Fourier-transform Infrared Characterization of Kaolin, Granite, Bentonite and Barite

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Abstract

Fourier transform infrared (FTIR) is a technique that is used to identify the functional group and the finger prints present in a particular sample. In this characterization, Kaolin clay from Wanka Kirfi and Granite from Kafin Tafawa in Bauchi state while Bentonite and Barite from free zone drilling company, Port-Harcourt,River state have been analyzed within the mid infrared region using Perkin Elmer 1310 infrared spectrophotometer. The result obtained showed that mineral contents of the samples free hydroxyl were within the spectra region of 3900-3820cm^{-1}. Diazonium salts at the peak region frequency of 3200-3100cm^{-1}, organic substance at peak region of 2900-2700cm^{-1}, by comparing the spectra obtained with those present in literatures. These indicate that the Si- O, Si-O-Al, Si-O-Fe, Al-Mg-OH, Si-OH, Ba-S-O and Si-O-Si groups prevailed in the FTIR spectral measurement of the samples which are indication of the finger prints and functional group based on their group. Other distinct spectra with octahedral, polyhedral stretching vibration and symmetric stretching bonds of SO_4^{2-} and CO_3^{2-} modes in barite and granite spectrum indicate the presence of the calcite group common to most clays.

Keywords: characterization, clays, infrared, minerals, spectroscopy.

Introduction

Infrared (IR) spectroscopy has a long and successful history as an analytical technique that is extensively used, mainly as a complementary method to X-ray diffraction (XRD) and other methods used to investigate clays and other minerals (Janes& Peter, 2001).

IR spectra can serve as a fingerprint for mineral identification, give unique information about the mineral structure, including the family of minerals to which the specimen belongs and the degree of regularity within the structure, the nature of isomorphic substituent, the distinction of molecular water from constitutional hydroxyl and the presence of both crystalline and non-crystalline impurities (Farmer, 1979).

Dispersive IR spectrometers are now slowly being replaced by quicker and more sensitive Fourier Transformed (FT) instruments. The greater sensitivity of the Fourier Transform Infrared (FTIR) spectrometers is related to the continuous detection of the entirely transmitted energy simultaneously (Koenig, 1992; Russell & Fraser, 1994).

FTIR spectroscopy has been for decades, a frequently used method to investigate the structure, bonding and chemical properties of clay minerals (Madejova, 2003). Clay deposits and other minerals vary in nature (Velde, 1992). Two deposits cannot have exactly the same clay minerals, and frequently, different samples of clay from the same deposits differ. The basic rocks from which clays are formed are complex aluminosilicates, during the weathering, these become hydrolyzed, the alkali and alkaline earth metal ions from soluble salts are leached out, the remainder consists of hydrated aluminosilicate of varying composition and structure and free silica (Bantignieset al., 1997). From the aforementioned, there is need to identify the functional group and the fingerprint using FTIR spectra analysis.

The FTIR provides greater advantages as means of identification over others in that it provides the mineralogy of specific aggregates and gives specific identification of minerals. FTIR can be used to identify unknown materials present in a specimen. It can be applied to minute quantities of materials, whether solid, liquid, or gaseous. When the library of FTIR spectra does not provide acceptable match, individual peaks in the FTIR plot may be used to yield partial information about specimen (Pittiglio & Doner, 2003).

The applicability/acceptability of clays and other minerals is however dependent on an appreciable knowledge of its mineral content and chemical composition. In most third world countries like Nigeria non-black fillers which include clays are largely imported whereas clay deposits abound, but there is paucity of information about their potentials (Ogbemudia et al., 2010).

This research work seeks to cover the FTIR characterization of bentonite and barite from Free zone drilling company, Port-Harcourt. Others include kaolin clay from Wanka Kirfi and granite from Kafin Tafawa, Bauchi State.

Kaolinite and its properties

Kaolinite has the chemical formula $Al_2Si_2O_5(OH)_4$. The different minerals are polymorphs, meaning that they have the same chemistry but different structures. The general structure of kaolinite group is composed of silicate sheets (Si_2O_5) bonded to aluminum oxide (hydroxide layers $Al_2(OH_4)$)called gibbsite layers. The silicate and gibbsite layers are tightly bonded together with only weak bonding existing between the S-S paired layers (Richard, 2005).

