P. Budhathoki et al. (2018) Int. J. Appl. Sci. Biotechnol. Vol 6(3): 238-243
DOI: 10.3126/ijasbt.v6i3.21171

ISSN (Online): 2091-2609
DOI Prefix: 10.3126/ijasbt

International Journal of Applied Sciences and Biotechnology (IJASBT)

Research Article

Assessment on the Characterization of Mineralogical Phase of Ceramic Tiles Available in Kathmandu Valley (Nepal) Using XRD and FTIR Analyses

Pramod Budhathoki[1], Gopal Paudyal[1], Rishiram Oli[1], Nirjan Duwal[2], Jagadeesh Bhattarai[1*]

[1*]Central Department of Chemistry, Tribhuvan University, GPO Box 2040, Kathmandu, Nepal
[2]St. Xavier College, Thapathali, Kathmandu, Nepal

Abstract

The mineralogical phase of eight different types of contemporary and historical ceramic tile samples used in Kathmandu valley of Nepal was analyzed using their X-ray diffraction (XRD) patterns and Fourier transform infrared (FTIR) spectra to assess their quality. Mineralogical phases existed in these eight different tile samples, i. e., three wall, three floor and two ancient tile sample specimens, used in this study are identified as quartz, feldspars, spinel, mullite and hematite including paragonite with the help of the corresponding Joint Committee for Powder Diffraction Standards (JCPDS) database files. The firing temperature applied during the time of these ceramic tiles production should be 1000° C or slightly more. The mineralogical compositions of the contemporary tile samples are found to be comparable with those of the ancient brick samples of the historical temples and monuments of Kathmandu valley of Nepal.

Keywords: Ceramic tiles; flexural strength; water absorption; porosity; XRD; FTIR

Introduction

It has been recently attracted more attention by ceramic materials than other two classes of metallic and polymeric materials in scientific community (Carter and Norton, 2007; Barsoum, 2003), because ceramic materials have advantageous physical, chemical, refractoriness, strength retention at high temperature, high melting point and good mechanical properties (Basu and Balani, 2011; Richerson, 2000; Kingery *et al.*, 1976). Ceramics are generally classified into two main groups of traditional and engineering ceramics on the basis of the field of their uses. The traditional ceramics are largely made by clay based and are typically involved low-cost fabrication processes, although the engineering ceramics are fabricated from high-purity ceramic powders and their properties can manipulate by varying process parameters. The engineering ceramics are more expensive than the traditional ceramics (Yanagida *et al.*, 1995). The traditional ceramics is a class of inorganic materials that have ionic and/or covalent bonding at high temperature (Basu and Balani, 2011; Kingery *et al.*, 1976). Historically, the use of the existing ceramic industries was dated back to 1500 BC. Early evidence of the use of clay- or pottery-based materials was found in Harappan, Chinese, Greek and many other civilizations (Basu and Balani, 2011; Richerson, 2000). One of the famous examples of the

Cite this article as:

P. Budhathoki et al. (2018) Int. J. Appl. Sci. Biotechnol. Vol 6(3): 238-243. DOI: 10.3126/ijasbt.v6i3.21171

***Corresponding author**
Jagadeesh Bhattarai,
Central Department of Chemistry, Tribhuvan University, GPO Box 2040, Kathmandu. Nepal
Email: bhattarai_05@yahoo.com

ceramics is the glazed tile which was used to decorate the wall of the famous *Tower of Babel* and the *Ishtar Gate* in the ancient *City of Babylon* about 562 BC (Basu and Balani, 2011).

