



Characterization of Magnetite and 2-line Ferrihydrite Using Laser Raman Spectroscopy

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Abstract

In this work, laser Raman Spectroscopy was used for the characterization of magnetite and 2-line ferrihydrite. These samples were irradiated using 5mW frequency doubled Nd-YAG laser with 532 nm at room temperature and their Raman spectra were recorded. The spectral database was used for the spectral analysis of the Raman shift of the two samples. The results obtained showed that different vibrations modes are appeared at (319 cm⁻¹, 543 cm⁻¹, 616 cm⁻¹ and 668 cm⁻¹) for magnetite while for 2-line ferrihydrite the vibrations are appeared at (707 cm⁻¹, 511 cm⁻¹ and 389 cm⁻¹). Other materials were appeared in the spectra of the two samples. A hematite band was recorded and this is because of ionization of magnetite and ferrihydrite. Thus Raman spectroscopy proved to be suitable method for the characterization of magnetite and 2-line ferrihydrite and could be used for characterization of other materials.

Keywords: Raman spectroscopy; Magnetite; 2-line ferrihydrite; characterization of iron compounds (;).

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1. Introduction

Raman spectroscopy is a spectroscopic method, which is complementary to IR spectroscopy. It is an analytical, nondestructive technique based on Raman effect and that provides information about the molecular structure of the investigated sample [1]. It relies on inelastic scattering, or Raman scattering of monochromatic light, usually from a laser in the visible, near infrared, or near ultraviolet range [2]. The Raman effect occurs when monochromatic light impinges upon a molecule and interacts with the bonds of this molecule. For the spontaneous Raman effect to take place, the molecule is excited by a photon from the ground state to a virtual energy state. The molecule can relax and return to the ground state by emission of a photon whose energy is the same as that of the exciting radiation resulting in elastic Rayleigh scattering. But a very small part (approximately 10^{-7} photons) of the scattered light can also have frequencies that are smaller than those of the elastically scattered part because a part of the energy of the incoming photons was employed to excite molecules to a higher vibrational state. As a result, the emitted photons will be shifted to lower energy, i.e., light with a lower frequency. This shift is designated the Stokes shift and it is a fingerprint of the molecules. The difference in energy between the original state and the final state corresponds to a vibrational mode far from the excitation wavelength. If the process starts from a vibrational excited state ($v = 1$) and relaxes to the ground state ($v = 0$), then the emitted photons will be shifted to higher frequency which is designated the Anti-Stokes shift. Compared with the Stokes-shifted light, the Anti-Stokes shifted radiation has a lower intensity because of the small population of the vibrational excited state compared to that of the ground state of the molecule at room temperatures. [3]. Raman Spectroscopy has different distinguished applications like characterization of different materials based on their Raman shift.

This work aimed to use laser Raman Spectroscopy for the characterization of magnetite and 2-line ferrihydrite.

2. Materials and Methods

Two samples of magnetite, and 2-Line Ferrihydrite were investigated in this work by laser Raman spectrometer in the range from (400 cm^{-1} to 4500 cm^{-1}).

2.1 Equipments

Figure (1) shows a diagram of the laser Raman microscope spectrometer model Burker sentra which was used in this work. Burker sentra microscope senterra is a high performance Raman microscope spectrometer designed for demanding analytical applications and research applications. The light source in this spectrometer is Nd-YA laser with wavelength of 532 and output power of 5mW. Raman spectra of these samples were recorded (the intensity of the scattered light as a function of Raman shift). The Raman shift, in

wavenumber, and the change in intensities in of the scattered light were compared with data in the references and previous studies .