Bentonite and its properties

Bentonite has the chemical formula: $Al_2O_34SiO_2H_2O$ which is a highly viscous jellylike structure, thus a form of sedimentary clay that is formed out of volcanic ash. When hydrated, it can change its molecular and electrical properties. This makes it porous and useful as a binding agent (Velde, 1992).

Barite and its properties

Barite ($BaSO_4$) is a widespread, normally occurring highly grainy mineral with a specific gravity ranging from 4.2 to 4.6 and a hardness index of 3.0 (Nusaed & Ahmed,2000). It is an accessory mineral to other minerals and can make a nice backdrop to brightly coloured crystals.

Celestine ($SrSO_4$) has the same structure as barite and forms very simple crystals the two are indistinguishable by ordinary methods, but a flame test can distinguish them. By scraping the dust of the crystal into a glass flame, the colour of the flame will confirm the identity of the crystal. If the flame is a pale green, it is barite, if red, it is celestine (Nusaed & Ahmed, 2000; Alibaba, 2010).

Barite is often used as incent filler due to its high bulk density, insolubility in water, resistance to acid and alkali, low abrasiveness and high refractive index. It is a good extender for primers having good filling properties and provides high chemical resistance and smoothness to under coats (Alibaba, 2010).

Granite and its properties

Granite is primarily composed of feldspar, quartz along with different other minerals in varying percentages, which are affirmed as follows: Nominal chemical composition of a variety of oxides are: silica (SiO_2) 70-77%, Alumina (Al_2O_3) 11-14%, Potassium oxide (K_2O_5) 35%, Soda (Na_2O) 35%, lime 1%, Iron (Fe_2O_3) 12%, (FeO) 13%, Magnesia (MgO) 0.51%, Titinia less than 1% (0.38%) and water (H_2O) 0.03%. Granite has an almost negligible porosity ranging between 0.2 to 4% (Anonymous, 2009).

Thermal stability: granite is highly stable thermally and therefore, it shows no changes with change in temperature. Granite is impervious to weathering from temperature and even from the air borne chemicals. It is the high resistance to chemical erosion that makes it useful for making tanks to store caustic materials.

Infrared characterization of minerals

The empirical identification of minerals by infrared spectroscopy requires a collection of spectra obtained from well characterized specimens. The identification of mineral and the recognition of its presence in mixtures are more certain when its absorption bands are numerous and sharply defined and if there appear a distinctive region of the spectrum. Sharp absorption band usually reflect a high degree of crystallinity and regularity in the structure, so that random isomorphous substitution which is a common feature in silicates, tend to broaden absorption bands and reduces detail in the spectrum; this particularly marked with aluminum for silicon substitution. The spectrum of a mineral cannot only define a mineral species, but place it accurately within its range of compositional variation and this with a sample which can with suitable techniques be less than 1μg (Velde, 1992).

Experimental section

FTIR spectra of the clay samples were measured with a Perkin Elmer 1310 Infrared Spectrophotometer. The mull technique as described by Gerhson et al., (1981) was used. The potassium bromide (KBr) cell was washed with ethanol, cleaned, and dried. The kaolin sample was further pounded (separately) with a dentist's "wiggle bug" and dissolved in Nujol. 150mg of the mixture (sample and Nujol) was weighed, spread on the potassium bromide cell and then placed at the light chamber of the spectrophotometer. The absorption spectrum of the resulted mull was obtained within three minutes scan time with a normal resolution of 20cm^{-1} in the 4000400cm^{-1} region. A reference spectrum of KBr was subtracted automatically with the system software to yield the final spectrum of the samples.

Results and Discussion

The spectra of the clays and other minerals are generally divided into two regions for ease of interpretation; the fingerprint regions with frequency (wave number) range of 400 to 1300cm^{-1} and the functional group region with frequency range of 1300 to 4000cm^{-1} for middle infrared analysis. The frequency assignment approach (conventional method) is used in the discussion of results (Gerhson et al.,1981).

FTIR spectrum of Bentonite clay

Figure 1 is the spectrum of bentonite clay used in this research and Table 1 gives the frequency assignment.

