



Mineralogical Characterization Studies of Ancient Potteries of Tamilnadu, India by FT-IR Spectroscopic Technique

R. RAVISANKAR^{*}, S.KIRUBA[#], P.ESWARAN[¶],
G. SENTHILKUMAR[§] and A.CHANDRASEKARAN

^{*}Post Graduate and Research Department of Physics,
Government Arts College, Tiruvanamalai-606603, Tamilnadu, India

[#]Department of Physics, St.Joseph's College of Engineering, Chennai-119, Tamilnadu, India

[¶]Department of Physics, Vel Tech Dr RR & SR Technical University, Chennai-62, India

[§]Department of Physics, University of College of Engineering
(A Constituent College of Anna University) Chennai, Arani- 632317, Tamilnadu, India

Department of Physics, Sacred Heart College, Thirupattur-635601, Tamilnadu, India

rrs_phy@rediffmail.com

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Abstract: We report the spectroscopic investigation of ancient potteries excavated in Tamilnadu. Qualitative analyses were carried out to determine the major and minor constituent minerals present in the samples from the band position or location of the peaks. From the prominent IR absorption peaks, the minerals were identified with the available literature are the quartz, orthoclase, albite, magnetite, hematite, kaolinite, montmorillonite, illite, gypsum and calcite. The interpretation of results is made from the IR characteristics absorption bands. Spectroscopic results indicates that these potteries were refired to a less than 900 °C.

Keywords: Ancient pottery, Archaeometry, FT-IR, Firing temperature, Mineralogical Characterization.

Introduction

Archaeometry is a multidisciplinary research branch which focuses on studying and solving the problem in the field of cultural heritage. This discipline is geared towards the extraction of information about the genesis and history of findings through the analysis of the material and dating techniques. Archaeometry includes studies about dating, authentication, conservation and restoring, provenance and the achievement of technological information about hand made articles manufactures as well. One of the most important areas of

archeology is the identification of the source and the origin of ancient artifacts. Knowing the origin is very important for tracking correctly ancient civilization and history. Ancient potteries are the most common artifacts found during excavation of archeological sites, so archaeologists are interested in the studies of pottery fragments. Most archaeologists have classified ancient artifacts (pottery) by their shapes and uses. The main ingredients of pottery are clays to which tempering materials are some time added during manufacture. The clay, shell, sand *etc.* from which pottery were fashioned can have a chemical composition which unique and thus reviles the local source from which they were taken. Potteries are made of clay minerals and the common major clay mineral used in making potteries is kaolinte. The study of thermal transformation of the clay mineral can thus help in determining the firing temperature of the potteries.

The dehydroxylation of kaolinte minerals was first studied by Ross and Kerr¹. According to their differential thermal analysis (DTA) results dehydroxylation takes place between 400 °C and 525 °C. A small amount of water can however persist up to 750 °C or 800 °C at which dehydroxylation is complete. Dehydroxylation of kaolinte was used by Prost *et al*² also using infrared spectroscopy. They observed that among the hydroxyl bands in the 3700-3600 cm⁻¹ region the bands at 3675, 3650 and 3630 cm⁻¹ persist after firing to a temperature of 327 °C (600 K). According to Ellass and oliver³, on heating kaolinte the intensity of bands 3700-3600 cm⁻¹ region decreases and at 500 °C only a weak broad band remains in the 3600 cm⁻¹ region. The thermal behavior of the bands due to hydroxyl groups in clay artifacts were studied by Maniatis *et al*⁴ also. They observed that clay minerals begin to lose their crystalline hydroxyl groups and start disorganizing at temperatures in the range 400-600 °C and for some minerals it can continue up to 800 °C. According to them the persistence of a weak band around 3600 cm⁻¹ indicates the presence of the iron hydroxyl still in the clay body and points to incomplete dehydroxylation.