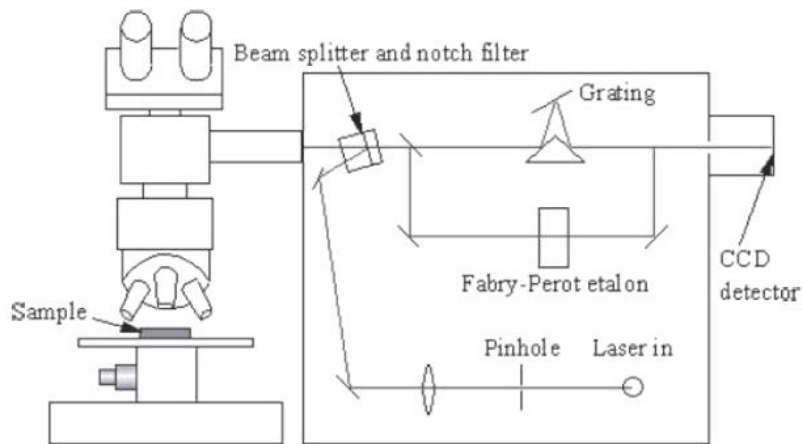


Figure 1: schematic diagram of Burker sentra laser Raman microscope spectrometer.

2.2 Samples preparation

Samples from magnetite and 2line Ferrihydrite were investigated here. These samples were prepared as follows:

2.2.1 Magnetite (Fe_3O_4)

One molar of 1ml Ferric nitrate ($Fe(NO_3)_3 \cdot 9H_2O$) was dissolved in 10 ml of distilled water to form a transparent yellow solution. Next, three different mineralizing agents were added into the ferric solution ; First was 5 ml of 10.67 molar KOH aqueous solution added drop wisely into the ferric solution . Second was 1 ml of ethylenediamine (EDA). The EDA was added gradually into the ferric solution. Third was a combination of KOH and EDA. The 5 ml of KOH solution at molar 10.67 was added first, followed by 1 ml of EDA. After adding these mineralizing agents, a brown $Fe(OH)_3$ suspension was obtained. Then, these solutions were all stirred for 30 min before transferring the mixture into a Teflon-lined stainless steel autoclave of 40 ml capacity and followed by heat treatments at 200°C for 9 h. After that, the autoclave was cooled down to room temperature in air. The precipitates were collected by centrifugation, washed with demonized water and ethanol several times to remove organic and impurities, and finally dried in air at 80°C for 12 h [5].

2.2. 2 2-Line Ferrihydrite

Fourty gm of Ferric nitrate($Fe(NO_3)_3 \cdot 9H_2O$) was dissolved in 500 ml distilled water and added with stirring, 330ml 1molar KOH to bring the pH to 7-8, centrifuge , then dialyze rapidly as possible to remove electrolytes and freeze dry [4].

3. Results and discussion

Figure (2) shows the Raman spectrum of magnetite after irradiation with Nd-YAG laser with wavelength of 532 nm and 5mW output power. The spectrum shows clear peaks and by comparison with the vibrations recorded in some references we found that these vibrations are attributed to some components of materials that are listed in

table (1).