The peaks at 3900 and 3820cm^{-1} are indicative of free OH (hydroxyl), probably due to water vapor at the light chamber of the spectrophotometer and that present in the clay. The sharp band at 3695cm^{-1} is attributed to OH stretching (Al-OH and Si-OH) for bentonite as it agree closely to 3689 and 3628cm^{-1} obtained by Hubicki et al. (2009) and Isci et al. (2006) respectively. The peak at 3420cm^{-1}was assigned to OH stretching which is close to 3424 to 3426cm^{-1} for bentonite spectra reported by Isci et al. (2006). The broad band 3200 to 3100cm^{-1} is an indication of diazonium compound (NH_4^+) which are reported by Franco et al. (1978) as common impurities in montmorillonite clay types of which bentonite is one. They also reported that they obtained the band range of 3150 to 3100cm^{-1} in their analysis. The peaks at 2960 and 2900cm^{-1} are assigned to alkyl CH stretching which is an indication of organic impurity and agreed closely with that obtained by Isci et al. (2006) and Franco et al. (1978) as 3000 to 2800cm^{-1} and 2953, 2926, and 2855cm^{-1} for CH stretching bands respectively. The bands at 1840 and 1760cm^{-1} are indicative of hydrogen bonding effect clearly in carbonyl stretching region (Isci et al., 2006). The peaks at 1590 and 1530cm^{-1} are attributed to OH deformation mode of water. The peaks at 1150, 1060 and 1030cm^{-1} are assigned to characteristic bands of silicates which are mostly related to stretching vibrations of M-O (where M = Si, Al) and agree closely with 1200400cm^{-1} and 11031036cm^{-1} reported by Hubicki et al., (2009) and Vlasova et al. (2003) respectively. The peak at 920cm^{-1} is responsible for Al-Al-OH group deformation and is close to 913 and 914cm^{-1} reported by Amin et al. (2010) and Hubicki et al. (2009) for the same assignment respectively. The peak at 900 and 850cm^{-1} are assigned to Al-Fe-OH which agree closely with 896 and 885cm^{-1} obtained by Hubicki et al., (2009) and Amin et al, (2010). At 840 and 820cm^{-1} there exist a signal of Al-Mg-OH band vibrations which agree with 835 and 842cm^{-1} reported by Akcay and Yurdakoc (1999) for the bond and the same clay type. At 800cm^{-1}, the peak is assigned to Mg^{+2}-Fe^{+3}-OH while Si-O vibrations and various modifications of silica and correspond to 795 and 800cm^{-1} reported by Akcay and Yurdakoc (1999) and Vlasova et al. (2003).