The main uses of the traditional ceramics are in various fields such as structural materials, ceramic tiles, table wares, bricks and so on. The ceramic tiles are thin/thick slabs made from clays, silica, fluxes, colouring and other raw materials and they are manufactured by grinding, sieving, mixing, moistening, shaped by pressing, extruding, casting or other processes, usually at room temperature. Then, they are dried and subsequently sintered at high firing temperatures. Chemico-sintering and mechanical properties of these tile bodies vary with their mineralogical phases contains and the degree of densification at high firing temperatures and so on. Different clays and admixtures are the principal raw materials for manufacturing of various tiles (Cultrone *et al.,* 2001). The mineralogical phase composition of the raw materials used for the production of ceramic tile is one of the main indicators of components selection for its final products. On the other hand, the mineralogical study of the clay-based tiles is one of the widely accepted tools for the approximate determination of their firing temperatures. In this context, present research work was focused to characterize the mineralogical phases developed in the fired-tile samples collected from local vendors of Kathmandu valley using XRD and FTIR techniques.

Materials and Methods

Total eight wall, floor and ancient ceramic tiles of different brands were collected from local tile dealers and two historical temple sites of Kathmandu valley were collected to carry out the present work. A small broken piece of each tile samples without glaze was thoroughly hand grounded to fine powder in agate mortar to make powder for XRD and FTIR analyses.

Mineralogical phase characterization of the ceramic tile samples was carried out at Nepal Academy of Science and Technology (NAST), Khumaltar, Lalitpur using XRD analysis on a D8 Advanced Diffractometer (Bruker, Germany) with Cu Kα radiation (λ = 0.15418 nm) at a scanning speed of 2°/minute in 2θ mode between 10° and 70°. Major and minor phases present in the tile bodies were identified from their basal spacing (d-spacing) values using corresponding JCPDS (Joint Committee on Powder Diffraction Standards) database files (JCPDS, 1999). The sample powder was loaded in a sample holder in a randomly orientated way to minimize preferred orientations of clay minerals. Characterization of the tile specimens were qualitatively determined using FTIR-A217053 and spectra was recorded at NAST using KBr pellet.

Results and Discussion

Identification of the mineralogical phases present in tiles by XRD patterns is relatively easy, although several factors make complication for accurate phase identification (Berry, 1994; Chung and Smith, 1974). Figures 1, 2 and 3 show the XRD patterns of the powder form of three different types of wall (TW-6, TW-13 and TW-37), floor (TF-2, TF-21 and TW-36) and ancient (TA-33 and TA-34) tile samples, respectively, collected from local vendors and historical temples of Kathmandu valley. The mineralogical phases present in all eight selected ceramic tile samples are identified as quartz, feldspars, spinel, mullite and hematite including paragonite in TF-21 sample (Fig. 2) with the help of the corresponding JCPDS database files (JCPDS, 1999).

The disappearance of feldspars diffraction peaks and appearance of spinel and mullite peaks is comparatively more pronounced in four tile samples of TF-2, TF-36 (Fig. 2), TA-33 and TA-34 (Fig. 3) than remaining other four tile samples of TW-6, TW-13 and TW-37 (Fig. 1). The result indicates that the firing temperature of these eight tile samples should not be same. It was reported that a spinel phase was appeared in ceramic bodies after fired at above 900°C and then the primary mullite phase begin to develop at about 1000–1100°C with diminishing XRD peaks of the spinel phase and finally well shaped mullite crystals was reported at firing to 1200°C or high temperatures (Ghorbel *et al.*, 2008; Bellotto *et al.*, 1995; Brindley and Nakahira, 1995; Sonuparlak *et al.*, 1987). However, the mullite phase in these eight tile samples analyzed in present is not well crystalline form. Consequently, it can be said that all the analyzed tile samples used in this study should be fired at high temperature of 1000°C or slightly high.

The development of miner with major mineralogical phases due to the impurities of clay raw materials have been reported a negative effect on the physico-sintering and mechanical properties of the fired ceramic bodies (El Nouhy, 2013). The XRD peak for hematite is mostly due the impurity of iron oxide in the tile making raw materials which is observed in all eight tile samples. However, there is no sign of the presence of calcite and dolomite phases in the presently analyzed all tile samples and the presence of spinel, mullite and residual forms of quart indicated that these tile samples should have good physico-sintering and mechanical properties which had reported by the present authors (Chapagain, 2017). It was reported that the mechanical strength of the ceramic bodies was due to the formation of mullite, residual quartz content and its particle size (Sokolár *et al.*, 2012; Traore *et al.*, 2007). In general, the mechanical properties of the tiles are worsening in presence of undesired phases observed in XRD patterns of the fired ceramic tiles. Therefore, it is assumed that the flexural strength of the fired tile bodies depends on their composition and void developed during the sintering at high temperature (Cultrone *et al.*, 2005; Tite *et al.*, 2001).

