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Raman spectroscopy of the transition of α -gallium oxyhydroxide to β -gallium oxide nanorods

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Abstract

The thermo-Raman spectra of synthesised α -gallium oxyhydroxide nanorods proves the transition of α -gallium oxyhydroxide to β -gallium oxide nanorods occurs above 350 °C but below 400 °C. Scanning electron microscopy proves the morphology of the α -gallium oxyhydroxide nanorods is retained upon calcination to β -gallium oxide. X-ray diffraction shows that the nanorods are α -gallium oxyhydroxide converting upon calcination to β -gallium oxide.

Intense Raman bands are observed at 190, 262, 275, 430, 520, 605 and 695 cm^{-1} which undergo a red shift of $\sim 5 \text{ cm}^{-1}$ upon heating to 350°C. Upon thermal treatment above 350 °C the Raman spectrum shows a significantly different pattern. Raman bands are observed at 155, 212, 280, 430, 570 and 685 cm^{-1} . The thermoRaman spectra are in harmony with the TG and DTG patterns which show the reaction of α -gallium oxyhydroxide to β -gallium oxide occurs at 365 °C.

KEYWORDS: Gallium oxide, oxyhydroxide, nanorods, nanofibre, Raman spectroscopy

INTRODUCTION

A variety of gallium oxide phases (α , β , γ , δ and ϵ) can be obtained from gallium oxyhydroxides ($\text{GaO}(\text{OH})$) by a simple dehydration process at low temperatures. Gallium oxide (Ga_2O_3) displays polymorphism similar to that of Al_2O_3 . It has been demonstrated that gallium oxyhydroxide nanostructures undergo isomorphous transformation to nanocrystalline gallium oxide during thermal treatment¹⁻⁴. Limited research has been published on the synthesis of 1D $\text{GaO}(\text{OH})$ nanostructures through hydrothermal processes. Hamada *et al.*⁵ reported the formation of monodispersed $\text{GaO}(\text{OH})$ particles with diameter of $\sim 100 \text{ nm}$ at the presence of sulphate by hydrolysis at elevated temperatures. Avivi *et al.*⁶ prepared scroll-like cylindrical layered $\text{GaO}(\text{OH})$ crystals with small amounts of metallic Ga enclosed inside via a sonochemical reaction. Tas *et al.*¹ synthesized quadrilateral prisms and spindle-like $\text{GaO}(\text{OH})$ single crystals by forced hydrolysis of Ga^{3+} ions in pure water or in the presence of decomposing urea. Patra *et al.*⁷ fabricated submicrometer-sized $\text{GaO}(\text{OH})$ rods by refluxing an aqueous solution of $\text{Ga}(\text{NO}_3)_3$ and NH_4OH in a microwave oven. Ristić *et al.*⁸ studied application of sol-gel method in the synthesis of $\text{GaO}(\text{OH})$ by hydrolysis of gallium isopropoxide and GaCl_3 in the presence of tetramethylammonium hydroxide in aqueous solution. Zhang *et al.*² synthesized $\text{GaO}(\text{OH})$ nanorods through hydrothermal route in a mixture of

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diethyleneglycol (DEG) and water solutions from GaCl₃-H₂O-NaOH in the pH range of 6~8.

Liu *et al.*⁹ prepared GaO(OH) nanorods via a hydrothermal route using Ga₂O₃ and NaN₃ as precursors. Zhang *et al.*³ reported a green hydrothermal method at 200 °C for the synthesis of GaO(OH) nanorods using Ga₂O₃ and water as starting materials without the presence of surfactant. One method of studying GaO(OH) nanomaterials is by the application of Raman spectroscopy. Raman spectroscopy has proven very useful for the study of minerals¹⁰⁻¹⁹. Indeed Raman spectroscopy has proven most useful for the study of diagenetically related minerals as often occurs with oxyhydroxide and carbonate minerals²⁰⁻²³. Some previous studies have been undertaken by the authors using Raman spectroscopy to study complex secondary minerals formed by crystallisation from concentrated solutions. Very few spectroscopic studies of nanomaterials have been forthcoming.

No Raman studies of GaO(OH) are available. The aim of this paper is to present the Raman spectroscopic study of the transition of α -GaO(OH) to β -Ga₂O₃ nanorods and to relate the spectra to the structure and morphology of the synthesised nanorods.