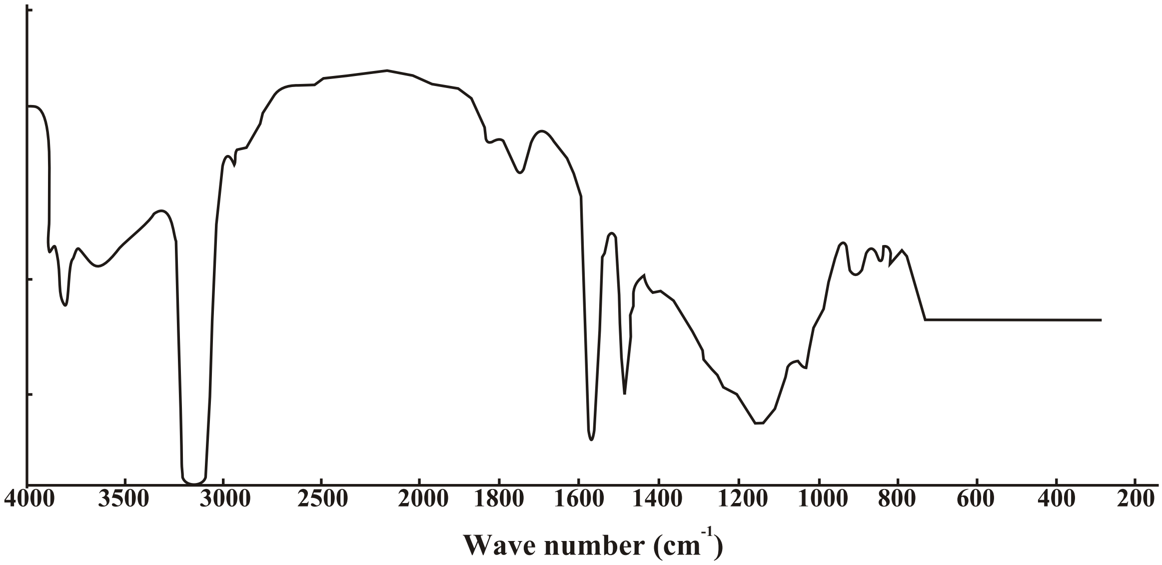

***Figure 1**: FTIR Spectrum of Bentonite*

***Table 1**: Vibrational frequency and assignment for Bentonite*

Band (cm^{-1})	Strength	Assignments
3960	Weak	Free OH
3880	Medium	Free OH
3695	Weak	-OH band stretch for Al-OH and Si-OH
3200-3100	Broad	Diazonium bond
1590	Broad	OH bending mode of absorbed water
1150	Broad	out-of-plain Si-O stretching for montmorillonite
1060	Broad	Si-O stretching bond vibrations
1030	Strong	Si-O stretching (in-plane) vibrations for layered silicates
900	Broad	Al-Fe-OH bending vibration
850	Medium	Al-Fe-OH bending vibration
840	Medium	Al-Mg-OH bending vibration
820	Medium	Al-Mg-OH bending vibration
800	Broad	Tridymite bending vibration (silicate, Mg-Fe-OH)
730	Broad	Twisting vibrations of Al-OH and Si-OH and stretching vibrations of Al-O

FTIR spectrum of Kaolin

Figure 2 shows the spectrum of Kaolin and the vibrational frequency assignment is given in Table 2.

The bands at 3700, 3660, and 3620cm^{-1} shows frequency peaks with medium absorbance strength of OH stretching. The peak at 3700cm^{-1} is assigned to inner-surface OH stretching and agreed with 3701cm^{-1} reported for kaolin from Alkaleri by Aroke et al. (2013). The peak at 3660cm^{-1} is attributed to inner-cage OH stretching of kaolinite and agreed closely with 3655cm^{-1} reported by Davarcioglu and Ciftci (2009). Inner-hydroxyl group is obtained at 3620cm^{-1} which is typical of high amount of Al-OH in the octahedral sheet and agreed with 3620 and 3626cm^{-1} reported by Gloria (2006) and Aroke et al.(2013) repectively. Thomas and Svoronos (1989) reported that the strong peaks at 2980, 2940, 2900, 2740, and 1730cm^{-1} are indications of organic impurities in the clay samples. The strong absorption band at 1130cm^{-1} is assigned to Si-O normal to the plane stretching of kaolinite which is close to 1125cm^{-1} reported by Davarcioglu and Ciftci (2009). The bands at 1050 and 1030cm-1are assigned to Si-O planar stretching common with kaolinite. The bands at 770 and 750cm^{-1} are indicative of Al-O-Si inner surface vibration and those at 705, 975, and 630cm^{-1} are hydroxyl stretching of quartz, hydroxyl deformation, and Si-O respectively. The bands at 846 and 805cm^{-1} are indicative of Al-Mg-OH deformations, showing the presence of illite mineral which is present in the kaolin as impurity, probably due to inefficient beneficiation or other purification method carried out on the raw kaolin clay.

