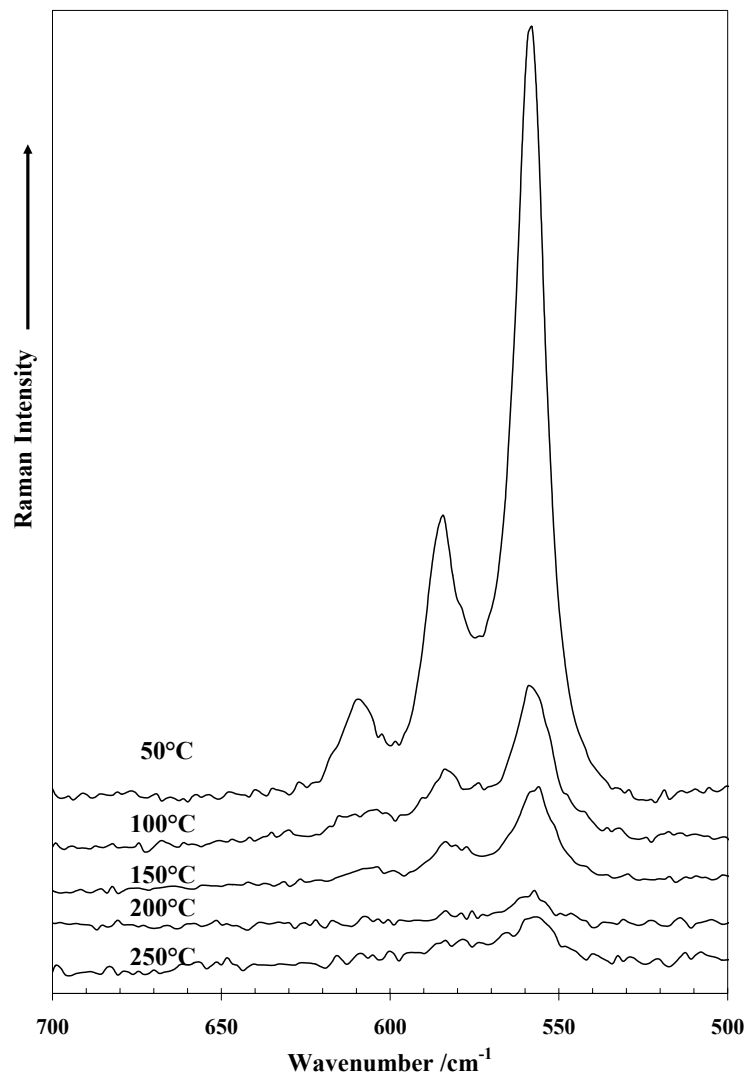
**Figure 3**



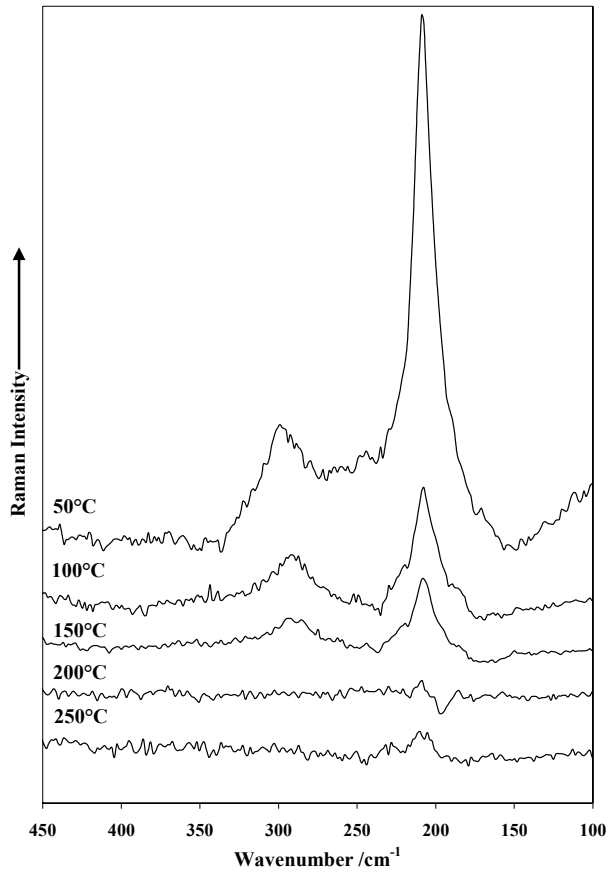
**Figure 4**



**Figure 5**



**Figure 6**



**Figure 7**