EXPERIMENTAL

Synthesis of GaO(OH) materials

Analytical grade Ga(NO₃)₃, NaOH, HNO₃ were used as precursor to prepare the gallium hydrate precipitate. A total amount of 0.004 mol Ga(NO₃)₃ was dissolved in ultrapure water to form a solution (A) with a metal ion to H₂O molar ratio of 1:100, and heated to 80 °C. With stirring, into solution A was added dropwise a 1.5 M NaOH solution. 0.012 mol NaOH, which is three times of the amount of Ga(NO₃)₃, were used to form a precipitate. The mixture was then sealed and put in a shaking bath at a shaking rate of 100 rpm at 80 °C for 2 hours; the resulting precipitate was recovered by centrifugation and washed with pure water several times to remove sodium nitrate. the samples were then transferred to autoclave and hydrothermally treated at 100 °C for 2 days, followed by water wash for several times and dried in air at 80 °C.

Raman spectroscopy

The crystals of GaO(OH) 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 633 nm laser 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^{22,24,25}.

Spectra at elevated temperatures were obtained using a Linkam thermal stage (Scientific Instruments Ltd., Waterford Surrey, England). Spectra were taken from

50°C at 100°C intervals up to a temperature of 300°C in order replicate the acquisition of data in the TGA-MS plots. Intervals of 50°C were used where there was no evident change in mass or the mass derivative. Acquisition intervals of 25°C were resumed from 350-425°C in order to record changes in the spectra as the sample began to thermally decompose. Spectral Manipulation such as baseline adjustment, smoothing and normalisation was performed using GRAMS[®] software package (Galactic Industries Corporation Salem, NH, USA)

RESULTS AND DISCUSSION

X-ray diffraction

The X-ray diffraction of the synthesised α -GaO(OH) and thermally treated products (β -Ga₂O₃) together with the standard reference patterns are shown in Fig. 1S. It is clear that the material synthesised after ageing but before hydrothermal treatment and the sample after two days hydrothermal treatment at 100°C correspond precisely with the reference pattern 01-07102778 which is the patterns of α -GaO(OH). The calcined products of α -GaO(OH) is purely β -Ga₂O₃. No other materials are present. Thermal treatment of α -GaO(OH) results in the formation of β -Ga₂O₃.

Raman microscopy

The Raman spectra of GaO(OH) nanorods as a function of temperature are shown in Fig. 1. Intense Raman bands are observed at 190, 262, 275, 430, 520, 605 and 695 cm⁻¹. There is a slight red shift of these bands as a function of temperature. The bands are observed at 187, 252, 269, 425, 518, 600 and 692 cm⁻¹ at 350 °C. After 350 °C the Raman spectrum changes significantly and is the spectrum of Ga₂O₃. Raman spectroscopy has been used to study gallium oxide nanomaterials²⁶⁻²⁸ but not GaO(OH).

According to Rao *et al.*²⁹ Raman bands observed at 653 and 764 cm⁻¹ are attributable to the ν_1 symmetric stretching bands of GaO₄ units. In this work no bands were found in these positions. The band at 695 is assigned to the ν_1 symmetric stretching bands of GaO₄ units. The band at 605 cm⁻¹ is assigned to O-Ga-O bending modes of the GaO₄ units. According to Rao *et al.* there is a blue shift in the wavenumbers of β -Ga₂O₃ nano-materials upon formation of nanorods²⁹. The results of the Raman spectra of the GaO(OH) prepared with the PEO surfactant are almost identical in intensity and position of the nanowires prepared by Rao *et al.* The Raman spectra of the GaO(OH) synthesized using PEO surfactant as a directing agent is that for a nanofibre. The band observed at 430 cm⁻¹ is assigned to the symmetric stretching mode of GaO₆ octahedra. The two bands at 262 and 275 cm⁻¹ are attributed to OGaO bending modes of the GaO₆ octahedra.