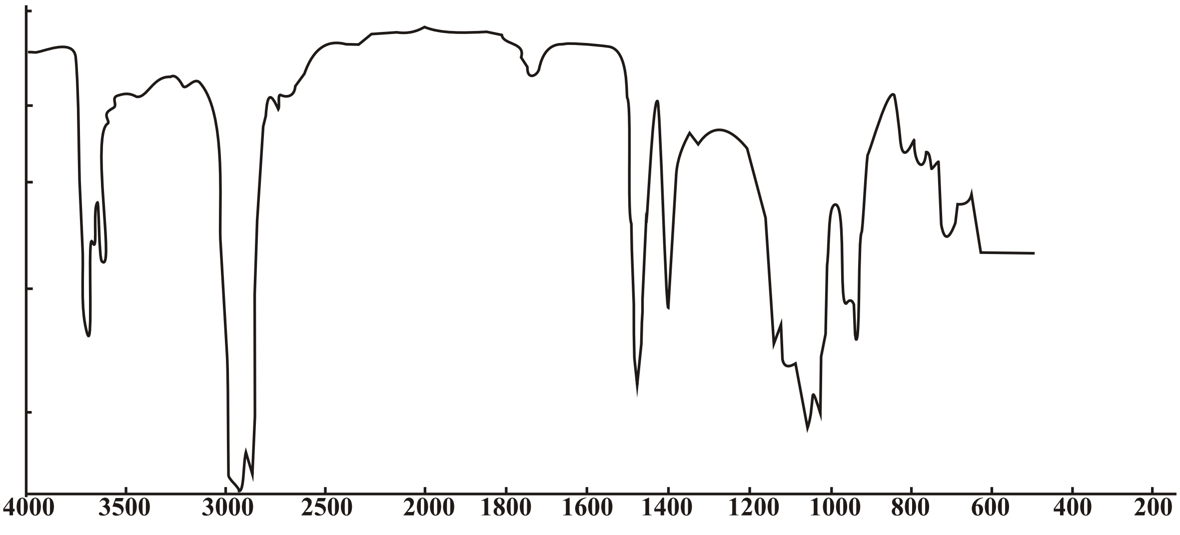

***Figure 1**: FTIR Spectrum of Kaolin*

***Table 2:** Vibrational frequency and assignment for Kaolin*

Band (cm^{-1})	Strength	Assignments
3700	Medium	Inner surface OH (Al-OH) stretching
3660	Medium	Inner cage OH stretching
3620	Medium	Symmetric OH stretching
1130	Strong	Symmetric (Si-O) normal to the plane stretching
1100	Strong	Symmetric (Si-O) normal to the plane stretching
1050	Strong	Symmetric (Si-O) planar stretching
1030	Strong	In-plane (Si-O) stretching
960	Medium	Inner surface Al-OH
846	Medium	Al-Mg-OH deformation
805	Weak	Al-Mg-OH deformation
675	Weak	OH deformation and Si-O (perpendicular)
630	Weak	OH deformation

FTIR spectrum of Granite

Figure 3 shows the spectrum of granite and the frequency assignment in Table 3.

Toshifumi et al. (2010) reported that an unexposed granite has an Orthoclase-type Albite structural formula of [$(NaK)AlSi_3O_8$] and Quartz (SiO_2) which are represented in the spectrum of this sample.

The peaks at 3680, 3580, and 3400cm^{-1} are due to OH bond stretching for Al-OH and Si-OH. The shoulders and broadness of the OH bands are mainly due to contributions of various structural OH groups occurring in the family of alkali feldspar group of which granite belongs (Dhanapandian and Gnanavel, 2009). The peak at 690 cm^{-1} is an indication of the presence of quartz which agreed closely with 695cm-1 reported by Dhanapandian and Gnanavel (2009). The peak at 750cm^{-1} is assigned to Al-O stretching which is in agreement with the range 776-725cm^{-1} reported by Toshifumi et al. (2010). The peak at 1390cm^{-1} reflected the amorphous sodium and potassium linkage to oxygen present in granite, but differ to some extent from 1420cm^{-1} obtained by Toshifumi et al., (2010). The broad band at 1170-1015cm^{-1} corresponds to the oxygen-bridging Si-O-Si asymmetric stretching and non oxygen-bridging Si-O stretching in granite (Toshifumiet al., 2010). The band observed at 1725cm^{-1} is attributed to H-O-H bending vibrations of absorbed water molecules, but differ from 1640cm^{-1} reported for granite by Dhanapandian and Gnanavel (2009) probably due to the variation in the amount of water or moisture present in the atmosphere at the time and place of the experiment and level of exposure of the sample to the atmosphere.

