Optik 125 (2014) 6375–6378

Contents lists available at ScienceDirect

Optik

journal homepage: www.elsevier.de/ijleo

Application of various spectroscopic techniques to characterize the archaeological pottery excavated from Manaveli, Puducherry, India

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ARTICLE INFO

Article history:
Received 28 October 2013
Accepted 2 June 2014

Keywords:
Archaeological samples
Firing temperature
FT-IR
XRD
DSC–TGA

ABSTRACT

This paper is focused on a spectroscopic study of some ancient pottery shreds from an archaeological site Manaveli village, Puducherry, India. Analytical characterization using Fourier transform infrared spectroscopy (FT-IR), X-ray diffraction (XRD) and differential scanning colorimetric coupled with thermo gravimetric analysis were carried out on red and black ware and red ware recently excavated from the above site. The experimental results of FT-IR and XRD are similar and allowed us to identify the mineralogical composition of pottery samples. In addition, TGA was applied in order to study the dehydration of hydroscopic water and decomposition of carboxyl group in the powdered pottery samples during heating. Moreover, this paper proves that all the above spectroscopic techniques are very useful analytical tool for the examination of ancient pottery, which is also suitable for the identification of its firing temperature and firing atmosphere.

1. Introduction

The most abundant materials found at archaeological sites are potteries, valuable source of information for the study of ancient civilizations in terms of their culture, technological knowledge and ancient trade patterns. The application of analytical techniques to characterize the ancient pottery has proved to be valuable information to the archaeological investigations, aiming to reconstruct the ceramic life cycle, i.e. to extract provenance information and rediscover manufacture technology and use [1]. Manufacturing process of potsherds involves several aspects of pottery making, such as the type of raw materials used, their processing to prepare the clay paste, the surface treatment, decoration, firing condition and temperature to obtain the finished item. The firing temperature of ancient pottery is normally estimated by investigating mineral phases or determining experimental parameters which are temperature-dependent [2]. From long list of instrumental techniques such as Fourier transform infrared spectroscopy (FT-IR), X-ray fluorescence spectroscopy (XRF), X-ray diffraction (XRD), thermo gravimetric analysis (TGA) and scanning electron microscopy coupled with energy-dispersive X-ray spectroscopy (SEM-EDX), may successfully answer the above issues [3–8]. Clay materials are usually analysed by the use of techniques such as X-ray fluorescence and X-ray diffraction in which case it is difficult to identify poorly crystallized kaolinite. Infrared spectroscopy is however becoming an important tool for such qualitative identification. The application of the IR spectroscopy greatly increased in many spheres of clay research by the introduction of Fourier transform instrumentation. Thermal studies of clay minerals using TG and DTA were mainly confined to the monitoring of the dehydration processes because shreds have been buried and easily exposed to absorbed water.

The present work focuses on the results of various spectroscopic study of pottery recently excavated from the archaeological site at Manaveli, Puducherry, India. The mineralogy and firing of temperature of the archaeological bodies were examined by FT-IR and XRD. TGA is the complementary technique used to examine the firing temperature from the thermal characteristic reactions.

2. Materials and methods

2.1. Sample collection

Manaveli is one of the archaeological sites in Puducherry, India, near the archaeological site of Arikamedu on the outskirts of Puducherry town. The pottery samples were excavated

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http://dx.doi.org/10.1016/j.ijleo.2014.06.099
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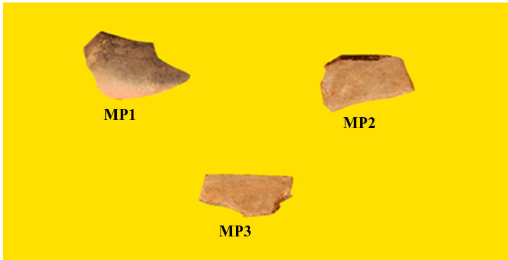

Fig. 1. Photograph of Manaveli pottery samples.

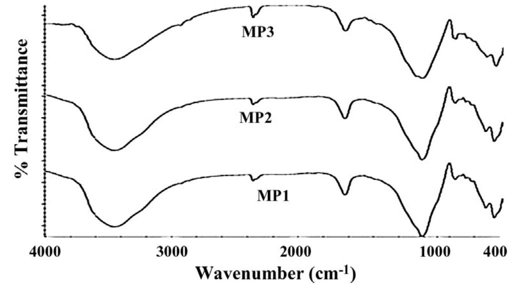

Fig. 2. FT-IR spectra of Manaveli potttery samples.

from Manaveli (11°53′26″N; 79°48′32″E) of Union Territory of Puducherry, India, by the Department of History, University of Pondicherry, Puducherry, India. The pottery shreds of Manaveli belong to the 5th century BC. Black and Redware, Red ware were collected in this site. The visual photograph of the collected pottery samples are shown in Fig. 1 The samples are designated as MP1, MP2, & MP3. After removal of an area of commercial clay extraction at a depth 30 cm to avoid the layer of surface vegetation, the pottery shreds were grounded into fine powder using agate mortar.