After 350 °C the Raman spectrum shows a significantly different pattern. Raman bands are observed at 155, 212, 280, 430, 570 and 685 cm⁻¹. Gao *et al.* published Raman spectra for β -Ga₂O₃ nanorods²⁷. These workers found Raman bands at 160, 194, 332, 409, 641 and 742 cm⁻¹ for β -Ga₂O₃ nanorods. They also published Raman spectra for powdered β -Ga₂O₃. The results of both materials differ from the data in this paper. Gao *et al.* found significant differences in the Raman

spectra of the β -Ga₂O₃ nanorods and that of the powdered β -Ga₂O₃. Chun *et al.* showed that the Raman spectra of the β -Ga₂O₃ nanorods and the β -Ga₂O₃ powder were the same²⁶. Chun²⁶ reported Raman bands at 321, 348, 417, 475, 632, 656 and 767 cm⁻¹. Rao *et al.* also published data on the Raman spectra of β -Ga₂O₃²⁹. These workers published data on the Raman spectra of β -Ga₂O₃ nanowires. Raman bands for the β -Ga₂O₃ nanowires were observed at 180, 213, 225, 387, 428, 470, 600 and 697 cm⁻¹.

The Raman spectra in the 900 to 2300 cm⁻¹ region are shown in Fig. 2. Raman bands are observed at 1124, 1327, 1437 and a broad band at 1885 cm⁻¹. In the 300 °C spectrum no bands are observed but in the spectra at temperatures higher than 350 °C, a band at 1562 cm⁻¹ is observed. For the hydrothermally treated GaO(OH) without surfactant and for the GaO(OH) hydrothermally treated with CTAB surfactant the Raman spectra shows a number of broad overlapping bands. The Raman bands are better defined for the PEO hydrothermally treated GaO(OH). As before it is proposed that this is the Raman spectrum of GaO(OH) nanorods. Raman bands at ambient temperatures are observed at 1071, 1118, 1283, 1303, 1441 and 1459 cm⁻¹. The Raman bands at 1071 and 1118 cm⁻¹ are assigned to the GaO(OH) OH deformation modes. For the bulk GaO(OH) infrared bands are observed at 1245, 1380, 1501 and 1641 cm⁻¹. After hydrothermal treatment without surfactant, increased band separation is observed and the bands are observed at 1235, 1263, 1381, 1463 and 1644 cm⁻¹. For the GaO(OH) hydrothermally treated with PEO surfactant increased band separation is observed. Infrared bands are observed at 1242, 1284, 1349, 1374, 1454, 1465 and 1634 cm⁻¹.

The Raman spectra in the 2750 to 3250 cm⁻¹ are shown in Fig. 3. The spectra show low signal to noise. Raman bands are observed at 2853, 2892, 2926 and 2962 cm⁻¹. These bands are attributed to OH stretching vibrations of the GaO(OH). The bands are of low intensity and by 200 °C the intensity approaches zero. The spectra are complex with a number of overlapping bands which may be ascribed to OH stretching vibrations of GaO(OH). For the hydrothermally treated GaO(OH) in the presence of the surfactant CTAB two sharp infrared bands are observed at 2948 and 2916 cm⁻¹. These bands are attributed to the GaO(OH) symmetric stretching vibrations. Cornelis-benoit assigned two infrared bands at 2840 and 2915 cm⁻¹ to the ν_{OH} stretching vibration³⁰. These two bands are observed in the infrared spectra of the bulk GaO(OH) at 2792 and 2968 cm⁻¹; to the hydrothermally treated GaO(OH) at 2818 and 2918 cm⁻¹; for the GaO(OH) hydrothermally treated with PEO surfactant at 2855 and 2920 cm⁻¹. The infrared bands observed at higher wavenumbers are assigned to water OH stretching vibrations. For the bulk GaO(OH) infrared bands are observed at 3178, 3276 and 3400 cm⁻¹; for the hydrothermally treated GaO(OH) infrared bands are observed at 3222, 3404 and 3482 cm⁻¹; for the hydrothermally treated GaO(OH) hydrothermally treated with PEO surfactant bands are observed at 3107, 3249, 3400 and 3472 cm⁻¹; for the hydrothermally treated GaO(OH) with CTAB surfactant bands are observed at 3233, 3405, 3479 cm⁻¹. These bands are all attributed to water OH stretching vibrations. It is noted that in the work reported by Dupuis³¹ two bands were observed at 2920 and 3205 cm⁻¹ which were attributed to GaO(OH) stretching vibrations. However this does not appear to be correct. Dupuis assigned a very broad band at 3380 cm⁻¹ to the water stretching bands³¹.