The transformation of the clay minerals during heating is reflected in the 1100-1000 cm⁻¹ region also. As the temperature is increased there is gradual destruction of the layer structures of the mineral. The bands at 1105 cm⁻¹ and 915 cm⁻¹ due to Al(OH) vibrations^{2,3,5} in the octahedral sheet structure begin to disappear with increasing temperatures and at 500 °C the band at 925 °C disappears completely³. This dehydroxylation is followed by crystal frame work collapse and the tetrahedral sheet disorder can be seen from the broadening of the Si-O stretching bands in this 1100-100 cm⁻¹ region.

The weak shoulder band observed at 875 cm⁻¹ in the spectra of iron rich clay mineral has been attributed to Fe(AlOH) group present in the clay mineral⁶. The presence of this group indicates the persistence of the octahedral sheet structure in the clay mineral, indicating incomplete dehydroxylation and thus firing temperatures below 800 °C as at 800 °C the dehydroxylation of kaolinte minerals are completed^{1,4}. However this band is observed only in the iron rich clay minerals⁶.

With these observations regarding the thermal behavior of absorption bands at round 3600 cm⁻¹ region and at 915 cm⁻¹, an attempt is made to establish the firing temperature of the archeological potteries in the present study by FT-IR spectroscopic technique.

Infrared spectroscopy of organic substances has been studied extensively, but its application to the study of inorganic materials, particularly of minerals, is relatively less attempted. Infrared spectra act as “finger print” technique and yield information about the atomic groupings present in the sample. Infrared spectroscopy, which acts as a research tool in mineralogy, is most powerful if used in conjunction with x-ray diffraction and other

techniques. Using the infrared spectra, unique information about the group of minerals in which the specimen belongs, the degree of crystalline and non-crystalline impurities and reactions of minerals with chemicals in their environment can also inferred.

Experimental

The samples were collected from two sites Nilgiri and Perumpor of Tamilnadu, India are named as PN & PP for identification. The samples were taken at depth from soil surface to about 6 m. After removal of surface layers, the pottery shards were grounded into fine powder using agate mortar. They were sieved using a 90 μm mesh. The major and minor minerals are qualitatively determined by FT-IR technique. The Perkins Elmer -1600 series available in Indira Gandhi Centre for Atomic Research (IGCAR), Kalpakkam, Tamilnadu is made use of in the present work for recording IR spectra of the samples at room temperature. The KBr pellet technique (1:20) pellets were followed for the mineral analysis. For each samples five to six pellet specimens were prepared and the spectra were taken in the mid region of 4000-400 cm^{-1} .

Results and Discussion

The ancient potteries of FT-IR spectra show in Figure 1. The absorption frequencies of the peaks in the spectra of each sample in wave number unit (cm^{-1}) are reported in Table 1.