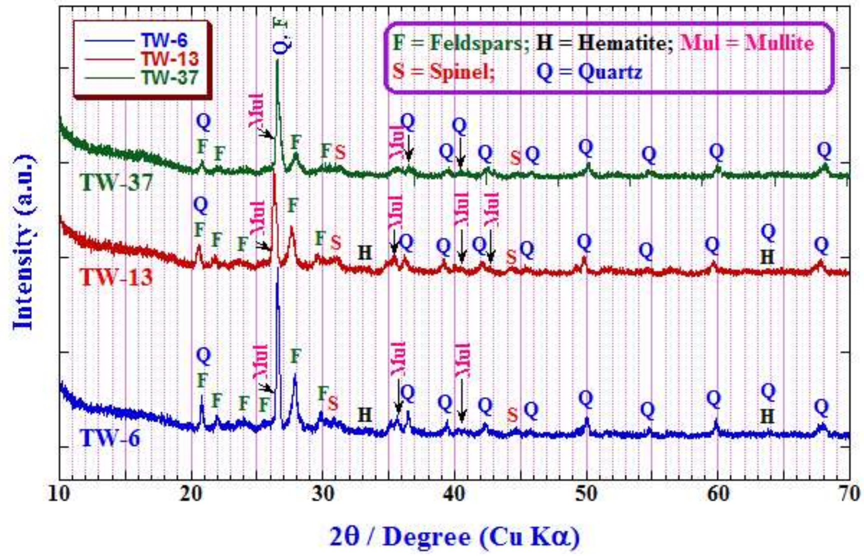

Fig. 1: XRD patterns of the contemporary wall tile samples of Kathmandu valley

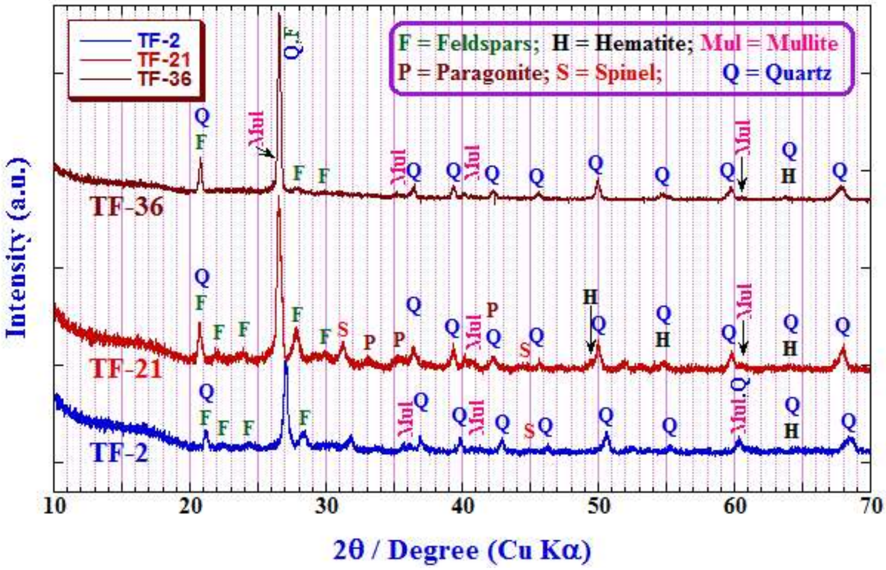

Fig. 2: XRD patterns of the contemporary floor tile samples of Kathmandu valley

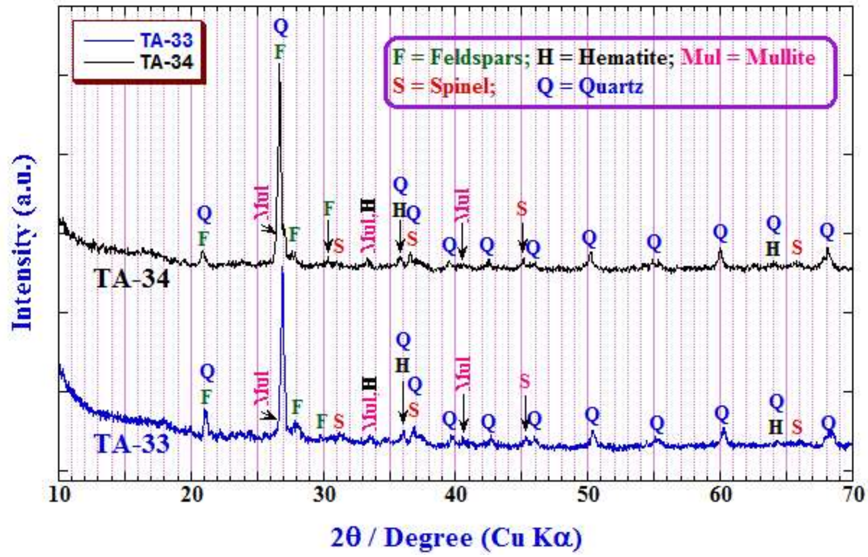

Fig. 3: XRD patterns of the ancient floor tile samples of the archaeological sites of Kathmandu valley

The FTIR spectra of some selected six tile samples were recorded to evaluate their mineralogical phases which are depicted in Fig. 4. The absorption peaks between 3750 and 3500 cm^{-1} are diminished and a broad absorption peak in the range of 3435–3450 cm^{-1} was clearly observed in the FTIR spectra of all the analyzed tile samples. It was reported that a broad band near 3420-3480 cm^{-1} represents to the OH stretching vibration along with a weak and medium absorption band at 1620-1650 cm^{-1} is typical absorbance band of adsorbed water molecule (Bantignies *et al.*, 1997). Hence, the broad band at 3435-3450 cm^{-1} for the aforementioned tile bodies is attributed to OH stretching vibration of hydroxide in the analyzed samples. This absorption band region is always accompanied by an absorption band at 1620 and 1626 cm^{-1} assigned to H-O-H bending of adsorbed water molecules.

In general, broadening of the FTIR spectra is also influenced the firing temperature range of the ceramic bodies such as ceramic tiles. Higher the firing temperature applied during the production of the tiles bodies, more broadening of the FTIR spectra of the tile samples at the region of the OH stretching vibration of hydroxide. It is clearly observed that the degree of broadening of the FTIR spectrum in the range of 3200-3700 cm^{-1} is almost same for all analyzed tile samples except TA-33 and TA-34 as shown in Fig. 4. This is probably due to the use of higher firing temperature at the time of manufacturing of the TA-33 and TA-34 than other four tile samples. The absorption peaks at 2359 and 2327 cm^{-1} should be affected by the measurement condition error, probably due to the room CO_2 gas. The similar result was reported in previous research works also (Alabarse *et al.*, 2011; Smith 1996).

