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Structural characterization of kaolin from Djebel Debbagh Mine using Fourier Transform Infrared Spectroscopy (FTIR)

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Abstract

The structural organization level of kaolinite is a useful parameter in the kaolin industry, the determination of the crystallinity index can somehow give an idea about the use of kaolin in a well-defined industry. Kaolinite has a number of structural defects, the abundance of which makes it possible to define a scale of crystallinity. Thus, well crystallized kaolinites, medium crystallized kaolinites and poorly crystallized kaolinites are distinguished. The objective of this study is to determine the crystallinity degree for three samples of kaolin (DD1, DD2 and DD3) selected from Djebel Debbagh mine, located in Eastern Algeria. In order to obtain the results envisaged; the three samples were analyzed by Fourier Transform Infra-Red (FTIR) method. According to the obtained results; the three kaolins have poor crystallinity, since the ratio P_O is greater than 1 and the ratio P_2 is less than 1,especially for DD2 and DD3 where a total absence of the 3652 and 3669cm^{-1} vibration bands was observed. Even the kaolin DD1 has two light shoulders at 3662 and 3633cm^{-1}, this sample remains poorly crystallized. In this study; it can be seen that the kaolin samples have a halloysite which is causing eventually this poor crystallinity and a poorly crystallized kaolinite also indicates the presence simultaneously of kaolinite and halloysite (mixed kaolin).

Keywords: Kaolinite, FTIR, Crystallinity Index, Djebel Debbagh mine.

Introduction

The structural disorder of kaolinites can be detected by differences in position and relative intensity of OH stretching and bending bands in IR spectrum[1-4].

The first zone corresponds to the high frequency bands between 3700-3400cm^{-1}, but the second corresponds to the lower frequencies in the 1500-400cm^{-1} (Figure-1). The high frequencies concern the vibrations of the O-H hydroxyls, whereas the bands of the small frequencies (right-hand part) concern the Al-OH, Si-O, Si-O-Si and Si-O-Al bonds.

Infrared spectroscopy is a very important tool for characterizing the crystallinity of clays by observing the relative intensities of the vibrational bands of the structural hydroxyls. Infra-red spectrometry was used to complement the other studies[6].

In general, the infrared spectrometry spectra depend on the structure of minerals. The properties of minerals, such as the types of bonds and their forces, the atomic masses of minerals, and the mode of stacking atoms in the crystal, determine the frequency of vibrations. These vibrations of the atoms around their equilibrium position also determine absorption bands. In any case; all defined minerals possess a characteristic infrared spectrum.

The infrared (IR) spectrum can be divided into three sub–regions; i. Near infrared: (13,000-4,000cm^{-1} or 0.8-2.5µm); ii. Mid Infrared: (4000-400cm^{-1} or 2.5-25µm); iii. Far infrared: (400-10cm^{-1} or 25-1000µm).

The near infrared domain is favorable to identify the typical bands of certain chemical groups or ions such as Fe^{2+}, H_2O, OH, and CO_3^{2-}.

In the middle infrared domain, the absorption or reflection bands are normally due to the various atomic groups of the minerals. The spectra in the middle infrared of a mineral always provide important information on the functional groups which constitute it. Most bands characteristic of minerals are found in the middle area of the infrared spectrum. As a result, research on minerals and gems is numerous in this field[7].

The Far Infrared domain is the area where the fundamental low-frequency bands of the different atomic groups are observed. This zone is not of this day well studied for the minerals[8].

These analyzes were carried out at the laboratory: “Metallogeny and Investigation Laboratory, Mining Exploitation and Prospecting Department, School of Mining, Energy and Materials Engineering of Oviedo, University of Oviedo, Spain.

