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INFRARED STUDY OF INFLUENCE OF TEMPERATURE ON CLAY MINERALS

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Abstract

The effect of temperature on the infrared absorption bands of different clay minerals has been investigated with a view to identify the thermal transformation occurring between 30 and 1000°C.

Keywords: clay minerals, IR

Introduction

Clay minerals are used since ancient times for making potteries and bricks. Haematite and/or magnetite are present in small quantities in all the clay minerals and they play a very important role in the characterisation of these minerals. Thermal transformation and the structural correlation of clay minerals have been a subject of thorough investigation by many authors [1–3]. In the previous paper [4] the infrared study of clay minerals from different parts of Tamil Nadu/Pondichery was reported with special reference to the order of crystallinity. It was found that well-ordered clay was predominantly kaolinite in structure. It is of interest to study the behaviour of the infrared absorption of the different chromophoric groups with the temperature of firing. This is presented in this paper.

Experimental

In the present study the clay minerals used for brick making were collected from five different places nearby villages of Chidambaram. The samples were cut into 8×8×8 cm^3 and were heated to 200°C using a muffle furnace. The heating rate was 200 $deg \cdot h^{-1}$ and the samples were kept for one hour at the top tem-

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perature and cooled to room temperature within one hour. This procedure was repeated for 400, 600, 700, 800 and 1000°C. A piece of each sample was removed everytime and well ground using an agate mortar for 3 min. The IR absorption spectra in KBr pellets were recorded using Pye Unicam SP3-300 Spectrometer. Absorption spectra of a representative (Sidhan salai) raw and the heated clay is shown in Fig. 1. The observed absorption frequencies at different temperatures for the same clay is given in Table 1 along with relative intensity and the probable vibrational assignments.

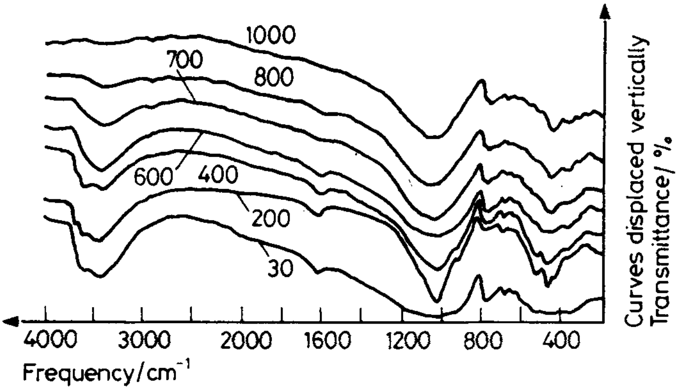

Fig. 1 Infrared absorption spectra of Sidhansalai clay (reperesentative) at different temperatures / °C

Results and discussion

Spectra of all the clay minerals are very nearly similar indicating that the constituents are almost the same. The absorption frequencies can be correlated with the frequencies for kaolinite. Keeling [7] pointed out that the clay minerals can be represented by means of general formula of the type.

$$O_6Si_4[O_4(OH)_2][(AlFe)^{3+}_{4-2n}X^{2+}_{n}]OH_{6-4n}$$

where the value of n lies between 0 and 1. One of the features of this series is that the proportion of outer (OH) groups decreases as n increases. The main features of the clay minerals absorption spectra are (1) the hydrogen bonding of the structural OH groups and (2) Si–O and Al–O vibration in the tetrahedral and octahedral sublayers and other associated oxide minerals.

Absorption between 3700 to 3400 cm^{-1}

In the present study there are absorption band at 3690 and 3620 cm^{-1} and a broad strong absorption band at 3420 cm^{-1}. The absorption band at 3690 cm^{-1}

has been assigned to free hydroxyl group which is the asymmetrical stretching vibration of H–O–H bonds [5, 6]. The absorption at 3690 cm^{-1} is due to inner hydroxyl group in the general formula for silicate structure. Farmer and Russel [7], and Miller [8] assigned the absorption band at 3620 cm^{-1} as due to hydroxyl group on the side of the tetrahedral sheet. The absorption band at 3420 cm^{-1} was assigned to hydrogen bonding [9]. For well ordered pure kaolinite the absorption bands observed are at 3689, 3668, 3649 and 3619 cm^{-1} [10, 11].