Thermal analysis

The thermal analysis of GaO(OH) rods is shown in Fig. 2S. The mass loss occurs at 365 °C and is assigned to the dehydroxylation of GaO(OH). The temperature corresponds to the change in the thermo-Raman spectrum of GaO(OH) between 350 and 400 °C.

CONCLUSIONS

Thermo-Raman spectroscopy has been used to study the transition of micro-sized α -GaO(OH) to β -Ga₂O₃ rods. By using soft chemical techniques and low temperatures micro-sized GaO(OH) nanorods were synthesised. Large crystals were readily obtained. GaO(OH) rod-like micro-sized crystal \sim 2.5 μ m in length and 1.6 μ m in width were prepared at 100 °C without surfactant via hydrothermal route when the initial Ga to OH ratio was 1:3. The growth of GaO(OH) crystal mainly occurred during ageing and the growth rate dramatically decreased once the nanosized particle aggregate disappeared and the relatively large rod-like crystals were formed. β -Ga₂O₃ crystals were obtained through calcination and the rod-like morphology of the GaO(OH) was retained.

Raman spectroscopy of α -GaO(OH) enabled bands at 2853, 2892, 2926 and 2962 cm^{-1} are attributed to the α GaO(OH) symmetric stretching vibrations. No intensity was observed in these bands after 200°C. Raman bands at 950 and 1010 cm^{-1} are assigned to the hydroxyl deformation modes of α -GaO(OH). After 350 °C the Raman spectrum shows a significantly different pattern to that of α -GaO(OH). Raman bands are observed at 155, 212, 280, 430, 570 and 685 cm^{-1} . These bands are assigned to β -Ga₂O₃. Bands at 262, 275, 430, 520 cm^{-1} are assigned to vibrational modes involving Ga-OH units.

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Figure 2S Thermal analysis of GaO(OH)