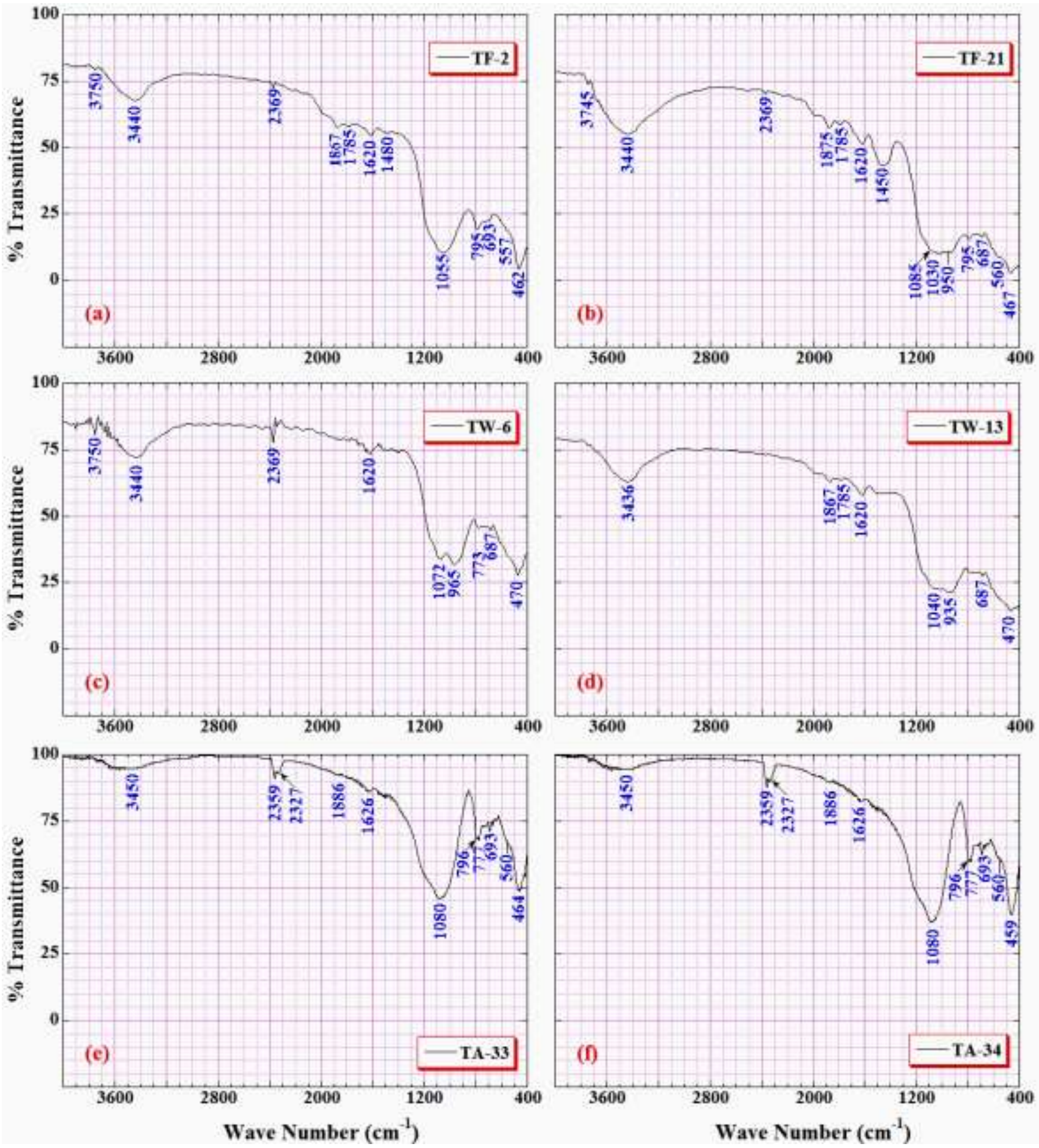

Fig. 4: FTIR spectra of contemporary floor tile (a & b), wall tile (c &d) and ancient floor tile (e & f) samples of Kathmandu valley

The FTIR spectra of all these fired clay brick samples show that they are mainly composed of quartz (796-773, 693-687 and 469–470 cm^{-1}). The absorption peak at 796-773 region became more intense for three tile samples of TF-2, TA-33 and TA-34 as shown in Figs 4 (a), 4 (e) and 4 (f) than other three tile samples analyzed here. It is meaningful for mentioning here that the previous research work reported a FTIR absorption peak chosen at around 779 cm^{-1} to be more suitable for qualitative amount of quartz in clay bodies (Reig *et al.*, 2002). On the other hand, the presence of feldspar can be explained by Si–O–Al compounded vibrations at 775–780 cm^{-1}. These assignments are in good agreement with that previously reported for quartz and feldspar (Hlavay, 1978). On the other hand, there is a weak and very broad absorption peak in the range of 550–545 cm^{-1} in the tile samples indicated that the fired tile bodies available in Kathmandu valley contains a trace amounts of hematite. The similar result of the FTIR absorption peak at 540-550 cm^{-1} due to the presence of hematite in the fired ceramic bodies was reported in previous works also (Velraj *et al.*, 2009a, 2009b).