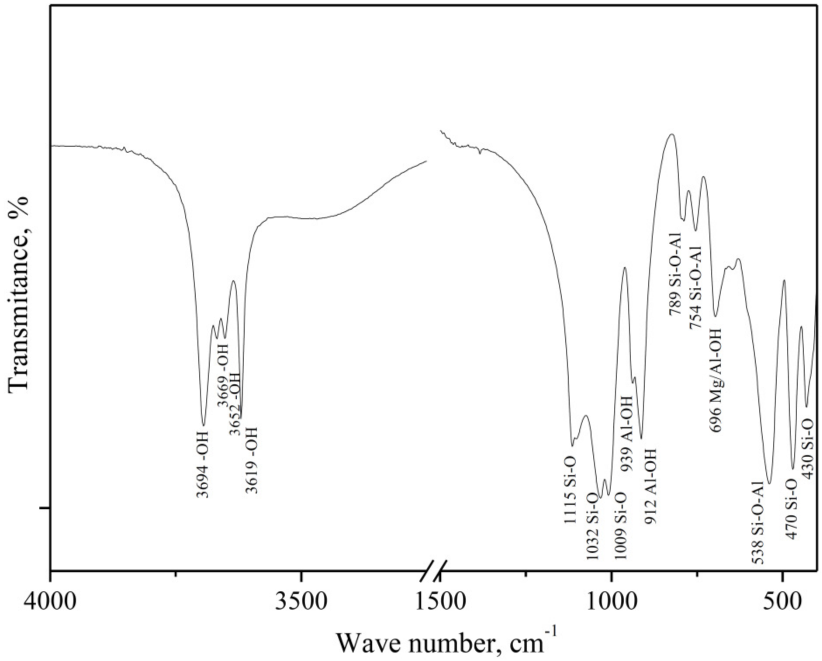

Figure-1: FTIR of the crystallized kaolin (MID-IR region: 4000-500cm^{-1})^5.

Materials and methods

To perform FTIR spectrometric analyzes; we selected three samples of Djebel Debbagh kaolin situated in East region of Algeria. The three samples are named DD1 (white sample), DD2 (gray sample) and DD3 black sample, respectively (Figure-2).

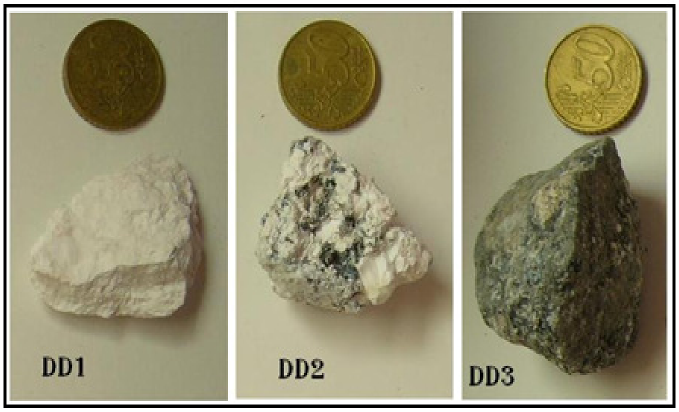

Figure-2: Photos of DD1, DD2 and DD3.

The three samples of kaolin are carefully prepared according to the KBr disc method, these samples are ground and sieved to less than 2µm, and then 1 mg of kaolin is introduced into 300mg of potassium-bromide. Subsequently and after introducing the mixture into a pelletizing mold, a very high pressure (about 12t/cm^2) is exerted with a hydraulic press for 4 minutes. Before carrying out the FTIR analyzes, the three pellets were dried at 105°C for 24 hours to eliminate the water adsorbed on KBr and kaolin samples.

The infrared spectra were recorded using a VIS-UV-IR PERKIN-ELMER λ-900 spectrophotometer equipped with a microcomputer; the numerical data acquired during the experiments were converted into spectra using Microsoft Excel.

Results and discussion

FT-IR technique investigates OH vibrations, whose absorption bands appear at different frequencies depending on the cations directly linked to the hydroxyls. Regarding to the kaolin's analysis, FTIR spectra are representing in Figures-3, 4, and 5 represent the IR spectra of the kaolin samples in a wavenumber interval between 500 and 4000cm^{-1}.

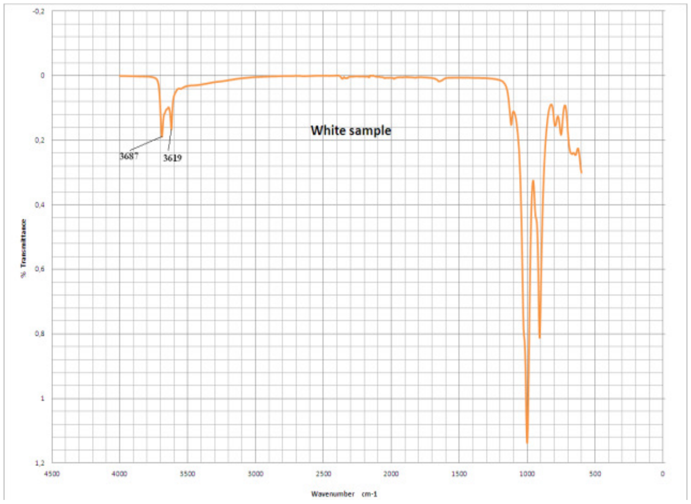

Figure-3: FTIR of kaolin DD1 (white sample).