2.2. FT-IR technique

FT-IR spectra on the pottery samples were recorded on a Bruker Alpha FT-IR spectrometer available in department of chemistry, Government Arts College, Tiruvannamalai, Tamilnadu, India, using KBr pellets technique in the wave number range from 4000 cm^{-1} to 400 cm^{-1}. The KBr pressed pellet technique was used by mixing the powdered samples with KBr in weight proportion of 1:20. The spectra were recorded in the mid region of 4000–400 cm^{-1} in the received state. The precision of the instrument is ±5 cm^{-1}.

2.3. XRD analysis

Powder X-ray diffraction data of the powdered pottery samples was carried out on a Siemens D500Advance diffractometer using Cu K_α radiation, equipped with a NaI(Tl) scintillation detector. The X-ray patterns of powdered pottery samples were recorded at room temperature. Diffraction data over a 2θ range of 10 to 70° were recorded by using diffractometer. Mineralogical composition of the studied samples is determined with the standard interpretation procedures of XRD.

2.4. Thermo gravimetric analysis (DSC–TGA)

As the thermo gravimetric analysis has gained wide analytical acceptance in recent years for compositional analysis, DSC–TGA study was carried out for the samples in SDT Q-600-V.8.0 thermal analyzer. The experiment was carried out by heating the samples from 30 to 1000 °C at 10 °C min^{-1} with flow of high purity nitrogen.

3. Results and discussions

3.1. FT-IR mineral analysis

The FT-IR spectra (4000–400 cm^{-1}) of the red, red and black pottery fragments of Manaveli are given in Fig. 2 The identified minerals by IR characteristics are shown in Table 1 In all the spectra, quartz is dominated phase with bands at 780, 700 and 460 cm^{-1}. The presence of the sharp band at 695 cm^{-1} indicates thin particles and in the case of thick particles, this band has shifted to 689 cm^{-1}. Since the spectrum of the clay sample shows this band at 687 cm^{-1} it is clear that this clay contains quartz of thick particle size [3]. The weak band observed at 2926 cm^{-1} (νCH) is along with the weak band at 2853 cm^{-1}, probably originated from organic residues [9]. The band around at 1030 cm^{-1} is assigned to Si—O stretching mode of silicates/clays. The SiO deformation band of the clays appears at 467 cm^{-1}. The clay minerals such as kaolinite and montomorilinte were identified by the presence of the peak at 1030, 1635 & 3440 cm^{-1}, respectively. The presence of bands 427, 591 and 1050 cm^{-1} are due to microcline, orthoclase at 465, 645 & 730 cm^{-1} and albite 725 cm^{-1} indicate feldspar group of minerals in the samples. The presence of absorption bands around 580 and 540& 476 cm^{-1} are due to magnetite and hematite, respectively, stated by Velraj et al. [10]. The weak band at 3445 cm^{-1} is along with 1645 cm^{-1} due to OH stretching of hydroscopic water. The spectroscopic results indicate that black colouration was due to concentrations of magnetite, red colouration due to concentration of hematite. The presence of haematite also indicates firing in the oxidising atmosphere [4]. The amount of the organic contribution is higher in red part in comparison with the black decoration part [11]. No calcite bands were observed in all the spectra of the samples which indication of non-calcareous clay type. FT-IR spectroscopic results reveal that the presence of minerals quartz, feldspars (microcline, orthoclase and albite), clay minerals (kaolinite and montormorlinite), iron oxides (hematite and magnetite) and organic compounds. The assignment has been made on the basis of the characteristic IR wave numbers of the minerals [12,13]. The analysis results of all the three archaeological materials are similar.

3.2. FT-IR firing temperature analysis

The absence of firing minerals namely, the IR absorption bands of plagioclase-anorthite, pyroxene-diopside, melilite-gehlenite and wollastonite in the archaeological body clearly indicate the low firing temperature. On the other hand, microcline (K-feldspar) is known to be stable up to a temperature ranges 500–750 °C [12]. The decomposition of kaolinite and formation of metakaolinite occurs in the temperature range 500–650 °C [3,14]. The appearance of kaolinite in all the samples reveals that the firing temperature was not high enough to complete the decomposition of this mineral indicating that the fi ring did not exceed 650 °C. The band at

Table 1
The observed absorption wave numbers and corresponding minerals from FTIR spectra of Manaveli pottery samples.

S. No.	Sample ID	Quartz	Feldspars	Clay minerals	Iron oxides	Organic carbon
1	MP1	776, 460	723, 641, 588, 427	1031, 3441, 1637	579, 538, 476	2926, 2854
2	MP2	776, 701, 460	728, 641, 590	1032, 3443, 1638	539	2920, 2853
3	MP3	777, 687, 458	1049, 646,590	1029, 1645, 3439	538	2926, 2849