



USAGE OF LASER RAMAN SPECTROSCOPY TO IDENTIFY THE UNSTABLE COMPOUNDS OF IRON OXIDES

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ABSTRACT

In this work laser Raman Spectroscopy was used to identify the unstable compounds in three iron oxides. These samples were irradiated using 5mW frequency doubled Nd-YAG laser with 532 nm at room temperature. Spectra database was used for the spectral analysis of the Raman shift of the three samples. The results obtained showed that the unstable compounds appeared in the spectra of the samples. Characteristic bands of hematite appeared in the spectra of goethite and akaganeite compounds while magnetite compounds appeared in the spectra of hematite. The laser power causes the bands to broaden and to undergo a small shift to lower wavenumbers. Other materials are appeared in spectra of the three samples like disulfide, alkyl disulfide and aliphatic fluoro. Raman spectroscopy proved to be suitable method for the identification of unstable compounds in hematite, goethite and akaganeite and could be used for other materials.

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INTRODUCTION

Raman spectroscopy is a spectroscopic technique used in condensed matter physics and chemistry to study vibrational, rotational and other low-frequency modes in a system [1]. It depends on the scattering phenomenon. In this context, scattering occurs due to collisions between photons and molecules. Generally, a photon collides with a substance, not necessarily only with a molecule. Irradiation of light with the frequency ν_0 upon a certain molecule brings a number of photons with the energy $E = h\nu_0$ to this molecule. Most photons colliding with molecules do not change their energy after the collision (elastic collision) and the ensuing radiation is called Rayleigh scattering. Rayleigh scattering consists of photons that have the same frequency as the incident light. A very small number of the photons that collide with the molecules exchange energy with them upon the collision (an example of in elastic collision). If an incident photon delivers an $h\nu_0$ quantum of energy to the molecule, the energy of the scattered photon reduces to $h(\nu_0-\nu)$ and the frequency of the scattering photon becomes $(\nu_0-\nu)$. On the contrary, when an incident photon receives the $h\nu$ energy from the molecule, the energy of the scattering photon rises to $h(\nu_0+\nu)$, and the frequency of the scattering photon becomes $(\nu_0+\nu)$. Scattering in which an incident photon exchanges energy with a molecule is known as Raman scattering [2].

Scattered light having the frequency of $\nu_0-\nu$ and that having the frequency of vibration $\nu_0+\nu$ are called “Stokes Raman scattering” and “anti-Stokes Raman scattering”, respectively. Stokes Raman scattering arises from interaction between a photon and a molecule that is in the ground state, while anti-Stokes Raman scattering is due to interaction between a photon and a molecule that is in the excited state [2]. At ambient temperatures, most molecular vibrations are in the ground state and thus the anti-Stokes transitions are less likely to occur than the Stokes transitions, resulting in the Stokes Raman scattering being more intense. For this reason, it is usually the Stokes Raman spectrum that is routinely studied [3]. Actually it is the finger print of the molecule so it can be used to identify different materials. This work aimed to use Raman Spectroscopy to identify the unstable compounds of three types of the iron oxides.

MATERIALS AND METHODS

Three samples of hematite, goethite and akaganeite, were investigated in this work by laser Raman spectrometer in the range from 400 cm^{-1} to 4500 cm^{-1} .

Equipments

In this work laser Raman microscope spectrometer model Burkert senttra, shown in the Figure (1) was used. The light source of this spectrometer is Nd-YAG laser with wavelength of 532 and output power of 5mW. The Raman shift in wave number, and the change in intensities in of the scattered light were compared with data in the references and previous studies.

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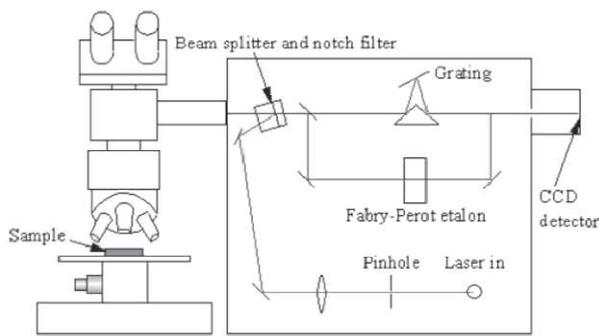


Figure 1 schematic diagram of Burker sentra laser Raman microscope spectrometer.

Samples preparation

Samples were prepared as follows

Sample1: Hematite (Fe₂O₃)

Fourty grams of Ferric nitrate (Fe (NO₃)₃. 9 H₂O) was dissolved in 500 ml of twice distilled water in polyethylene flask. Then , 300 ml of one molar (1M) potassium hydroxide (KOH) was added to the flasked followed by 50 ml of one molar (1M) sodium bicarbonate (NaHCO₃) . The mixtures were heated to 90C⁰, till formation of red brown precipitates of ferrihydrite. The flask and the content was allowed to stand for 48 hours. During this time the red brown suspension of ferrihydrite transformed to hematite with pH of 8 to 8.5 [4].