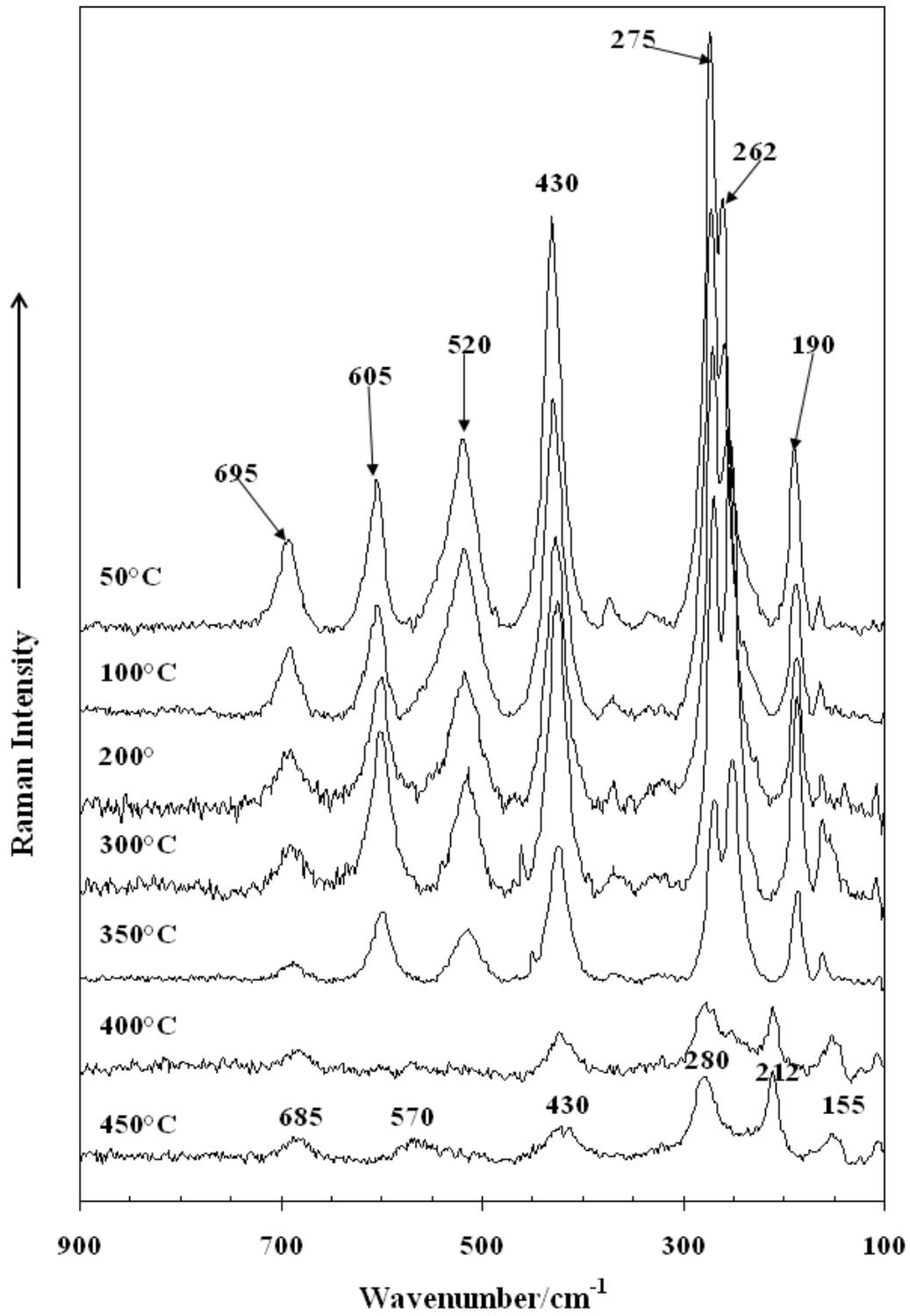


Figure 1

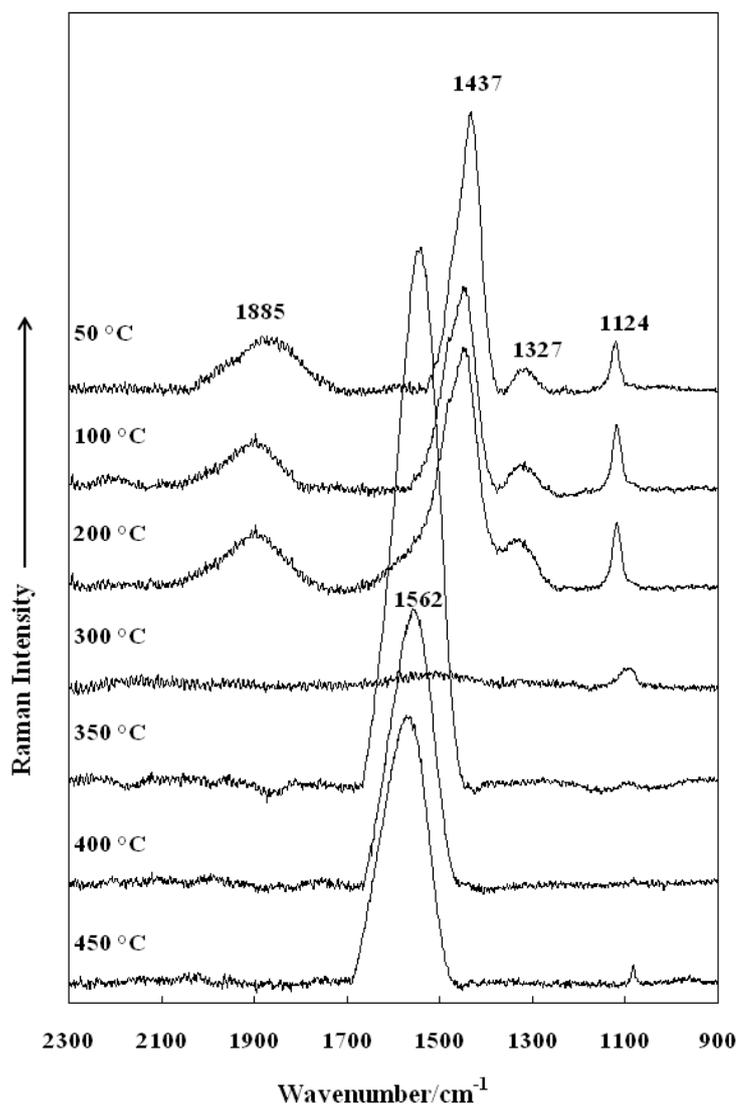