Conclusions

The mineralogical phases present in six contemporary ceramic tiles available in Kathmandu valley and two ancient ceramic tile samples from the historical temples of Bhaktapur and Patan were characterized using XRD and FTIR techniques in this study. Following conclusions are drawn from the above results and discussion.

I. Mineralogy phases present in the ceramic brick samples are found to be composed mainly of quartz, feldspars, spinel, mullite, paragonite and hematite based on the XRD patterns and FTIR spectra analyses.

II. It can be assumed that the disappearance of diffraction peaks for feldspars and appearance of mullite peaks through the alumina-rich spinel phase in all eight brick samples used in this study indicated that the firing temperature of these bricks should be around 1000°C or high.

Acknowledgement

The University Grants Commission-Nepal (UGC-Nepal) is highly appreciated for awarding the Faculty Research Grant-2072/073 to conduct this research work.

References

Alabarse FG, Conceicao RV, Balazaretti NM, Schento F and Xavier AM (2011) In-situ FTIR analyses of bentonite under high pressure. *Appl Clay Sci* **51(1/2):** 202–208. DOI:10.1016/j.clay.2010.11.017

Bantignies JL, dit Moulin CC and Dexpert H (1997) Wet ability contrasts in kaolinite and illite clays: Characterization by infrared and X-ray absorption spectroscopy. *Clays Clay Miner* **45(2):** 184–193. DOI:10.1346/CCMN.1997.0450206

Barsoum MW (2003) Fundamentals of Ceramics. Taylor & Francis, Boca Raton, USA.

Basu B and Balani K (2011) Ceramics: Definition and Characteristics, in Advanced Structural Ceramics. 1st edition, The American Ceramic Society, John Wiley & Sons Inc., pp. 1–13, New York, USA.

Bellotto M, Gualtieri A, Artioli G and Clark SM (1995). Kinetic stud of the kaolinite-mullite reaction sequence. Part I: Kaolinite dehydration. *Phy Chem Miner* **22(4):** 207-217. DOI:10.1007/BF00202253

Berry IG (1974) Selected Powder Diffraction Data for Mineralogy. Joint Committee on Powdered Diffraction Standard, Swanshmore, USA.

Brindley GW and Nakahira M (1959) The kaolinite-mullite reaction series-III: the high temperature phases. *J Am Ceram Soc* **42:** 319-324. DOI:10.1111/j.1151-2916.1959.tb14316.x

Carter CB and Norton MG (2007) Ceramic Materials. Springer, New York, USA.

Chapagain YP (2017) Study on the physic-mineralogical, sintering and mechanical properties of bricks of Kathmandu valley. M. Sc. Dissertation, Central Department of Chemistry, Tribhuvan University, Kathmandu, Nepal.

Cheng H, Liu Q, Yang J, Ma S and Frost RL (2012) The thermal behavior of kaolinite intercalation complexes-a review. *Thermochimica Acta* **545**: 1–13. DOI:10.1016/j.tca.2012.04.005

Chung FH and Smith DK (1974) A Hand Book of Industrial Applications of X-ray Diffraction. Marcel Dekker, Inc., New York, USA.