Sample2: Goethite(αFeOOH)

100 ml of one molar (1M) Ferric nitrate (Fe(NO₃)₃) solution was added into 2 liter polyethylene flask, then 180 ml of five molar (5M) potassium hydroxide (KOH) was added rapidly with stirring, till formation of Red brown precipitates of ferrihydrite at once. The suspension was diluted with twice stilled water and holded in a closed polyethylene flask maintained at 70 C⁰ in an oven for 60h. At the end of this period of time the red-brown suspension of ferrihydrite transformed in to a compact yellow precipitate of goethite [5].

Sample 3: Akaganeite(βFeOOH)

0.1 molar (0.1M) of FeCl₃ solutions hold in to 2 liter in closed vessel at 70C⁰ for 48h. During this time the pH of the system drops from 1.7 to 1.2 and compact yellow precipitate of akaganeite was formed [5].

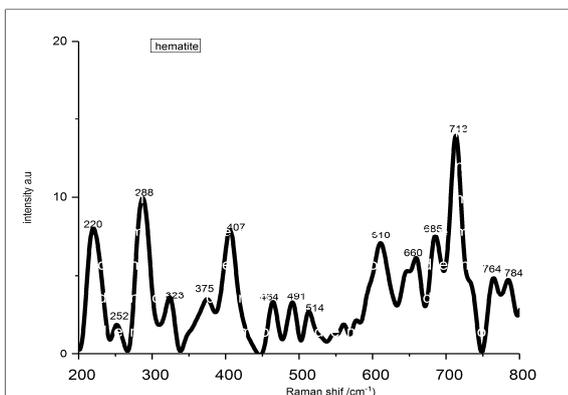


Figure 2 Raman spectrum of hematite in the range from 200 8-00 cm⁻¹

RESULTS AND DISCUSSION

Figure (2) shows the Raman spectrum of hematite 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 hematite compounds beside unstable components of hematite and some components of materials that are listed in table (1).

Table 1 The analyzed data of Raman spectrum of the hematite

Raman shift (cm ⁻¹)	Intensity (a.u)	Assignment	references
220	8.51	FeII-O	[10,11]
252	2.8	FeII-O	[10,11,12]
288	10.7	FeII-O	[10,11]
323	4.6	FeIII-O	[15]
375	4.85	Se-Se	[6,7,8]
407	8.07	FeII-O	[10,11]
464	4.31	Si-O-Si	[6,7,8,9]
491	4.36	FeII-O	[10,11,12]
514	3.09	S-S	[6,7,8]
610	7.3	FeII-O	[13]
660	6.26	FeIII-O	[14]
685	7.8	C=S	[6,7,8]
713	14.1	FeIII-O	[13]
764	5.0	C-F	[6,7]
784	5.2	C-F	[6,7]

Figure (3) shows the Raman spectrum of goethite after irradiation with Nd-YAG laser with wavelength of 532 nm and 5mW output power. The vibrations of goethite are appeared in the spectrum beside the vibrations of unstable components of goethite beside other materials. These vibrations are consistent with many previous studies as listed in table (2)

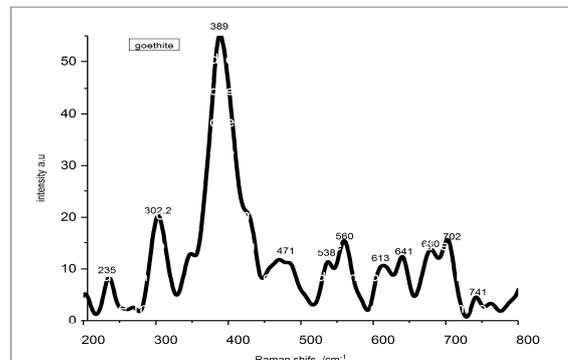


Figure 3 Raman spectrum of goethite in the range from 200 to 800 cm⁻¹

Table 2 The analyzed data of Raman spectrum of the goethite

Raman shift (cm ⁻¹)	Intensity (a.u)	Assignment	References
235	10.6	α Fe-OH	[5,14]
302.2	23.4	α Fe-OH	[5,14]
389	56	α Fe-OH	[5,14]
471	14.8	α Fe-OH	[5,14]
538	14.4	Si-O-Si	[6,7,8,9]
560	16.0	α Fe-OH	[5,14]
613	13.7	FeII-O	[10]
641	15.3	C=S	[6,7,8]
680	15.7	α Fe-OH	[14]
702	18.2	FeII-O	[16]
741	6.8	C-F	[6,7]

Figure (4) shows the Raman spectrum in the range from 200 to 800 cm^{-1} of akaganeite. The vibrations of akaganeite are appeared in spectrum beside some unstable components and some other materials. These vibrations are consistent with many previous studies as listed in table (3).

