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INVESTIGATION ON THE MINERALOGICAL PHASE OF ANCIENT BRICK SAMPLES OF KATHMANDU VALLEY (NEPAL) USING XRD AND FTIR ANALYSIS

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ABSTRACT
The total eight clay brick samples including five archaeologically importance samples from different historical sites and three samples from more than a century old buildings of Kathmandu valley were collected and their mineralogical phases were characterized using X-ray diffraction and Fourier transform infrared spectroscopic methods in this study. Mineralogical phases existed in these archaeological and ancient clay bricks are identified as quartz, feldspars, spinel, muscovite, margarite and hematite in accordance with the powder diffraction standard files. The degree of the disappearance of feldspars phase and appearance of the spinel phase in all the brick samples is found to be different indicating that the firing temperature applied to produce these brick specimens should not be same. The firing temperature applied for the production of the eight clay brick samples should be in the range of 900°-1000° C. Most of the archaeological clay brick samples used in this study should be produced by firing at the high-temperature comparison with those brick samples used in old buildings of Kathmandu valley.
Keywords: Archaeological brick, Characterization, X-ray diffraction, FTIR, Quartz, Feldspars

INTRODUCTION
Brick is one of the men made the oldest structural materials and it has been widely used all most all countries of the world mainly due to easy availability of its raw materials in the world. It was reported that different properties of the clay bricks depended on the mineralogy of the clay materials used to manufacture it, the manufacturing process and firing temperature[1]. The fired clay bricks are extremely durable and hence, there have been numerous archaeological masonry buildings standing for centuries as a testimony of the survival of the clay-based fired bricks. In general, clay bricks are classified into various groups based on their mineralogy. Previous research works also reported that the main factors to manufacture such type of bricks are clay raw material types and the firing temperature during their production that affects the quality and durability of bricks.[2-5]
The clay brick is used extensively in the construction industry all over the world. The global brick production is estimated at about 1.5 trillion annually[6] and Asian countries only account about 89-90 % of the global production, i. e., about 1.35 trillion bricks[7]. The clay brick production in Kathmandu valley is estimated more than 3.3 billion units[8] and with increasing demands of the clay bricks for the construction industry, bricks quality and cost become more important nowadays. The brick manufacturing techniques were depended on the supervisors and it was considered as the hereditary gifted knowledge passed on to generations from their forefathers[9]. This is the main reason that the knowledge about the ancient ceramic materials and their application techniques which were so successfully used in the past has now disappeared without any documentation in our part of the world. Furthermore, the mineralogical phase characterization of the historical bricks provides valuable information for restoration purposes to formulate new specific bricks using available raw materials. The clay brick is mostly homogeneous, harder and stronger due to the ceramic bond from the sintering phase of the silica and alumina clay

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constituents. It is reported that the brick was used as a fundamental building material since the Mesopotamian, Egyptian and Roman period[10]. It is known that the properties of the archaeological clay brick rely essentially on the properties of the brick units, which depend on the quality of the raw materials used, together with the manufacturing process technology. Numerous historical brick buildings have been existed until the 21st century, which testifies to the strength of such ancient brick materials along centuries of rain storms, snow, thaw-freezing cycles, high temperatures and human-induced deterioration. A large number of studies have been reported about the ancient brick structures and materials to foster their cultural and economic importance as well[11-19].

The archaeological clay bricks preservation has given rise to considerable interest of scientists, architects, engineers and archaeologists recently, because the archaeological masonry needs to be restored with the substitution of bricks when they damage. A good characterization of such archaeological clay brick specimens gives us a possibility to predict advance the chemico-mineralogical phases, physico-sintering and mechanical behavior of the newly formed building system. To learn about the historical understanding is not just to analyze and preserve such archaeological objects but also to investigate and understand the knowledge and skills used to produce and use them[20].

It was reported that the firing temperature was one of the key controlling factors of the physicomechanical properties of the bricks, not so much affected by firing time[21]. The physicomechanical properties of the bricks vary with their mineralogical phases and the degree of densification at high firing temperatures and so on. The mineralogical phase composition of the clay raw materials used for brick production is one of the main quality indicators of its final products. Hence it is considered that the mineralogical phase analysis of the clay-based bricks is one of the widely accepted tools for the approximate estimation of their firing temperature range, physico-sintering properties and durability so on. In this context, the main objectives of the present research work were to characterize the mineralogical phases developed in the ancient brick samples collected from historical sites of Kathmandu valley using X-ray diffraction (XRD) and Fourier transform infrared (FTIR) spectroscopic methods and also to understand the knowledge and skills used to produce these brick samples.