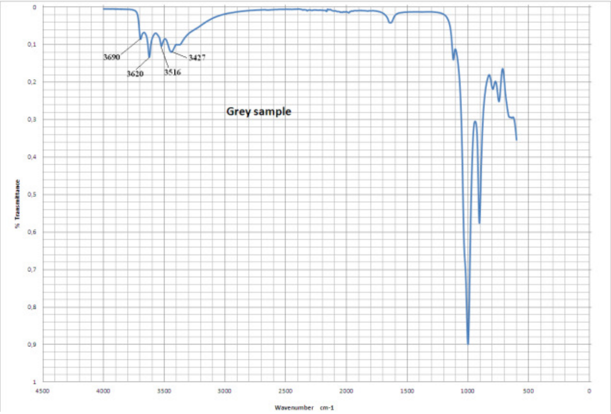

Figure-4: FTIR of kaolin DD2 (grey sample).

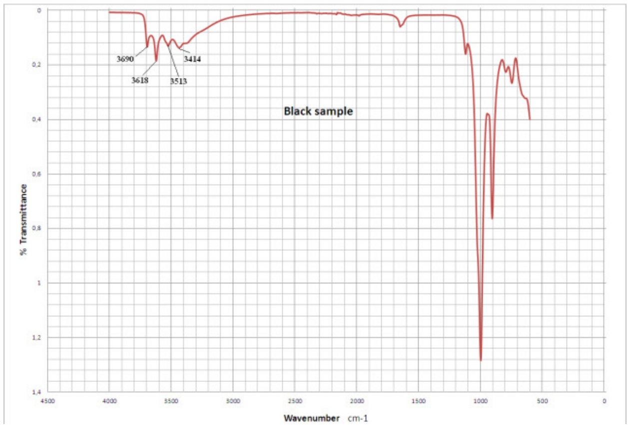

Figure-5: FTIR of kaolin DD3 (black sample).

The infrared spectrum of kaolinite and particularly its OH stretching region are very sensitive to interlayer modifications. The hydroxyl deformation modes of kaolinite are important in the spectroscopic analysis of intercalated kaolinite. Kaolin clay minerals contain two types of hydroxyl groups (I) the outer hydroxyl groups, or so-called inner surface hydroxyls and (II) the inner hydroxyl groups. These hydroxyl groups were designated Ou OH and In OH, respectively. The Ou OH groups are situated in an outer, unshared plane, whereas the In OH groups are located in the plane shared with the apical oxygen atoms of the tetrahedral sheet**.**

The 3695, 3620cm^{-1} doublet is characteristic for the kaolin group in general. In the case of a well-crystallized kaolinite on the Figure1 (Mid-IR.), presents four OH stretching bands It has been shown by deuteration of intercalated kaolinitethat the band observed at around 3625-3620cm^{-1} is due to the hydroxyl groups located inside the sheet (inner hydroxyl), the three other bands, observed around 3695, 3670 and 3655cm^{-1}, are due to hydroxyl groups constituting one side of the sheet, sometimes referred to as inner-surface hydroxyls[9].

Absorption bands located at: 1003cm^{-1}; and 3691cm^{-1} indicates the presence of kaolinite[10-13]. All peaks values FTIR of the three samples are represented in Table-1.

Table-1: Peak values (cm^{-1}) and corresponding groupings observed for the three kaolins and their assignments.

DD1 (cm^{-1})	DD2 (cm^{-1})	DD3 (cm^{-1})	Assignments
3687	3691	3691	Hydroxyl O-H
3662	--	--	Hydroxyl O-H
3633	--	--	Hydroxyl O-H
3620 (3619,7)	3620	3620	Hydroxyl O-H
3529	3518	3517	OH stretching of water
--	3428	3420	OH stretching of water
1631	1620	1631	H-O-H bends of water
1120	1116	1116	Si-O-Si stretching of kaolin
1000 (999)	1000 (998)	1000 (995)	Si-O-Si stretching of kaolin
906	905	902	Al-OH bonds of kaolinite.
787	790	787	Si-O stretching of quartz
746	740	740	OH translation
652	655	--	AL-O-Si bonds of feldspar
636	624	623 weak pic	Si-O stretching of gehlenite

In the first zone of FTIR spectrum of the DD1 kaolin (white sample) there are the valence vibrations of the (OH) groups which reflect the presence of four absorption bands located at 3687, 3662, 3633 and 3620cm^{-1}. The OH stretching mode of the only inner surface hydroxyl group (Ou OH) is assigned on the higher frequency band 3687. The valence vibrations of the (OH) groups for the samples DD2 and DD3 (grey and black kaolin) the absorption bands are located only at 3691and 3620cm^{-1}.