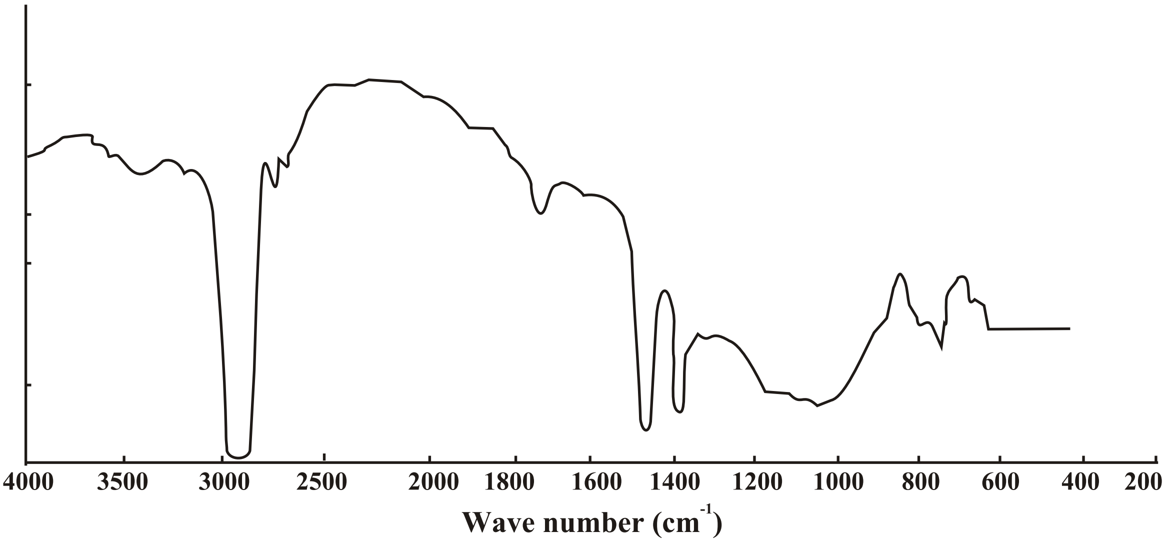

***Figure 1**: FTIR Spectrum of Granite*

***Table 3**: Vibrational frequency and assignment for Granite*

Band (cm^{-1})	Strength	Assignments
3680	Broad	-OH band stretching for Al-OH
3580	Weak	-OH band stretching for Si-OH
3400	Broad	-OH stretching of absorbed water
1900-1870	Broad	Si-OH stretching mode in quartz
1725	Weak	H-O-H bending vibrations
1465	Strong	Organic-inorganic hybrid bond
1390	Strong	Amorphous Na and K linked to Oxdes
1170-1015	Broad	Asymmetric oxygen-bridging Si-O-Si
800	Medium	Si-OH stretching
750	Medium	Al-O stretching
630	Medium	-OH deformation

FTIR spectrum of Barite

Figure 4 shows the experimental spectrum of barite and frequency assignment in Table 4.

The sulphate group has four fundamental vibrational modes. The frequency characteristic vibrations occur at 1180, 1130, 1090 and 990cm^{-1}. The peak at 1180cm-1 is assigned to asymmetric stretching vibration of sulphate group, 1130cm^{-1} is assigned to triply S-O stretching mode commonly found in barite groups (Janaki and Velraj, 2011), 1090cm^{-1} is assigned to symmetric stretching of SO_4^{2-} group and 990cm^{-1} is assigned to symmetric stretching of SO_4^{2-} tetrahedral. The vibrational frequencies falls within 11971076cm^{-1} range reported by Ramaswamy et al. (2010) for barite except for the peak at 990cm^{-1} which might be attributed to the difference in the particle size of the clay and the interaction of the tetrahedral SO_4^{2-} and metallic oxides (Al-O, Si-O etc.) present as impurities in the clay. In this spectrum, the sample showed a reasonably sharp peak at 3600 and 3410cm^{-1}, which can be assigned to O-H stretching due to crystalline hydroxyl group and absorbed water (Janaki and Velraj, 2011).

Mayer et al. (2006) assigned the peak at 644 and 630cm^{-1} to BaO_{12} octahedral stretching vibration in the spectra of supergene and endogen Barite samples analyzed with FTIR spectrometer. This agrees closely with 640cm^{-1} for the sample in this study. The peak at 2030cm^{-1} is assigned to Ba-S-O stretching and bending vibrations which suggests a "sheet" a structure for the Ba-S-O bonding, while 2000cm^{-1} was reported by Mayer et al., (2006). The peak at 880cm^{-1} was assigned to symmetric modes of CO_3^{2-} stretching which is present in calcite and suggests the presence of some traces of calcite in the barite clay sample as an impurity and this agreed closely with 874cm^{-1} reported by Mayer et al. (2006).