EXPERIMENTAL

Total eight clay brick samples including five archaeological brick samples from different historical sites and more than a century old three brick samples used in ancient buildings of Kathmandu valley were collected to carry out their mineralogical phase characterization in the present study. The detail descriptions of these eight clay brick sample specimens are summarized in Table-1.

Table-1: Description of the Clay Brick Samples

S. No.	Sample Name	Location of Brick Sampling Site	Brick Types
1	CTB-1	Ghanta Ghar (Clock Tower) Building	Historical
2	DTB-2	Dharaharaa (Kathmandu Tower) Building	Historical
3	BDB-3	Basantpur Darbar Square	Historical
4	RTB-4	Balgopaleshwor Temple (Ranipokhari)	Historical
5	BTB-5	Baghbhairav Temple (Kirtipur)	Historical
6	TOB-6	Tripureshwor	Ancient
7	POB-7	Patan (Mangal bazaar)	Ancient
8	KOB-8	Kirtipur (Panga)	Ancient

A small broken piece of each brick samples was thoroughly hand grounded in an agate mortar to make a fine powder for XRD and FTIR analyses as described elswhere[22]. Mineralogical phase characterization of the clay brick 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 CuKα radiation (λ = 0.15418 nm) at a scanning rate of 2°/minute in 2θ mode between 10° and 70° as described elswhere[22, 23]. The powder form of the brick sample was loaded in a sample holder in a random orientation to minimize the preferred orientations of the clay materials for XRD analysis. Mineralogical phases present in the selected eight brick powders were identified from their basal spacing (d-spacing) in accordance with Joint Committee for Powder Diffraction Standards (JCPDS) database files[24]. The prepared powder form of each brick sample was loaded in an XRD sample holder in a randomly orientated way to minimize preferred orientations of clay minerals. In addition, FTIR spectra of these eight archaeological and old brick samples were recorded in a wide range of wave number from 400 to 4000 cm^{-1} by using both the FTIR-A217053 at NAST and the IR-Tracer-100 (Shimadzu, Japan) in Central Department of Chemistry, Tribhuvan University, Kirtipur to know their mineralogical compositions.

RESULTS AND DISCUSSION

The use of XRD patterns of the ceramics like brick bodies is one of the relatively easy methods to identify their mineralogical phases, although several factors make complication for accurate phase identification from overlapping the peak values[25,26]. XRD patterns of the powder form of five different archaeological brick samples of different historical sites and three ancient (more than a century old) brick samples of local buildings collected from different parts of Kathmandu valley are shown in Fig.-1 and 2, respectively. The common mineralogical phases present in all eight clay brick samples are quartz, feldspars, spinel and hematite in CTB-1, RTB-4, BTB-5 brick samples including muscovite type of mica mineral phase in samples of BDB-3, TOB-6, POB-7 and KOB-8 (Fig.-1 and 2) and the mineralogical phase of margarite specially in the brick samples of DTB-2 and BDB-3 (Fig.-1) with the help of the corresponding JCPDS database files[24]. The disappearance of feldspars diffraction peaks and appearance of the alumina-rich spinel phase is comparatively more pronounced in four archaeological brick samples of CTB-1, DTB-2, BDB-3 and BTB-5 (Fig.-1) than other three ancient brick samples of TOB-6, POB-7 and KOB-8 (Fig.-2) including one archaeological brick sample of RTB-4 (Fig.-1).

These results indicated that the firing temperature of these eight brick samples should not be the same. Furthermore, XRD patterns of three old brick samples of TOB-6, POB-7 and KOB-8 (Fig.-2), and one archaeological brick sample of BDB-3 (Fig.-1) show clearly the muscovite type of mica minerals with a residual form of quartz, feldspars and less amounts of spinel phase including hematite, although remaining other four archaeological clay brick samples have developed well-formed alumina-rich spinel phase in additions of residual quartz, feldspars and hematite. These results revealed that four archaeological clay brick samples except BDB-3 sample should be produced by firing at higher temperature range as a comparison with other remaining four clay brick samples as mentioned above.