The band observed at 3620cm^{-1} for the three samples (DD1, DD2 and DD3) is assigned to the stretching mode of an inner hydroxyl group (In OH), which is in the plane common to both the tetrahedral and octahedral sheets, in this wave number value, the band also is typical for the stretching of the internal OH groups in kaolinite, The FTIR of the kaolin DD2 and DD3 shown the absence of two bands situated at the wavenumber of 3668 and 3653cm^{-1},which indicates that the kaolin samples have a disordered structures (poor crystalinity index)[14].

The vibration bands located at 3529, 3420 for DD1, 3518, 3428 for DD2, and 3517, 3420 for DD3 are corresponding to the OH stretching of water. The bands located at 1631, 1620 and 1620 cm^{-1} for the samples DD1, DD2 and DD3 respectively are attributable to the flexion of the H-O-H bonds of the structural water molecules. Between the band 1000cm^{-1} and 500cm^{-}1; the important main groups are Si-O and Al-OH. The absence of the 912cm^{-1} band for the three samples (attributable to the flexural vibrations of the Al-Al-OH and Al-Mg-OH groups), indicating the absence of smectite[15,16]. The bands at 1120 and 1000cm^{-1} for DD1, 1116 and 1000cm^{-1} for DD2 and DD3 are attributed to the deformation vibrations of the Si-O-Si bonds. The absorptions peaks situated at 906, 787 and 746cm^{-1} for DD1, 905, 790 and 740 for DD2 and 902, 787 and 740 for DD3; are attributed to the Al-OH bonding vibrations of kaolinite.

According to Van Olphen and Fripiat the band near to the wave number of 750cm^{-1} (746, 740, 740cm^{-1} respectively for DD1, DD2 and DD3) assigned to the OH translation and indicates the presence of Illite. The small bands situated at 652 and 655cm^{-1} for DD1 and DD2 represent the symmetrical elongation vibrations of the Al-O-Si bonds of feldspar, except in DD3 which this band don't exist[17].

According to Russel and Fraser the two bands of low and nearly equal intensity, located at 790cm^{-1} and nearly 740cm^{-1} observed for all samples, assigned to Si-O stretching of quartz and indicate the presence of kaolinite. The absorption bands observed at 636, 624 and 623cm^{-1} in the three samples may be assigned to Si-O stretching of gehlenite. The characteristic bands observed at (< 623cm^{-1}) assigned to (Si–O–Al) bonding are missing in the three samples.

Infrared spectroscopy is a tool for mineralogists to characterize the crystallinity of clays by observing the relative intensities of the vibration bands of structural hydroxyls. Delineau T. provides an estimate of the crystallinity of kaolin from their infrared spectra[18].

The unit cell of kaolinite has four hydroxyls. The valence vibrations of these OH groups result in the presence of four absorption bands centered on the frequencies 3695, 3669, 3652 cm^{-1} (external OH) and 3619cm^{-1} (internal OH).

Depending on its origin, kaolinite has a mineral network, either organized or disorganized, a consequence of the presence of crystallinity or its absence. Crystallinity can be estimated from the infrared spectrum of kaolinite[19]. According to certain authors the distinction of a doublet with 3669 and 3652cm^{-1}, sign of an ordered kaolinite and an enlargement on the zone of the hydroxyl groups is necessary (Figure-6).

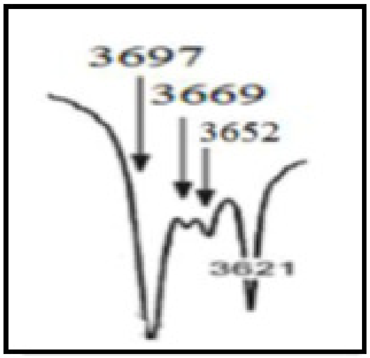

Figure-6: Enlargement of the hydroxyl group in the range 3700-3600cm^{-1}.

When the disorder of the kaolinite increases, there is a progressive disappearance of the stretching vibration band at 3669cm^{-1}. This disappearance is preceded by a reversal of the intensities of the bands at 3652 and 3669cm^{-1}. The ratios P_0 and P_2 of the bands intensities of valence vibration at 3619 and 3695cm^{-1} on one hand and 3652 and 3669cm^{-1} on other hand, measure the crystallinity of kaolinite[20]. P_0 greater than 1 and P_2 less than 1 are synonymous for the well-crystallized kaolinite [21].