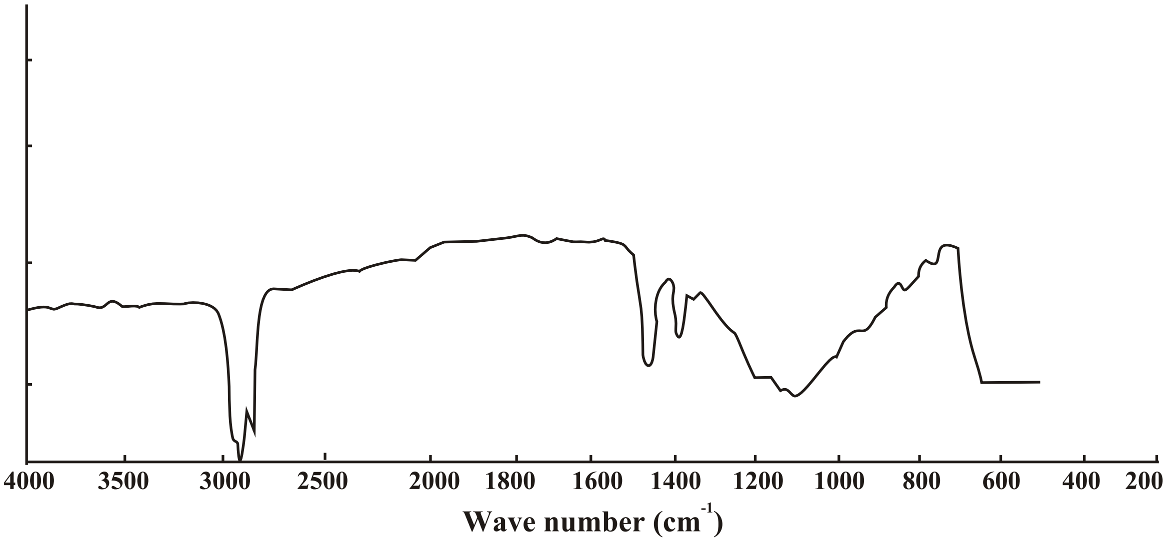

Figure 4: *FTIR spectrum of Barite*

Table 4: *Vibrational frequency and assignment for Barite*

Band (cm^{-1})	Strength	Assignments
3600	Medium	-OH stretching
3410	Medium	-OH stretching
2030	Medium	Ba-S-O stretching and bending vibrations
1180	Strong	Asymmetric stretching and bending vibrations
1710	Medium	Stretching vibrations of Oxygenous groups
1130	Strong	Triply asymmetric S-O stretching mode
1090	Strong	Symmetric stretching of SO_4^{2-}
990	Strong	Symmetric stretching of SO_4^{2-} tetrahedral
880	Strong	Symmetric stretching of Co_4^{2-} in calcite
640	Strong	Ba-S-O_{12} polyhedral stretching vibration (sheet structure)

Conclusions

This research provides general, supporting data or supplementary information for existing clay mines within regions where these minerals were sourced.

The spectrum of bentonite reveal the presence of free hydroxyl from absorbed water, Diazonium salt as an impurity and organic compounds also present as impurities. Further industrial application of these clay types for ceramics, bricks, sanitary wares, insecticides, cosmetics etc. required beneficiation and characterization.

The spectrum of kaolin showed a very heavy presence of organic impurity at the peaks between 2980-1730cm^{-1}, showing a relatively higher purity than Bentonite and other peaks are those common with Kaolinite clay groups which find application mostly in the ceramic industries and the cosmetics.

The granite and barite spectrum showed distinct spectra with octahedral, polyhedral stretching vibrations and symmetric stretching bands of SO_4^{2-} and CO_3^{2-} modes in calcite clay groups. Granite showed amorphous Na and K linked to oxides at 1390cm-1 peak which is present in most calcite clay groups.

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