On heating the sample to 200 and 400°C there is no perceptible change in the absorption bands either in intensity or in frequency. However, when the temperature was raised to 600°C the bands at 3690 and 3620 cm^{-1} disappear. There is also considerable decrease in the intensity of the broad absorption band around 3420 cm^{-1}. This behaviour may be correlated to the dehydroxylation during heating. Similar result on heating kaolinitized samples of st-leger du Bois has been reported by Elass and Oliver [12]. Fripiat and Toussaint [13] observed that the loss of water was rapid after 450°C and was complete at 600°C using the differential thermal analysis. De [3] concluded that the tetrahedra silicate layer is very stable even at 600°C. At this temperature they observed an endothermal reaction. The endothermal reaction was identified as due to the removal of structural water followed by semicrystalline metaphase formation which is known as metakaolinite. Miller [8] interpreted the formation of metakaolinite during early stages of dehydroxylation, on the basis of the disappearance of the absorption bands at 3718 and 909 cm^{-1}.

The dehydroxylation of the clay minerals occurs around 400–800°C. The transformation temperature depends upon the type of clay minerals. The octahedral lattice breaks down with the formation of iron oxides. Such a behaviour should be reflected in the infrared spectrum. The fact that OH bands disappear at 600°C in all the clay minerals may be the indication of dehydroxylation and resultant spectral characteristics of lower frequencies. The infrared absorption bands at 1620 cm^{-1} has been assigned to H–O–H bending [14–16]. From the spectra at different temperature it is observed that intensities of this band gets weakened as the temperature is increased and disappeared completely around 700°C. This decrease in intensity may be attributed to two processes that may take place during their transformation, dehydroxylation up to 500°C and the collapse of crystal frame work. These patterns should also be reflected in the low frequency region.

Absorption between 1200–800 cm^{-1}

In this region three absorption bands are observed 1100, 1010 and 910 cm^{-1} for raw clay samples. The absorption at 1100 cm^{-1} has been assigned to Si–O assymmetrical out of plane stretching vibration [7, 17–19].

Table 1 Infrared absorption frequencies (cm^{-1}) and intensities for representative clay (Sidhansalai) at different temperature

30°C		200°C		400°C		600°C		700°C		800°C		1000°C		Tentative assignment
Freq.	Int.*	Freq.	Int.	Freq.	Int.	Freq.	Int.	Freq.	Int.	Freq.	Int.	Freq.	Int.	
		3690	m st	3680	m br									Outer OH [6, 9, 24]
3560	st br	3620	m st	3620	m st	3600	v w	3610	v w	3610	v w			Inner OH [6, 9, 10]
3420	st br	3420	st br	3420	st br	3420	st br	3420	m br	3420	m	3420	w	Adsorbed water [6, 9]
1620	m st	1620	m st	1620	m st	1620	m st	1620	m w	1620	m w	1620	v w	H–O–H [6]
								1170	w	1160	w	1165	w	Si–O of SiO_4 [10]
1110	w sh	1110	w sh	1110	w sh	1110	w sh	1110	vw			1100	w	Si–O [10]
1030	st br	1030	st br	1030	st br	1040	st br	1040	st br	1065	st br	1080	st br	Si–O–Si [28, 7, 8]
		1010	st					1000	vw sh			1020	st br	Si–O [10]
935	v w													OH deformation [5]
910	v w	910	st	910	m sh									$[Al–O(OH)]_6$ [10]
		880	w sh											–
790	w sh	790	vw sh	790	v w	790	w	790	w sh	790	sh	790	w sh	Si–O of SiO_4 [10]
775	st	775	m st	775	st	775	st	775	st	775	st	775	st	$Si–O–Al^{vi}$ [17, 31]
725	w sh					735	w sh	730	w sh	730	w sh	730	w sh	Quartz [18]
690	m	690	m	690	m	690	m w	690	w	690	w	690	w	Si–O of SiO_4 [10] Quartz

Table 1 Continued

30°C		200°C		400°C		600°C		700°C		800°C		1000°C		Tentative assignment
Freq.	Int.*	Freq.	Int.	Freq.	Int.	Freq.	Int.	Freq.	Int.	Freq.	Int.	Freq.	Int.	
635	w					640	w	640	w	635	w	635	v w	Al_2O_3 [28]
575	w					575	w	575	w sh	575	w	575	v w	FeO of Fe_2O_3 [32]
530	m w	530	m st	520	m st	530	v w	530	w			545	v w	Si–O–Al^{vi} [12, 31]
460	st br	460	st	460	m st	460	st br	460	st br	460	st br	460	st	Si–O–Si [10]
		420	w	430	w sh							430	w sh	Al_2O_3 [28], OSi–γ_t(OH) [31]
		390	v w											OH [31]
370	w br	370	v w	360	w	360	w br	370	m w	370	m	370	m w	Fe_2O_3 [18]
330	w br	330	w			320	v w	325	w br	330	m w	330	w	Fe_2O_3 [18]

* Abbreviations of intensity: st-strong, m-medium, w-weak, br-broad, sh-shoulder, v-very.