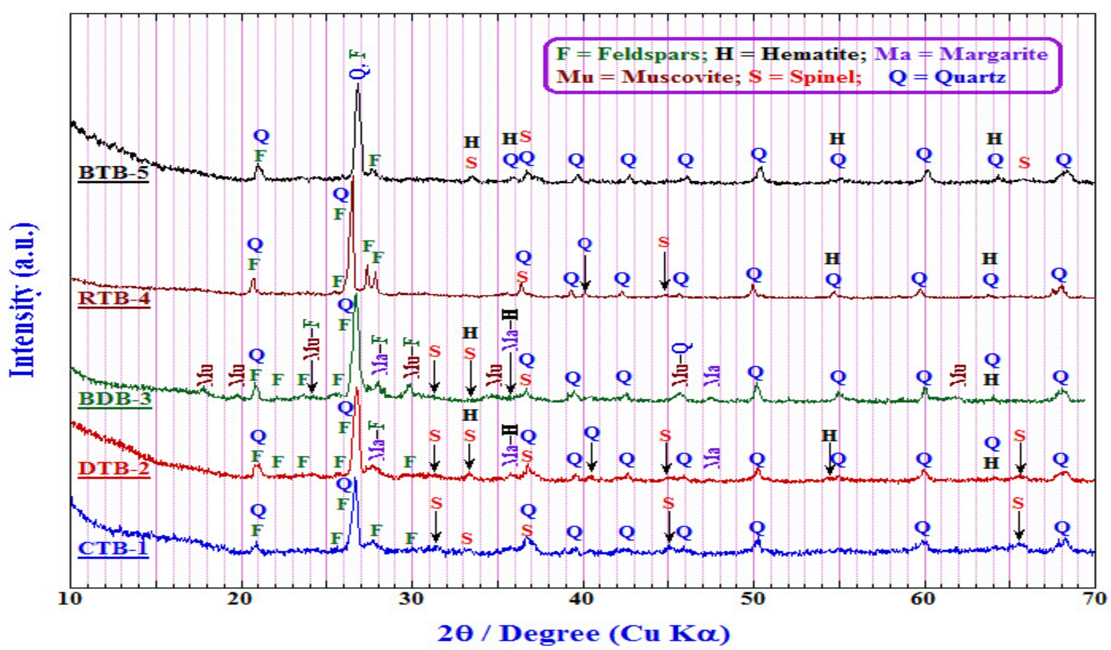

Fig.-1: XRD Patterns of the Archaeological Brick Samples from Different Historical Sites of Kathmandu Valley

An alumina-rich spinel and primary mullite phases were developed at above 900°C and about 1000–1100°C, respectively, while such phases were completely diminished by forming a well-shaped mullite crystals at 1200°C or high firing temperatures.[27-29] However, these eight brick samples used in this study did not show the development of even primary mullite phase from XRD analysis. Consequently, it can be said that all the analyzed archaeological and ancient bricks might be produced at the firing temperatures between 900° to 1000°C. The development of miner phases due to the impurities like hematite, calcite and dolomite so on in ceramic raw materials were reported a negative effect on the physico-sintering and mechanical properties of the fired clay bodies[30-36]. The XRD peak for hematite is mostly due to the impurity of iron oxide and no sign of the presence of calcite and dolomite phases in all eight archaeological and ancient clay brick samples indicates that the worsening of the mechanical properties of these brick samples generally expected mostly due to the presence of undesirable phase of hematite only in these brick samples. It is significant to mention here that the presence of hematite in ceramic bodies of tile samples showed the adverse effects in their physicomechanical properties like water absorbtivity, apparent porosity, bulk density and flexural strength[30].

