Available online at www.sciencedirect.com
ScienceDirect
Ceramics International 36 (2010) 909–916
CERAMICS INTERNATIONAL
www.elsevier.com/locate/ceramint

Pyrophyllite as raw material for ceramic applications in the perspective of its pyro-chemical properties

T.K. Mukhopadhyay *, S. Ghatak, H.S. Maiti

Central Glass & Ceramic Research Institute, Council of Scientific & Industrial Research, Kolkata 700032, India

Received 19 February 2009; received in revised form 4 September 2009; accepted 19 October 2009
Available online 20 November 2009

Abstract

General pyro-chemical properties of pyrophyllite were studied using one Indian variety as sample. In addition to normal routine analysis, thermal expansion, infrared spectroscopy, DTA, XRD and SEM studies were also employed to understand the pyro-chemical properties of the specimen at different temperatures. The results indicate that the specimen contains pyrophyllite as major phase with sericite, quartz and diaspore as minor phases. Unlike kaolinite, pyrophyllite contains low alumina and high silica which on heating mainly produces mullite and amorphous silica. Mullite crystallization from pyrophyllite is rather easy than that from kaolinite. The silica in turn yields large amount of viscous liquid at high temperature. It is suggested that pyrophyllite may be utilized in such compositions favourably where mullite is a desirable phase by partial replacement of china clay which is a viable alternative particularly in the background of depleting reserves of kaolinite and its continuous cost escalation. Additionally amorphous silica produced in the reaction system may acts as an in situ produced filler material that reduces the use of quartz in such system.

Keywords: Pyrophyllite; XRD; SEM

1. Introduction

Pyrophyllite is a chemically inert hydrous alumino-silicate $Al_2O_3{\cdot}4SiO_2{\cdot}H_2O$ [$Al_2Si_4O_{10}(OH)_2$], composed of 67% SiO_2, 28% Al_2O_3 and 5% H_2O. It is an early stage metamorphic mineral and is actually quite common. Pyrophyllite is largely an overlooked raw material available in huge quantities in nature. This is mainly due to the fact that other comparable alumino-silicate raw materials like china clay are available in much purer form.

Huge reserves of pyrophyllite is found in various parts of the globe among which the most important locations are USA, New Zealand, China, South Africa, Australia, Brazil, etc. In India, pyrophyllite mineral is found mainly in the states of Uttar Pradesh, Madhya Pradesh and Maharashtra [1,2]. An estimated reserve of 1.0 million tons of pyrophyllite is available only in Maharashtra. The mineral is extensively used as filler in rubber, paper, soap, cosmetics, asbestos products and insecticides; however, use of pyrophyllite in ceramic industries is very much restricted.

Studies on pyrophyllite have been carried out by several investigators throughout the world, although its use as a ceramic raw material is not yet widely accepted. This is probably due to the fact that the mineral seldom occurs in pure state like kaolinite and the characteristics of associated minerals (quartz, kyanite, sericite, diaspore) can influence its properties and behaviour. Literature indicates that most investigators studied the properties of pyrophyllite and its utilization based on well-known sources, i.e. pyrophyllite from Hillsboro, NC, USA [3], Coromandel Peninsula, New Zealand [4], and from coastal region of Southeast China [5].

Most of the investigations on pyrophyllite were confined to its utilization in whiteware body as a replacement of quartz, clay or feldspar [6–15]. However, there is little information regarding thermal transformation of pyrophyllite mineral. Bradley and Grim [16] and later Heller [17] studied the thermal transformation of pyrophyllite to mullite. Nakahira and Kato [18] also studied the thermal reactions of pyrophyllite by transmission electron microscopy (TEM). The investigations were carried out to evaluate the crystallographic structure of

* Corresponding author.
E-mail address: tapas@cgcri.res.in (T.K. Mukhopadhyay).