Naryan Roy [20] observed that when aluminium was substituted for silicon, 1100 cm^{-1} absorption generally shifted to 960 cm^{-1}. It may be presumed to be due to the Si–O stretching motion modified by the presence of Al^{3+} as a cation co-ordinating the oxygen. This oxygen is strong when the amount of Al^{3+} is low in tetrahedral position [12]. When the temperature is increased to 200°C the broad absorption band is resolved into 1100, 1030 and 910 cm^{-1}. This might be due to ordering that takes place due to dehydration [12]. For samples fired to 600°C the absorption band at 1100 cm^{-1} is poorly resolved and got fused in the main absorption at 1020 cm^{-1}. This may be due to increase of Al^{3+} in the tetrahedral side [12] and an increase of perturbation on Si–O by Al–O bond vibration [20].

Miller [8] assigned the band at 1100 cm^{-1} as due to Al–OH vibration. Absorption at 1020 cm^{-1} is broad and intense for raw clay samples. Stubican and Roy [21], and Farmer and Russel [7, 22] assigned this band to Si–O–Si in plane stretching vibration. Percival [10] assigned this absorption to Si–O vibration of tetrahedral sheet. When the temperature is increased to 200°C this absorption band is clearly resolved. When the temperature increased to 400 and 600°C this absorption band becomes broadened and shifted to higher frequencies when the samples were heated to 700, 800 and 1000°C. The shifting of absorption maximum at 1020 cm^{-1} towards higher frequencies can be ascribed to condensation of the Si–O tetrahedra, breakdown of Si–O–Al bond and the dehydroxylation of the Si–OH groups [23]. The thermal reaction of $Si–O_2–Al_2O_3$ in the temperature region 500 to 1200°C has been investigated [24–26]. The absorption band at 1020 cm^{-1} shifted towards higher frequencies when the samples were fired to higher temperatures. This shift was considered to be due to the substitution of Al_2O_3 for $Si–O_3$ in this amorphous solid [18].

Absorption band at 910 cm^{-1} for raw clay sample is not clearly resolved. This absorption was assigned for Al–O(OH) vibration [5, 8, 10]. When the firing temperature was increased to 200°C the absorption band was well resolved. This may be due to the presence of residual water. This residual water may be removed by dehydration after firing to 200°C [12]. When the temperature was increased to 400°C this band decreased in intensity and disappeared at 600°C. The disappearance has been attributed to be destruction of octahedral layer [8, 10].

A relationship existing between the ratio of I_{910} and I_{1030} with temperature, is shown in Fig. 2. It becomes zero at 600°C consistent with the fact that 910 cm^{-1} due to Al–O(OH) of the octahedral sheet which breaks down at 600°C. The disappearance of absorption band may be understood [3] by comparing the peak areas (calculating the radial distribution function from X-ray diffraction intensities). Corresponding to the Si–O and Al–O distances, the coordination number of Si atom remains unchanged while that of Al decreases as

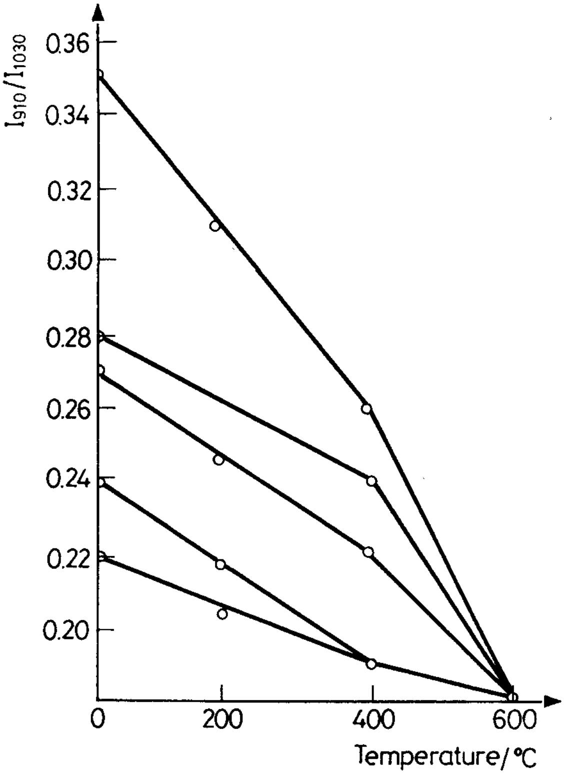

Fig. 2 Ratio of intensity of absorption frequencies at 910 cm^{-1} and 1030 cm^{-1} for clays at different temperatures

dehydration proceeds. This obviously confirms the stability of the tetrahedral silicate layer and gradual collapse of the octahedral Al–O(OH) with raise of temperature, owing to the expulsion of (OH) groups which initiate the collapse of kaolin layers to form semicrystalline metaphase.