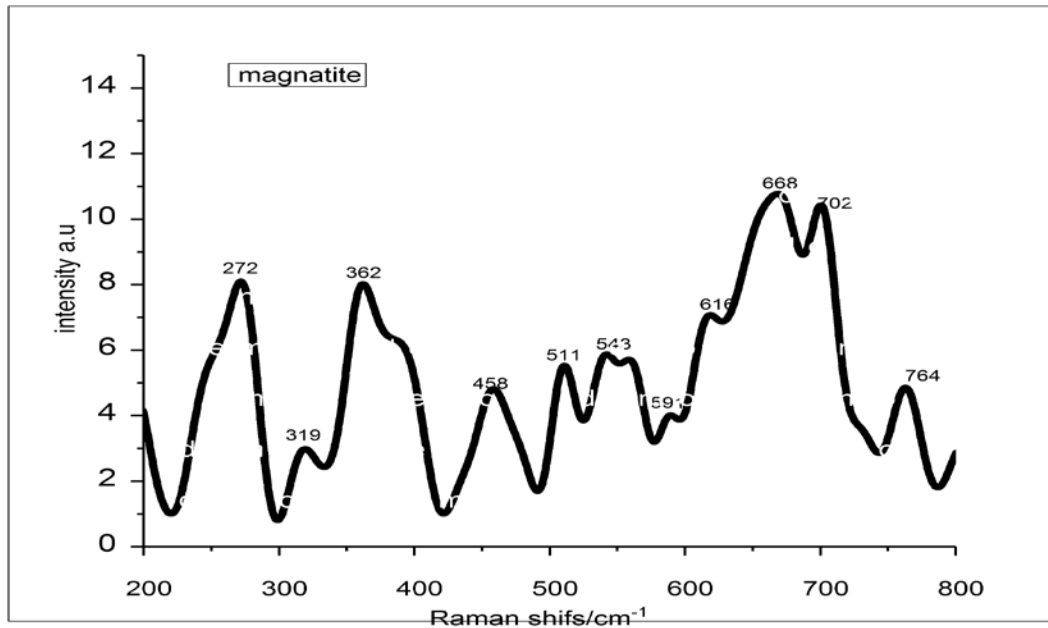


Figure 2: Raman spectrum of magnetite in the rang (200 cm^{-1} to 800 cm^{-1}).

Table1: The analyzed data of Raman spectrum of the magnetite

Raman shift(cm^{-1})	Intensity (a.u)	Assignment	References
272	8.6	FeII-O	[10,11]
319	4.3	FeIII-O	[12]
362	8.34	Se-Se	[6,7,9]
457	5.84	Si-O-Si	[6,7,8,9]
511	6.61	S-S	[6,7,8]
543	7.3	Fe III-O	[13,11,14]
591	4.5	C=S	[8,9]
616	8.4	FeIII-O	[12]
668	11.98	FeIII-O	[13,11]
702	11.5	FeII-O	[10]
764	5.31	C-F	[8,9]

Figure (3) shows the Raman spectrum in the range from (200 cm^{-1} to 800 cm^{-1}) of 2-line ferrihydrite sample after irradiation with Nd-YAG laser with wavelength of 532 nm and 5mW out power . This spectrum shows peaks of 2-line ferrihydrite molecules and some components of other materials that are listed in table (2)

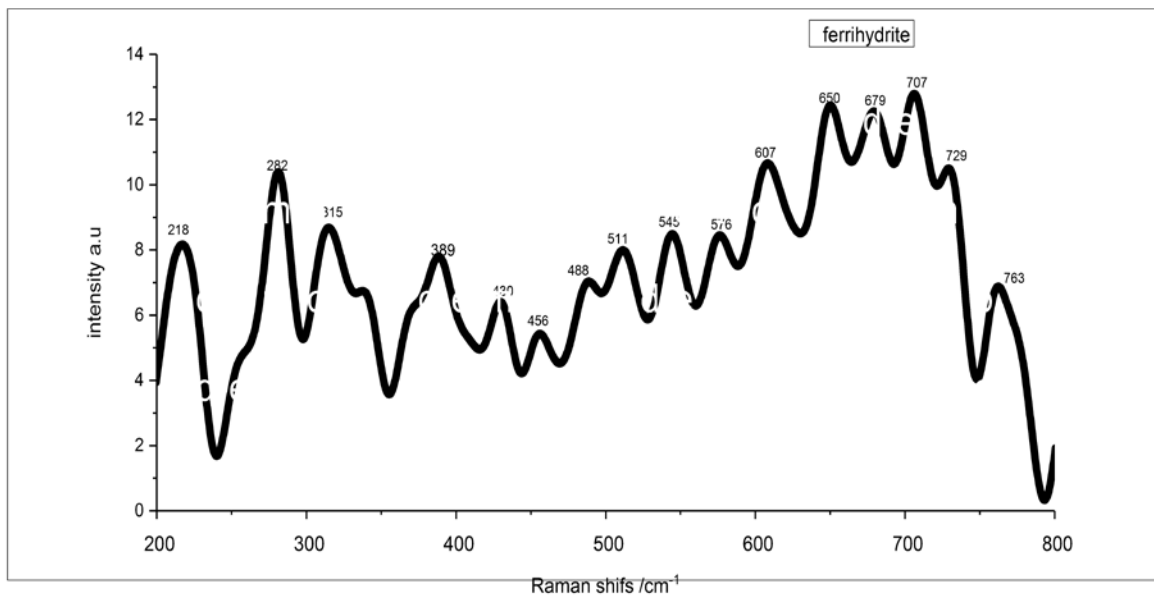


Figure 3: Raman spectra of ferrihydrite in the range from (200 cm^{-1} to 800 cm^{-1})