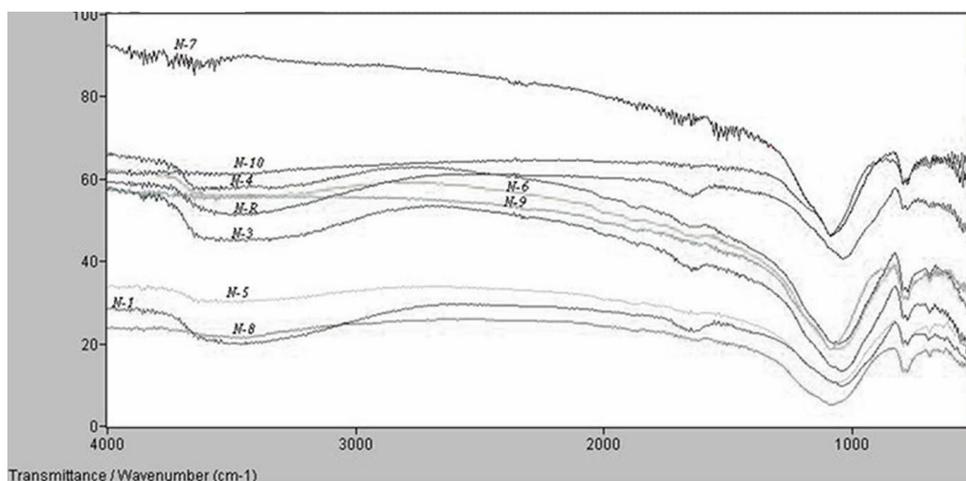


Figure 1. Typical FT-IR spectra of ancient potteries

Table 1. Observed absorption frequency in the region of 400-4000 cm^{-1}

S. No	Observed IR absorption bands (cm^{-1})
PN	405, 415, 435, 445, 475, 490, 535, 545, 580, 605, 635, 645, 675, 695, 715, 775, 795, 875, 1030, 1080, 3420, 3620, 3660, 3690
PP	405, 415, 435, 445, 475, 490, 545, 580, 635, 605, 645, 675, 715, 775, 795, 875, 1030, 1030, 1080, 1425, 3420, 3620, 3690

The assignment has been made on the basis of characteristics IR wave numbers in minerals. By comparing the observed frequencies with the available literature, the different types of inclusions were identified in the pottery samples such as quartz, orthoclase, albite, hematite, magnetite, kaolinite, calcite, gypsum, montmorillonite and illite⁷⁻⁹. The mineral wise discussion is as follows.

Quartz

Quartz is a silicate mineral. It could be observed from the Table 1. The IR absorption peaks of quartz are at 445, 695, 775 & 795 cm^{-1} may be due to the presence of quartz in the samples¹⁰⁻¹³. Out of the four peaks observed for quartz, the bands at 795-800 cm^{-1} and 775-780 cm^{-1} may be assigned symmetrical stretching modes and those at 695-700 cm^{-1} and at 445-450 cm^{-1} may be due to symmetrical bending mode and asymmetrical bending respectively. Out of these two stretching modes and two bending modes 795-800 cm^{-1} and 695-700 cm^{-1} are widely used as the diagnostic peaks for quartz.

The presence of quartz gives information about the origin of the potteries; quartz was used in piedmont for covering of engobed pottery, while kaolin was used elsewhere for the same purpose. The presence of quartz may give information about the samples comes from piedmont or not. It is not possible to state that findings showing quartz inclusions do not being piedmont area. But in the present study the largest parts quartz from the I.R studies may indicate that these samples are common origin.

Feldspar

From the spectra of the samples in this investigation, the absorption frequencies of the peaks of feldspar were measured together with the literature values. The IR absorption frequency of the bands at 405, 435, 535 and 635 cm^{-1} may suggest the presence of feldspar^{14, 15}. The peaks at 435 & 635 cm^{-1} and 405 & 535 cm^{-1} are indicating the presence of orthoclase and albite. Feldspar is a common component of clay minerals. The presence of feldspar, as a common component of potteries, does not give relevant information about the techniques used for their production.

Magnetite and hematite

Magnetite (Fe_3O_4) can be identified by band around 670 and 580 cm^{-1} which is typical spined structures. Hematite (Fe_2O_3) is observed¹⁶ by the presence of peaks at 540 and 475 cm^{-1} . The presence of magnetite and hematite provides interesting information about the firing atmosphere. Iron oxides are very influenced by the firing atmosphere; in fact they differ in colour according to firing conditions. When oxygen is almost absent in the kiln *i.e.* under reducing conditions, reduced compounds as magnetite (black colored) form, on the contrary, under the influence oxidizing conditions, the oxidized form as hematite (reddish) prevail. The presence of hematite in some findings could give further information about the provenance of the clay used for the mixture.