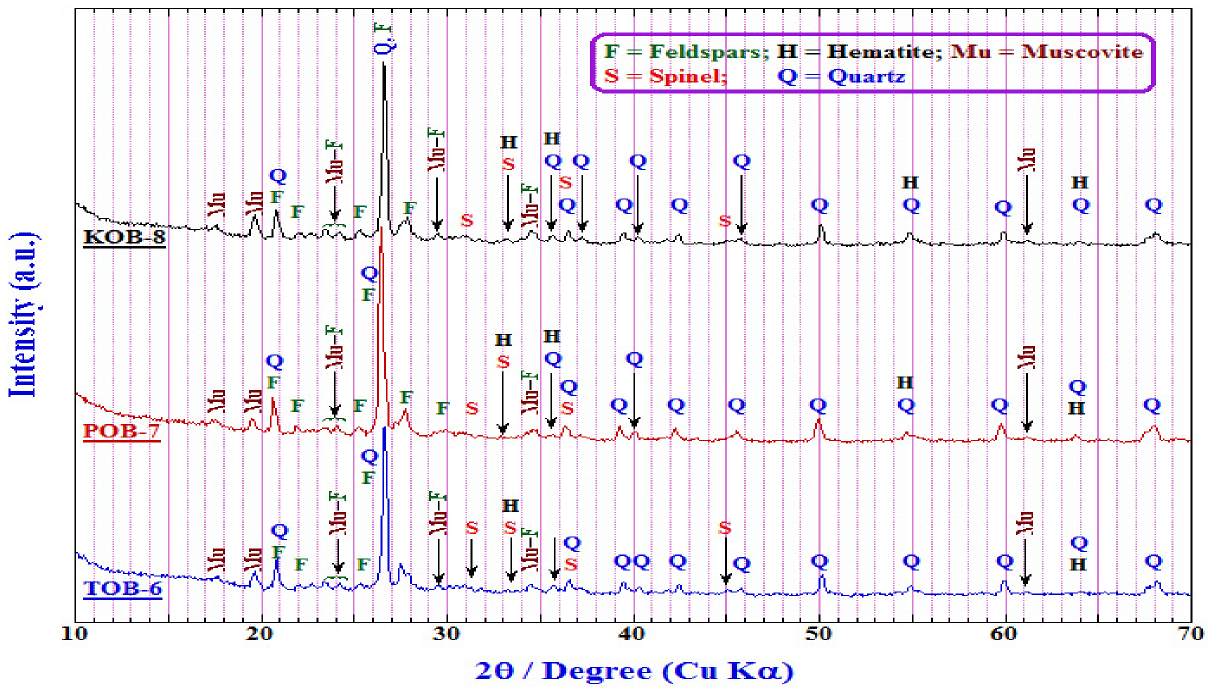

Fig.-2: XRD Patterns of a Century Old Brick Samples Collected from Different Parts of Kathmandu Valley

Figure-3 shows the recorded FTIR spectra of the six selected brick samples for their mineralogical phase characterization. The peak between 3800 and 3400 cm^{-1} for the archaeological and ancient brick samples except for one sample (i. e., DTB-2) is disappeared as sown in Fig.-3(b). A very broad absorption peak at 3470 cm^{-1} is clearly observed for the brick sample DTB-2 which is assigned to OH stretching vibration of hydroxide in the brick sample. This absorption band region is accompanied by an absorption band at 1640 cm^{-1} assigned to O-H bending and this FTIR peak is found to be more pronounced for the DTB-2 sample than other five brick samples as shown in Fig.-3.

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 due to the presence of adsorbed water molecule.[37-39] However, the absorption bands in these two wavelength regions are nearly diminished, because the broadening of the FTIR spectra of the brick samples should generally be influenced by the firing temperature applied during their production and hence it can be assumed that the firing temperature used to produce the brick sample of DTB-2 should be lowered than that of other brick samples analyzed in this study. The FTIR absorption peak at 2955 cm^{-1} particularly for the brick samples BDB-3, TOB-6 and KOB-8 as depicted in Fig.-3(c), 3(e) and 3(f), respectively, indicated that these three brick samples should contain a small amount of organic matters which is appeared to diminish by firing at about 1000 °C or high temperature. The similar observation was reported in previous research works also[40]. The strong band at 1015–1054 cm^{-1} attributed to the Si–O stretching vibration of the tetrahedral sheet of the fired brick samples.[39-41]