Absorption in the region 800 and 200 cm^{-1}

A strong absorption band centred around 770 cm^{-1} with weak shoulders at 790 and 730 cm^{-1} a medium intense band at 690 cm^{-1}, weak absorption at 635 and 575 cm^{-1} were observed. A broad absorption band centred at 460 cm^{-1} with weak absorption at 530 and 420 cm^{-1} another medium intense band at 370 cm^{-1} with weak absorption at 390 and 330 cm^{-1} was also observed.

Absorption at 790 cm^{-1} may be assigned for Si–O of SiO_4 [10]. Manghani [27] assigned this vibration as due to Si–O–Si bridged stretching between SiO_4 tetrahedra. Later Eissa [28] assigned this frequency for Si–O of SiO_2. Stubican and Roy [21] assigned the absorption band at 535 cm^{-1} as due to Si–O–Al^{vi} vibration for montmorillonite and beodilite. Helvye [17], observed this absorption at 540 cm^{-1} and assigned it to $Si–O–Al^{vi}$ compounded vibration. Percival [10] assigned it to Al–O band of $Al(O–(OH)_6)$ stretching. After heat treatment of the clay they observed this absorption at 545 cm^{-1} and assigned for condensed AlO_6 group. Elass and Oliver [12] assigned this absorption at 535 cm^{-1} to bending vibration of $Si–O–Al^{vi}$ in surmouline and petite chaume samples. They also found that the frequency is inversely proportional to the radius of octahedral cation [12]. Siddheswaran [29], observed this absorption at 541 cm^{-1} and assigned it to $Si–O–Al^{3+}$ stretching vibration. Kanchan [30] studied the infrared absorption for $Na_2–V_2O_5–Fe_2O_3$ glass and observed a peak at 540 cm^{-1} and assigned to Fe_2O_3. On the basis of the above absorption the absorption at 530 cm^{-1} in the present duty may be assigned to Si–O–Si bending and O–Si–O bending vibration of silicates [12]. Zwinkels [31] assigned the absorption at 430 cm^{-1} due to OSi–OH vibration. Absorption bands at 415, 435 and 450 cm^{-1} were assigned to Fe–O vibration and 560 cm^{-1} was assigned to the characteristic absorption of $\alpha–Fe_2O_3$ by Eissa [28]. Absorption at 420 and 635 cm^{-1} were assigned to $\gamma–Al_2O_3$.

In the present study weak absorption at 580 cm^{-1} may be assigned to $\alpha–Fe_2O_3$. Bogdanovich [22] assigned 580, 520 and 475 cm^{-1} as due to $\alpha–Fe_2O_3$. In addition to 580 cm^{-1} absorption at 370 cm^{-1} may also be assigned to the presence of haematite in clays [28]. All the samples at room temperature show the presence of bands at 575, 375 and 325 cm^{-1} which can be attributed to the presence of Fe–O group of α-FeOOH and β-FeOOH. On the basis of earlier observations [31, 32] in clays the hydroxyl get separated due to dehydroxylation resulting in the formation of Fe_2O_3.

From the present study the following conclusions are drawn:

(1) All the clay minerals studied in the present investigation are disordered form of kaolinite.

(2) The bands at 3695 cm^{-1} and 3620 cm^{-1} assigned to outer and inner hydroxyl stretching vibration of the kaolinite structure is present in all the samples.

(3) The presence of aluminium AlO(OH) is indicated by the absorption band 910 cm^{-1}.

(4) The presence of Fe_2O_3 and/or FeOOH is indicated by the band at 575 cm^{-1}.

(5) On heating, the dehydroxylation takes place with the inner and outer hydroxyl group getting separated. The dehydroxylation is complete around 600–700°C. This result is in agreement with the observations of Simopoulos [33, 34].

(6) The disappearance of Al(OH) band at 910 cm^{-1} with the appearance of the band at 635 cm^{-1} around 600°C is indication of the formation of Al_2O_3.

(7) The presence of weak absorptions at 3420 cm^{-1} even at 800°C indicates that the hydrogen bonded system is still strong even at 800°C. The symmetric nature of the band at 1080 cm^{-1} may be indicative of the formation of silicate structure.

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Zusammenfassung — Im Hinblick auf die Identifikation der thermischen Umwandlungen im Temperaturbereich 30 bis 1000°C wurde der Einfluß der Temperatur auf die IR-Absorptionsbanden verschiedener Tonmineralien untersucht.