Cultrone G, Rodriguez-Navarro C, Sebastian E, Cazalla O and La Torre MJD (2001) Carbonate and silicate phase reactions during ceramic firing. *Eur J Miner* **13**: 621–634. DOI:10.1127/0935-1221/2001/0013-0621

Cultrone G, Sebastian E and de la Torre MJ (2005) Mineralogical and physical behavior of solid bricks with additives. *Con Build Mater* **19(1):** 39–48. DOI:10.1016/j.conbuildmat.2004.04.035

El Nouhy HA (2013) Assessment of some locally produced Egyptian ceramic wall tiles. *HBRC Journal* **9(3):** 201–209. DOI:10.1016/j.hbrcj.2013.08.001

Farmer VC (2000) Transverse and longitudinal crystal modes associated with OH stretching vibrations in single crystals of kaolinite and dickite. *Spectrochimic Acta; Part-A: Mol Biomol Spectro* **56(5)**: 927–930. DOI:10.1016/S1386-1425(99)00182-1

Ghorbel A, Fourati M and Bouaziz J (2008) Microstructural evolution and phase transformation of different sintered kaolins powder compacts. *Mater Chem Phy* **112(3):** 876–885. DOI: 10.1016/j.matchemphys.2008.06.047

Hlavay J, Jonas K, Elek S and Inczedy J (1978) Characterization of the particle size and the crystallinity of certain minerals by IR spectrophotometry and other instrumental methods-

II; Investigations on quartz and feldspar. *Clays Clay Miner* **26(2)**: 139–143. DOI:10.1346/CCMN.1978.0260209

JCPDS (1999) Joint Committee on Powder Diffraction Standards.

Kingery WD, Bowen CR and Uhlman A (1976) Introduction to Ceramics. 2nd edition, John Wiley & Sons Inc., New York, USA.

Reig FB, Gemino-Adelantado JV and Moya Moreno M C (2002) FTIR quantitative analysis of calcium carbonate (calcite) and silica (quartz) mixtures using the constant ratio method: application to geological samples. *Talanta* **58(4)**: 811–821. DOI:10.1016/S0039-9140(02)00372-7

Richerson DW (2000) Magic of Ceramics. Wiley-American Ceramic Society, Westerville, USA.

Smith BC (1996) Fundamentals of Fourier Transform Infrared Spectroscopy. pp 28-30, CRC Press LLC, New York, USA.

Sokolár R, Vodova L, Grygarova S, Štubňa I and Šín P (2012) Mechanical properties of ceramic bodies based on calcite waste. Ceram Inter **38(8)**: 6607–6612. DOI:10.1016/j.ceramint.2012.05.046

Sonuparlak B, Sarikaya M and Aksay IA (1987) Spinel phase formation during the 980°C exothermic reaction in the kaolinite-to-mullite reaction series. *J Am Ceram Soc* **70(1):** 837-42. DOI:10.1111/j.1151-2916.1987.tb05637.x

Tite MS, Kilikoglou V and Vekinis G (2001) Strength, toughness and thermal shock resistance of ancient ceramics and their influence on technological choice. *Archaeo* **43(3):** 301–324. DOI:10.1111/1475-4754.00019

Traore K, Ouédraogo GV, Blanchart P, Jernot J–P and Gomina M (2007) Influence of calcite on the microstructure and mechanical properties of pottery ceramics obtained from a kaolinite-rich clay from Burkina Faso. *J Eur Ceram Soc* **27(2–3)**: 1677–1681. DOI: 10.1016/j.jeurceramsoc.2006.04.147

Velraj G, Janaki K, Musthafa AM and Palanivel R (2009a) Spectroscopic and porosimetry studies to estimate the firing temperature of some archaeological pottery shreds from India. *Appl Clay Sci* **43(3):** 303–307. DOI:10.1016/j.clay.2008.09.005

Velraj G, Janaki K, Musthafa AM and Palanivel R (2009b) Estimation of firing temperature of some archaeological pottery shreds excavated recently in Tamilnadu, India. *Spectrochimica Acta Part-A: Mol Biomol Spectro* **72(4):** 730–733. DOI: 10.1016/j.saa.2008.11.015

Yanagida H, Koumoto K and Miyayama M (1995) The Chemistry of Ceramics. John Wiley & Sons Inc., New York, USA.