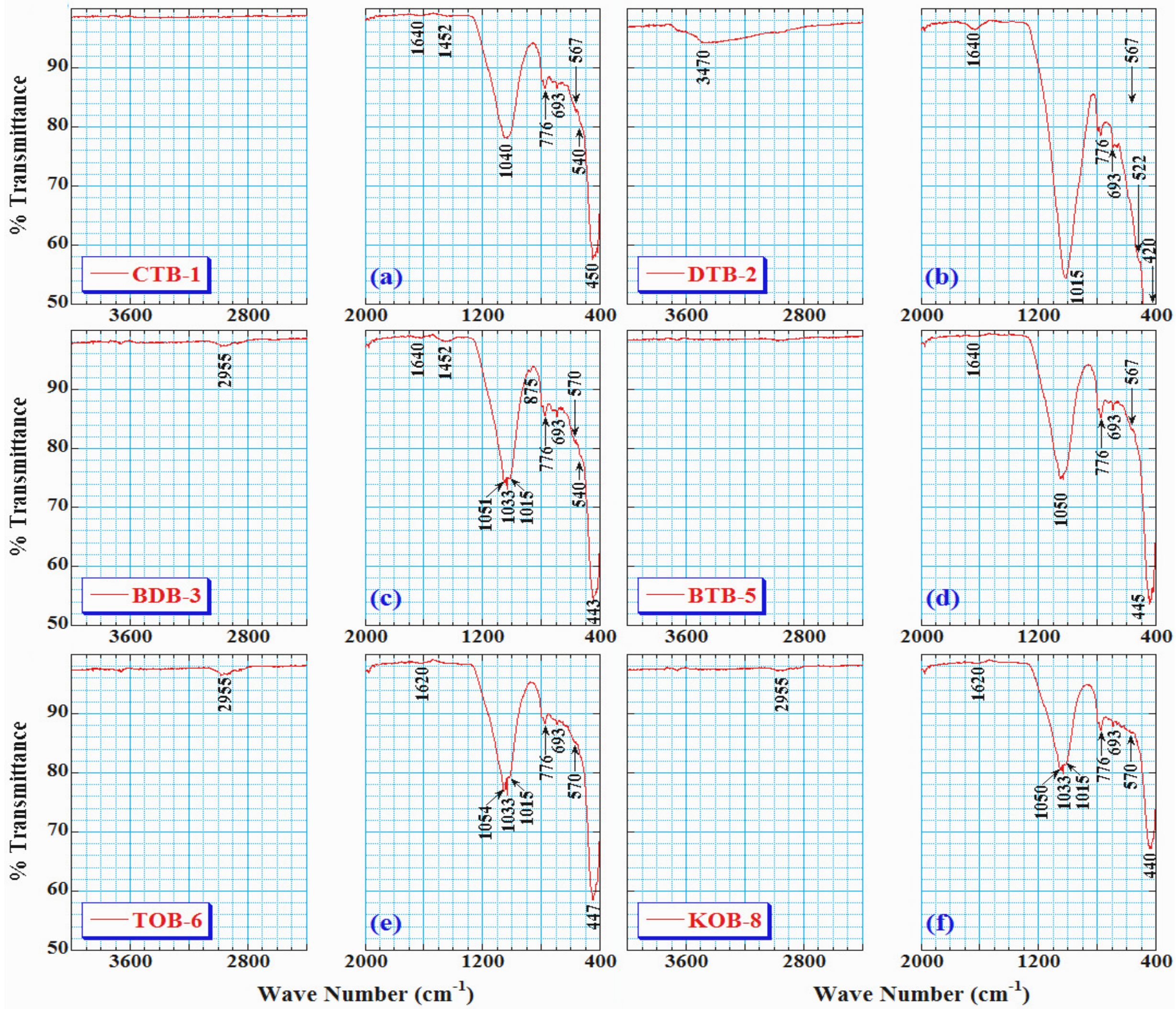

Fig.-3: FTIR Spectra of Four Archaeological (a-d) and Two Ancient (e and f) Brick Samples of Kathmandu valley

The FTIR spectra of all these six archaeological and ancient clay brick samples show that the absorption peaks at 796-776, 693 and 420–450 cm^{-1} are mainly of quartz. It is meaningful for mentioning here that the previous research work was reported an FTIR absorption peak chosen at around 779 cm^{-1} to be more suitable for quantitative amounts of quartz in clay bodies[42]. On the other hand, the presence of feldspar can be explained by Si–O–Al compounded vibrations at 775–780 cm^{-1} and these assignments are in good agreement with that previously reported results[43]. Similarly, there is a weak and very broad absorption peak in the range of 550–545 cm^{-1} in all the brick samples analyzed here indicated that the fired bricks available in Kathmandu valley contain 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.[22,23,44]

CONCLUSION

The mineralogical phases of five archaeological bricks from five different historical places and more than century-old three ancient brick samples of Kathmandu valley were characterized using their XRD patterns and FTIR spectra analysis in this study. Following conclusions are drawn based on the results and discussion.

i. Mineralogy phases in the analyzed brick samples are found to be composed mainly of quartz, feldspars, spinel with muscovite, margarite and hematite from XRD and FTIR analyses.

ii. The disappearance of diffraction peaks of feldspars and appearance of the alumina-rich spinel phase in all eight brick samples indicated that the firing temperature of these bricks should be around 900°-1000° C.

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