Table2: The analysis of Raman spectrum of 2-line ferrihydrite

Raman shift(cm^{-1})	Intensity (a.u)	Assignment	References
707	13.3	Fe-OH	[13]
679	12.9	C=S	[8,9]
650	13.0	FeII-O	[16]
607	10.95	FeII-O	[16,11]
576	8.7	C-Cl	[8,9]
545	9.09	Si -O- Si	[8,9]
511	8.4	Fe-OH	[13]
488	7.6	FeII-O	[14,17]
456	6.62	Si-O-Si	[6,7,8,9]
430	7.0	S- S	[8]
389	8.2	Fe-OH	[13]
315	8.97	FeIII-O	[14]
282	10.9	FeII-O	[14,17]
218	8.6	FeII-O	[14,17,16]
763	7.12	C-F	[6,7]
729	11.19	C-F	[6,7]

Through the analysis of the two spectra, it was found that some vibration modes of some materials are appeared as follows:

1. FeIII-O appeared in the spectra of the two samples at different intensities (4.3, 7.3, 8.4, 11.98, and 8.97).
2. FeII-O appeared in the spectra of the two samples with different intensities (8.6, 11.5, 13, 10.95, 7.6, and 10.9).
3. Fe-OH appeared in the spectra of 2line ferrihydrite at different intensities (13.3, 8.4, 8.2).
4. Si -O- Si appeared in the spectra of the two samples with different intensities (5.84, 6.62).
5. C= S appeared in the spectra of the two samples with different intensities (4.5, 12.9).
6. S- S appeared in the spectra of the two samples with intensities (6.61, 7.0).
7. C-F appeared in the spectra of the two samples with different intensities (5.31, 7.12, 11.19).
8. C-Cl appeared in the spectrum of the ferrihydrite with intensity (8.7).
9. Se-Se appeared in the spectrum of the ferrihydrite with intensity (8.97).

Table (1) illustrate that most of the Raman shift for vibrations mode of materials were found between 200 -800 cm^{-1} . Four vibrational modes of FeIII-O at 668 cm^{-1} , 543 cm^{-1} , 616 cm^{-1} and 319 cm^{-1} are assigned to magnetite and mentioned in the literatures (Oh and his colleagues 1998) [14] . Very high intensity of FeII-O vibration modes are appeared in the spectra at 272 cm^{-1} and 702 cm^{-1} and assigned to hematite and mentioned in the literatures (Thibeau and his colleagues a 1978) [17]. Also other vibration modes of materials like Si-O-Si appeared at 457 cm^{-1} and assigned to silicate, S-S vibration mode at 511 cm^{-1} and assigned to dialkyl disulfide, C=S vibration mode appeared at 591 cm^{-1} and assigned to alkyl sulfides , Se-Se vibration mode at 362 cm^{-1} and vibration mode of C-F at 764 cm^{-1} assigned to Aliphatic Fluor chemicals.

For the peaks of 2-line ferrihydrite listed in table 2, three vibration modes of Fe-OH are appeared at 707 cm^{-1} , 511 cm^{-1} and 389 cm^{-1} and assigned to ferrihydrite and this agreed with the results of other research (Hanesch M. 2009)[13]. Other peaks are appeared at 282 cm^{-1} , 650 cm^{-1} , 607 cm^{-1} , 218 and 488 cm^{-1} and assigned to hematite as mentioned by (De Faria and his colleagues a 1997) [16] . The laser power of 5mW is sufficient to convert the ferrihydrite to hematite in addition to the appearance of vibration mode at 315 cm^{-1} attributed to magnetite according to (Oh and his colleagues 1998) [14] . Other materials vibration modes were found at 458 cm^{-1} and assigned to silicate , 679 cm^{-1} and assigned to alkyl sulfides, 430 cm^{-1} and assigned to dialkyl disulfide , 576 cm^{-1} and assigned to primary chlorolkanes and 763 cm^{-1} and 729 cm^{-1} which are assigned to Aliphatic fluorine [6,7,8,9].

4. Conclusions

Raman spectroscopy provides useful information about the contents of magnetite and 2line ferrihydrite and also can distinguish between the magnetite and 2line ferrihydrite

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