Figure 2

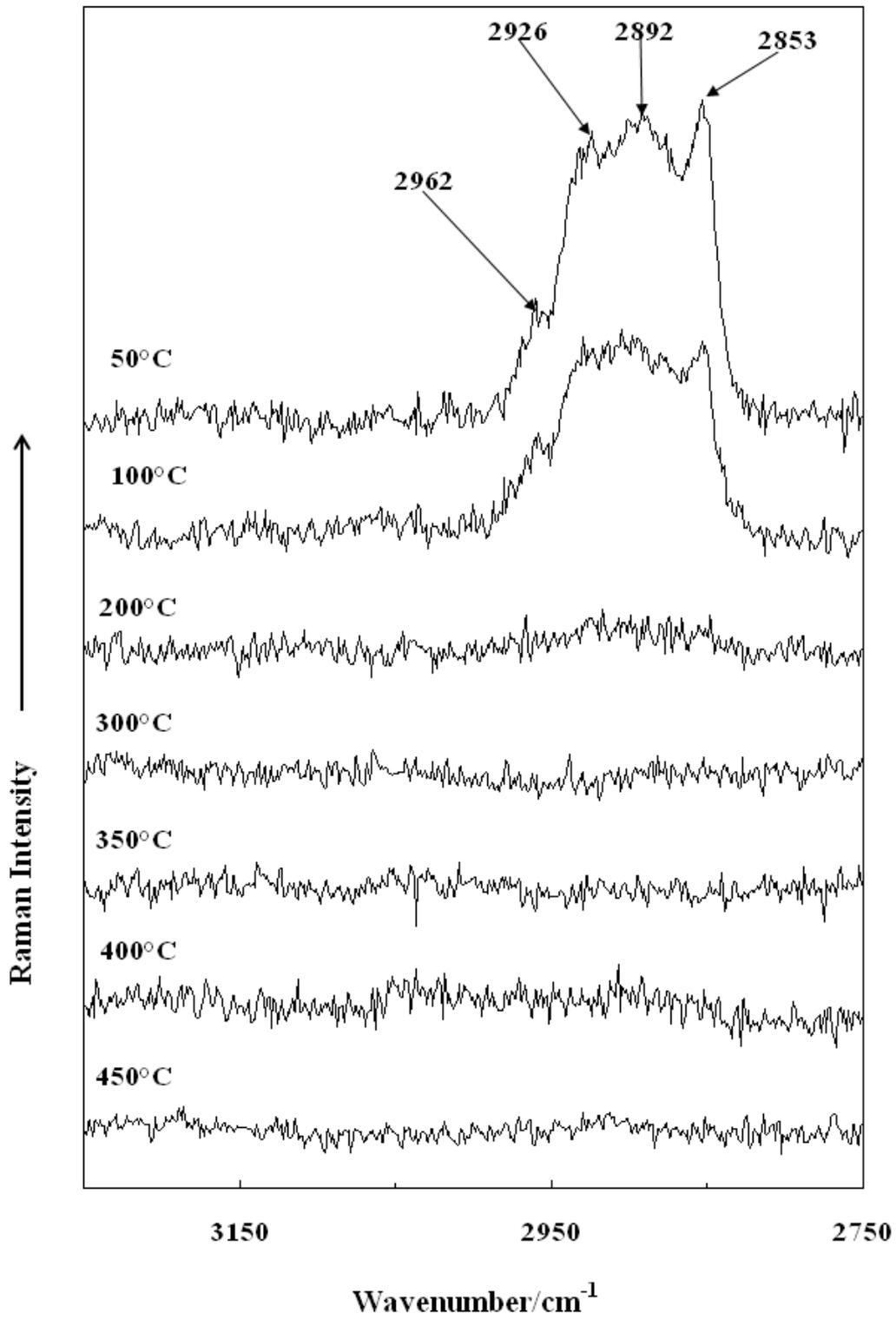


Figure 3