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Spectroscopic and thermal analysis of red clay for industrial applications from Tamilnadu, India

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HIGHLIGHTS

- Firing transformations of red clay were investigated by DT-TGA, FTIR, and XRD.
- Kaolinite, quartz, hematite, and goethite are presented in the red clays.
- The firing promotes the formation of new minerals such as mullite.
- FTIR technique is very suitable to analyze mullite environment.
- The studied clay has adequate characteristics for ceramic fabrication.

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ABSTRACT

FTIR spectroscopy is a powerful tool for assessing both chemical and mineralogical composition of the clay and fired materials. In the present study an attempt has been made to investigate the thermal transformation of red clay. Fourier transform infrared (FTIR) spectroscopy has been used to find the mineralogical transformations of red clay due to firing in the range of 400–1100 °C. From this analysis, red clay has relatively well crystalline kaolinite, rich in quartz, goethite, and hematite. The increasing firing temperatures lead to the vanishing of kaolinite and the development of mullite. Mullite is developed from silica and clay mineral. Finally, in order to demonstrate the reliability of FTIR attributions, XRD and TG-DTA were performed. The results show that the FTIR technique has the potential to become applicable for the characterization of natural clay, fired clay materials and high temperature minerals.

1. Introduction

From the ancient times, the clay is one of the most used natural materials in the ceramic industry with very different applications such as pottery, tiles, cement and brick. There is a great interest in the science and technology of gaining inspiration from natural clay for the design and manufacture of ceramic materials. In all types of ceramic manufacturing and other types of applications, clay is used as a main material. It consists of a multitude of different minerals, which are formed by the weathering of rocks and sediments. These weathering products consist mainly of hydrous aluminium silicates with a layer structure. Kaolinite and illite are the most widely used clay mixture in the ceramic industry [1]. During the firing process, these minerals change their structure, they decompose and finally new minerals are formed. The technological properties of these products are influenced by the chemical and mineralogical composition of natural clay materials as well as firing conditions (heating temperature, atmosphere and heating rate) [2]. Different clays from different regions around the world have been previously characterized due to its importance for industrial applications. FTIR spectroscopy is a relatively simple technique which is extremely sensitive to OH stretching vibrations [3,4]. It is widely used as analytical technique and extensively employed in the field of clay mineralogy to get information about the structural and chemical/physical properties at molecular level. This paper intends to show how FTIR spectroscopy to assess the mineral transformations occurring during firing. Also XRD and TG-DTA were used as a complementary technique in order to confirm the reliability of assignments made on the basis of the FTIR results.

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2. Materials and methods

2.1. Preparation of specimens

Two outcrops of natural red clay materials used in this study were taken from clay mine at Vadalure (VDR) (lat: 11 33°N, long: 79 32°E) and Patherakottai (PKI) (lat: 11 43°N, long: 78 37°E) in Tamilnadu. Initially the air dried clay samples were mixed with sufficient amount of water for the formulation of ceramic pastes and kept at room temperature a day to reach the optimum water content for good plasticity. The test specimens were prepared by hand shaping, molding and hand pressing. The samples obtained with these techniques were $5.0 \times 2.5 \times 2.5$ cm^3 rectangular bars. The shaping technique is simulation of the industrial processing performed at a laboratory scale. The specimens were initially dried at room temperature for a day and then sun dried for 2 days. Drying was carried out before firing to remove the moisture content. Finally the specimens were fired in an electrical furnace, at temperature ranging from 400 to 1100 °C. After reaching desired temperature, the specimens were kept in furnace for 4 h, followed by natural cooling to room temperature. The fired specimens were subjected to FTIR and XRD techniques to understand the formation of micro-crystalline phases during heating at different temperatures.

2.2. Analytical techniques

The Fourier transform infrared spectra (FTIR) were recorded in the 4000–400 cm^{-1} range using the Perkin Elmer RX1 FTIR spectrometer, the for all clay and fired samples.

Thermogravimetric analysis and differential thermal analysis (TG-DTA) were carried out with a SDT Q 600 V. 8.3 Thermal Analyzer with thermal advantage software. The experiment was carried out by heating the samples up to 1200 °C with a heating rate of 10 °C min^{-1} under high purity Argon atmosphere.

Mineralogical characterization was performed by X-ray diffraction (XRD) using Seifert (JSO-DEBYEFLEX 2002). X-ray diffractometer having a curved graphite crystal diffracted monochromator, with a source of CuKα radiation and NaI (Tl) scintillation counter detector. The experimental pattern was compared with patterns obtained from the JCPDS database [5].