Calcite

This mineral is characterized¹⁷⁻¹⁹ by the presence of the peaks at 715, 875, 1085 & 1425 cm^{-1} (Table 1). The presence of calcite (CaCO_3) in the findings may occur essentially for two reasons; a low firing temperature or a post burial deposition processes. Calcite exists up to 800 °C, when the CaO formation is promoted, followed by the formation of the so-called "high-temperature crystalline phase" made of Ca-silicates or Ca-Al-silicates such as gehlenite ($\text{CaAl}_2\text{SiO}_7$), diopside ($\text{CaMgSi}_2\text{O}_6$) and anorthite ($\text{CaAl}_2\text{Si}_2\text{O}_8$). The simultaneous presence of calcareous clays of calcite and high temperature minerals clearly rules out any hypothesis of primary calcite, strengthening the assumption of a secondary origin due to deposition induced by water of the burial soil. Clearly in non-calcareous clays calcite is not expected.

Clay minerals

The presence of kaolinite, montmorillonite and illite minerals in the samples are from a group of clays. The absorption peaks appearing at 3690, 3660, 3620 and 1030 cm^{-1} in the samples were attributed to kaolinite¹⁶. The characteristic feature of kaolinite is the O-H stretching band at about 3690 and 3620 cm^{-1} which can be diagnostic distinguishing kaolinite from other clay minerals. The peak appearing at 3690 cm^{-1} is the most suitable for both qualitative and quantitative investigation. The absorption band at 3690 and 3620 cm^{-1} is attributed to the stretching vibrations of inner surface OHs and inner OH respectively.

The most distinguishing feature of the montmorillonite is the broad absorption bands at the ranges from 3300 to 3500 cm^{-1} . This band typically centered around 3400 cm^{-1} may be due to H-O-H stretching of water molecules present in the interlayer region of montmorillonite. From the Table 1, the presence of montmorillonite is shown²⁰ by the absorption bands at 3420 cm^{-1} and 470 cm^{-1} . The IR absorption bands for illite are rarely diagnostic because they are variable in chemical composition. The presence of peak at 490 and 415 cm^{-1} is attributed to illite²⁰.

The gypsum and MnO_2 is identified by the absorption peaks (Table 1) at 605 cm^{-1} and 645 cm^{-1} respectively²¹. Recently De Benedetto *et al.* reported the mineralogical compositions of ancient potteries depending upon the IR spectroscopic results. Our results are agreement with those of De Benedetto *et al.*⁸.

The IR spectra indicates that all the samples contain calcite in different amounts. Calcite is present as impurity of local clays. Observation of calcite (CaCO_3) bands allows us to draw conclusion on firing temperature. The processing temperature should be below²² the decomposition temperature of calcite that is about 700°-900 °C. According to mendelovici *et al.*⁶, the infrared absorption band around 3600 cm^{-1} is due to hydroxyl groups, which persist up to 800 °C. In the received state PP shows absorption band at 3621 cm^{-1} which indicates that samples might have been fired below 800 °C when other sample PN did not show an absorption band at 3621 cm^{-1} indicating that they would have been fired to temperature 800 °C or above.

The above results can also be confirmed with the bands at 915 cm^{-1} and 875 cm^{-1} . The band at 915 cm^{-1} is due to Al(OH) vibrations in octahedral sheet structure, which begins to disappear with increasing temperature and at 500 °C the band disappears completely. None of the samples taken for the present study showed the band at 915 cm^{-1} . This implies that all the samples were fired to the temperature above 500 °C. The broad absorption bands at 580 and 540 cm^{-1} have been attributed to magnetite and hematite¹⁶. The amount of magnetite and hematite indicates atmospheric condition of firing²³. The FT-IR spectra of PP and PN showed the absorption of hematite indicating that these samples were fired in the open air or perfectly oxidizing atmosphere at the time of manufacture.

Conclusion

Application of IR spectroscopy to ancient pottery shows great potential for understanding technological conditions implemented for production of potteries and found to give useful information about composition of potteries. Quartz, kaolinite and calcite were detected in all the samples. Spectroscopic results indicated that the potteries were fired to a temperature less than 800°C in oxidizing atmosphere.

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