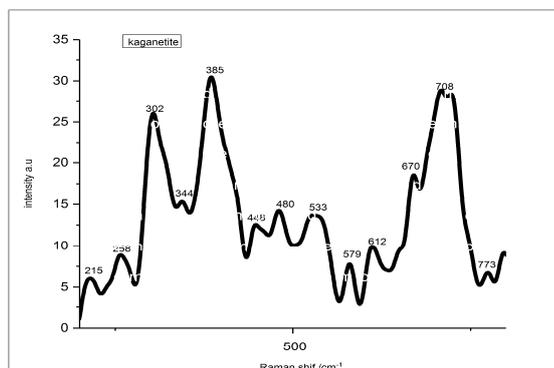


Figure 4 Raman spectrum of akaganeite in the range from 200 -800 cm^{-1}

Table 3 The analyzed data of Raman spectrum of the akaganeite

Raman shift (cm^{-1})	Intensity (a.u)	Assignment	References
215	8.6	FeII-O	[[10,11]
258	11.3	FeII-O	[10]
302	26.3	βFeOOH	[5,13]
385	30.6	$\beta\text{Fe-OH}$	[5,13]
344	17.2	Se-Se	[6,7,8,9]
448	14	S-S	[6,7,8,9]
480	16.1	$\beta\text{Fe-OH}$	[13]
533	16	$\beta\text{Fe-OH}$	[13]
579	10.34	C=S	[6,7,8,9]
612	11.15	$\beta\text{Fe-OH}$	[13]
670	20.5	$\beta\text{Fe-OH}$	[13]
708	29.3	$\beta\text{Fe-OH}$	[5,13]
773	8.31	C-F	[6,7]

Through the analysis of the three samples it was found that the vibration modes of some materials are appeared as follows:

1. FeII-O appeared in the spectra of the three samples at different intensities (10.7, 8.51, 2.8, 8.07, 4.36, 7.3, 13.7, 18.2, 8.6, 11.3).
2. FeIII-O appeared in the spectrum of the hematite at different intensities (4.6, 6.26, 14.1).
3. $\alpha\text{Fe-OH}$ appeared in the spectrum of the goethite with different intensities (10.6, 23.4, 56, 14.8, 16, 15.7).
4. $\beta\text{Fe-OH}$ appeared in the spectrum of the akaganeite with different intensities (26.3, 30.6, 16.1, 16, 11.15, 20.5, 29.3).
5. Si -O- Si appeared in the spectra of the hematite and goethite samples with different intensities (4.31, 4.4).
6. C= S appeared in the spectra of the three samples with different Intensities (7.8, 15.3, 10.34).
7. Se-Se appeared in the spectra of hematite and akaganeite with different Intensities (4.85, 17.2).
8. S- S appeared in the spectra of the hematite and akaganeite with different intensities (3.09, 14).
9. C-F appeared in the spectra of the three samples with different intensities (5.0, 5.2, 6.8, 8.31).

The bands that proved to be useful for the identification of the investigated hematite are listed in Tables (1). Six vibration modes of FeII-O at 288, 220, 407 cm^{-1} , 491, 610 and

252 cm^{-1} are mentioned with the literatures (Thibeu *et al.* 1978, De Faria *et al.* 1997), [10,11]. Also vibrational modes at 713 cm^{-1} , 660 cm^{-1} and 323 cm^{-1} were observed. These are assigned to Magnetite and this agreed with the results of other research (Shebanova ON *et al.* 2003, Oh *et al.* 1998) [13, 14]. Vibration modes of other materials are observed at 464 cm^{-1} and assigned to silicate, 685 cm^{-1} assigned to alkyl sulfides, 514 cm^{-1} assigned to dialkyl disulfide, 774 cm^{-1} and 784 cm^{-1} which are assigned to Aliphatic fluoro according to [6.7.8.9].

In the Raman spectrum of Goethite high intensity vibrational modes of $\alpha\text{Fe-OH}$ are appeared at 389 cm^{-1} , 235, 302.2, 389, 471, 560 and 681 cm^{-1} and are assigned to goethite as mentioned in the literatures (Oh *et al.* 1998) [14]. Also we found vibrations mode of FeII-O that appeared in the spectra at 702 and 613 cm^{-1} and assigned to hematite and mentioned in the literatures (Thibeu *et al.* 1978, De Faria *et al.* 1997), [10,11]. Other vibration modes at 538 cm^{-1} and assigned to silicate, vibration mode at 641 cm^{-1} attributed to alkyl disulfide and mode at 741 assigned to aliphatic fluoro and those findings agreed with the results of other research's [6.7.8.9]. For akaganeite, seven vibration modes of $\beta\text{Fe-OH}$ appeared at 302, 385, 708 cm^{-1} , 490, 533, 612 and 670 cm^{-1} are assigned to akaganeite as presented in the literatures (Oh *et al.* 1998), [14]. In addition vibration modes at 215 and 258 cm^{-1} are recorded which attributed to hematite according to (Thibeu *et al.* 1978, De Faria *et al.* 1997), [10,11]. Other vibration modes were observed at 448 cm^{-1} and assigned to dialkyl disulfide, 579 cm^{-1} and assigned to alkyl disulfide, 773 cm^{-1} and assigned to aliphatic fluoro according to [6,7,8,9].

CONCLUSIONS

The results presented in this work show that Raman spectroscopy technique is an efficient method to identify unstable compounds of hematite, goethite and akaganeite. It provides precise information about other materials found in the three samples.

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