3. Results and discussion

3.1. FTIR analysis

FT-IR spectroscopy is a physical method applied to study the mineralogy and mineralogical change of clay materials due to firing. The great advantage of FTIR spectroscopy is high sensibility that permits the determination of many components, even in very small amount. Infrared technique has been frequently used for the identification of natural clay minerals [6–11] as well as the synthetic clay minerals [12,13]. With the help of the FTIR, apart from crystalline, also non-crystalline inorganic and organic fabrics can be identified [8]. Frequencies (cm^{-1}) obtained from recorded spectra of two clay samples are tabulated with corresponding minerals in Table 1.

The red clay samples VDR and PKI had similar mineralogical compositions. In the present study, the minerals such as kaolinite, quartz, goethite, hematite and organic carbon were identified in both VDR and PKI samples by comparing the observed wave numbers with available literature. As seen from Fig. 1 two red clay samples show a broad absorption band around at 3440 cm^{-1}. The band at 3440 cm^{-1} along with the weak band at around 1640 cm^{-1} are due to absorbed water [8–11]. The inter layer hydrogen bonding in clay is assigned by a characteristics band at 3625 cm^{-1}. Most of the bands such as 3698 cm^{-1}, 3670 cm^{-1}, 3654 cm^{-1}, 3645 cm^{-1}, 3625 cm^{-1}, 1033 cm^{-1}, and 914 cm^{-1} show the presence of kaolinite [10]. Kaolinite is the major constituent of clays which gives sharp absorption bands in the 3700–3600 cm^{-1} region. Inner hydroxyl groups, lying between the tetrahedral and octahedral sheets, gives the absorption near 3623 cm^{-1}, the other three groups reside at octahedral surface of the largest and from weak hydrogen bonds with the oxygens of the Si–O–Si bonds on the lower surface of the next layer. A strong band at 3695 cm^{-1} is related to in phase symmetric stretching vibration, two weak absorptions at 3669 and 3653 cm^{-1} are assigned to out of plane stretching vibrations. In the present study, for the both red clays the peaks are observed at 3698, 3654, 3645 and 3625 cm^{-1} which indicate that presence of minerals in an ordered state [6]. The band at 1040 cm^{-1} is due to asymmetric stretching vibrations of silicate tetrahedron [6–10].

Quartz is one of the non clay minerals. The presence of quartz in the sample can be explained by Si–O symmetrical stretching vibrations at around 778 and 796 cm^{-1} while Si–O symmetrical bending vibrations arise around 694 cm^{-1} due to low level of Al for Si substitution. According to Elsass and Oliver [14], the presence of the sharp band at 694 cm^{-1} indicates thin particles and in the case of thick particles, this band has shifted to 689 cm^{-1}. Since the red clay shows this band at 694 cm^{-1} it is clear that this clay contain quartz of thin particle size. The band at 540 cm^{-1} was due to hematite [6], as may be seen in Fig. 1, was indistinguishable. It overlaps into one broad absorption band centered at 535 cm^{-1} assignable to Al–O–Si present in kaolinite.

The broad absorption band around at 469 cm^{-1} was due to Si–O–Si bending vibration [11]. The region between 2850–3000 cm^{-1} was indicates that presence of organic matter in investigated clay sample. The pair at 2925 and 2855 cm^{-1} corresponded to the C–H stretching vibrations of some organic contribution [14,15]. Carboxyl groups were the most important functional groups in natural organic matter. The organic substances have a high specific surface and good molding capacity, improving the plasticity of the clays [15].

Fourier Transforms Infrared spectra of samples heated at increasing temperatures allows for studying the mineral transformations, the breakdown of the clay structure and the formation of new minerals in the high-temperature region. Fig. 1 also shows

Table 1
The observed absorption wave numbers and corresponding minerals from FTIR spectra of red clay and fired samples.

Si. No.	Observed wave numbers (cm^{-1})	Mineral name	Unfired clay sample	Fired clay sample							
				400 °C	500 °C	600 °C	700 °C	800 °C	900 °C	1000 °C	1100 °C
1	3698, 3654, 3645, 3625, 1033, 914 and 535	Kaolinite	(+)	(+)	(+)	(−)	(−)	(−)	(−)	(−)	(−)
2	1080, 778, 796, 694 and 469	Quartz	(+)	(+)	(+)	(+)	(+)	(+)	(+)	(+)	(+)
3	2925 and 2855	Organic matter	(+)	(+)	(+)	(+)	(−)	(−)	(−)	(−)	(−)
4	540	Hematite	(+)	(+)	(+)	(+)	(+)	(+)	(+)	(+)	(+)
5	1165 and 553	Mullite	(−)	(−)	(−)	(−)	(−)	(−)	(−)	(+)	(+)

(+) – present, (−) – absent.