$P_0 = [I/I_0\ (3619)] / [I/I_0\ (3695)]$

$P_2 = [I/I_0\ (3669)] / [I/I_0\ (3652)]$

With; I/I_0 (x)= T(x): transmitance a x cm^{-1} (%),T(x)= 10 $^{-A(x)}$, A(x) = Absobance a x cm$^{-1.}$

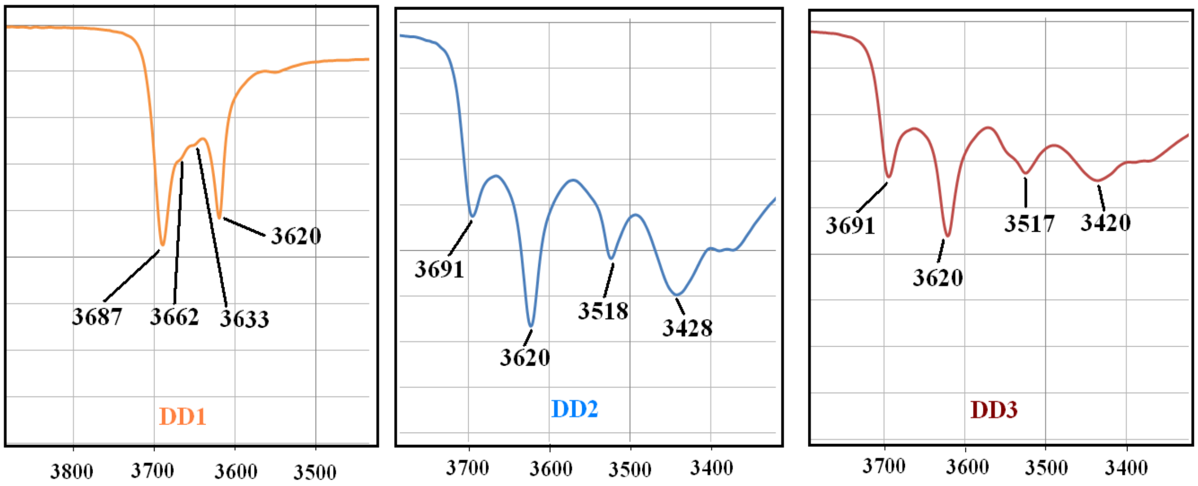

Figure-7: Enlargement of the hydroxyl group's zones of the three samples.

The ratios P_0 and P_2 characterizing the crystallinity of the three kaolin calculated on the absorption spectra are summarized in the following Table-2.

Table-2: The ratios P_0 and P_2 of the three samples.

Ratios	DD1	DD2	DD3
P_0	0,981	0,980	0,980
P_2	1,008	00	00

These results revealed; the three spectra are almost similar. The differences observed in the shape and position of the absorption bands may be related to the stacking difference of the various layers of kaolinite and halloysite[22].

From the spectra of the analyzed materials, the ratios of the intensities of the lines at 3620 and 3695cm^{-1} give values of P0 equal to 0.981, 0.980 and 0.980 for the samples DD1, DD2 and DD3 respectively, the index P2 is equal to 1,008 for DD1, for DD2 and DD3 the PO values have not been defined since the absorption bands at 3669 and 3652cm^{-1} will not appear on the relevant spectra. The values of P0<1 and P2>1 indicate that the kaolinite samples have poor crystallinity[23-25]. With this method; it can be seen that the kaolin samples have a Halloysite which is causing this poor crystallinity and According to Churchman, a poorly crystallized kaolinite also indicates the presence simultaneously of kaolinite and Halloysite (mixed kaolin)[26].

Conclusion

The three samples of kaolin and their associated minerals were investigated by FTIR-spectroscopy method.

According the obtained results; the three: FTIR patterns of DD1, DD2 and DD3 from Djebel Debbagh deposits contains mainly of kaolinite and are almost similar. The band observed at 3620cm^{-1} for the three samples is assigned to the stretching mode of an inner hydroxyl group, which is in the plane common to both the tetrahedral and octahedral sheets, in this wavenumber value , the band also is typical for the stretching of the internal OH groups in kaolinite, The FTIR of DD2 and DD3 shown the absence of two bands situated at the wavenumber of 3668 and 3653cm^{-1}, which indicates that the two samples have a poor crystallinity index more than DD1, this latter it has a poor crystallinity. The values of the ratio P_O and P_2 confirm that the three samples have a poor crystallinity. The poorly crystallized kaolinite indicates the presence simultaneously of kaolinite and halloysite (mixed kaolin), which influences the bending region and in OH stretching.

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