0272-8842/$36.00 © 2009 Published by Elsevier Ltd and Techna Group S.r.l.
doi:10.1016/j.ceramint.2009.10.026

pyrophyllite and its dehydroxylate. Kersey and Jerner [19] studied the mechanical properties of pyrophyllite as a function of firing temperature up to 1050 °C in air as well as in hydrogen atmosphere and tried to correlate the properties with microstructure. Sanchez-Soto et al. [20] studied the effect of mechanical treatment on pyrophyllite followed by thermal treatment. They concluded that there was possible segregation of amorphous silica and that mullite formation was rapid at lower temperature. Scanning electron microscope (SEM) studies were used by the same researchers [21] to understand different morphologies developed when pyrophyllite was progressively transformed by heating. However, very little information about the thermal transformations of pyrophyllite over a range of temperatures has been published with particular emphasis on thermo-mechanical properties as well as the content and crystallinity of mullite.

In our earlier communications one particular variety of pyrophyllite from Maharashtra was incorporated in a triaxial porcelain composition as a replacement of quartz and china clay [22–24] and the effect on the vitrification, mechanical properties and microstructure was studied. It was observed that pyrophyllite could be used in the tune of 15–22% as a replacement of quartz and china clay. In continuation to the same study, pyro-chemical properties of pyrophyllite mineral was evaluated and analyzed to understand the compatibility of the mineral, in general, during use in combination with other constituents in the triaxial porcelain system. The investigation will open up avenues to understand the mineral and its subsequent utilization due to depleting resources of standard alumino-silicate minerals.

2. Experimental

The sample of pyrophyllite was obtained from Maharashtra, India. Standard methods of coning and quartering were adopted for obtaining representative samples from the bulk. Specific gravity of the sample was determined with (−)200 mesh powder following usual procedure [25] using specific gravity bottle.

The pyrophyllite sample was ground to 300 mesh and then mixed with 1% poly vinyl alcohol (PVA) solution to obtain a mix with moisture content in the range of 6–8%. Discs of about 50 mm diameter and 10 mm thickness were pressed at 250 kg cm^{-2} in a semi-automatic hydraulic press. The discs were initially dried at room temperature to avoid cracking. The air dried discs were then finally dried in an electric oven by gradual rise of temperature up to 110 °C in 6 h and left for overnight. The samples were then cooled in the desiccators and their diameter measured to determine the dry linear shrinkage. Average of five samples was reported as the measured value. Dry test specimens were fired in an electrically heated muffle furnace at six different temperatures between 1100 °C and 1350 °C with 50 °C interval and 2 h soaking time at respective peak temperatures. Fired linear shrinkages, water absorption and bulk density of the fired specimens were determined following the standard procedure [26].

Thermal expansion of green as well as fired (1200 °C) pyrophyllite samples was investigated by an Orton Automatic Dilatometer, Bosch & Lamb, UK make, and at a heating rate of 2 K/min. Green samples were prepared by cutting raw pyrophyllite with diamond wheel followed by grinding and polishing. DTA, X-ray diffraction and chemical analyses of the samples were carried out for identification of possible mineral phases present. Chemical analysis was carried out following wet chemical as well as instrumental analysis. SiO_2 was estimated gravimetrically [27], Na_2O and K_2O flame photometrically [28] and other oxide constituents were estimated [29] using Inductively coupled plasma atomic emission spectrometer, Spectro Analytical Instrument, Spectro Ciros Vision model, Germany. DTA was performed using Netzsch Thermal Analyzer, model STA 409 with DTG mode determining DTA and TG simultaneously. Both DTA and TG of the samples were studied under identical conditions up to 1200 °C at a heating rate of 10 °C/min in alumina crucible and using α-alumina as the reference. The X-ray diffraction studies were carried out with powder (−200 mesh BS sieve) of each of the samples. 'X'Pert Pro' MPD diffractometer (PANalytical) attached with secondary monochromator, automatic divergence slit and nickel filter was used and operating at 45 kV and 40 mA to get monochromatic Cu-Kα radiation. The instrument was run at step scan mode with step size (0.02) and 8 s time per step, with 2θ angle 10–60°. The collected data was refined using Profit software. X-Pert plus and Quasor software based on Rietveld were used to calculate the percentage of mullite and quartz, where standard quartz and mullite were used as reference materials. The weight percentage of glassy phase was estimated by substracting sum of the wt% of quartz and mullite from 100. For reliability of data, each sample was scanned several times. The fitted curve matched well with the raw data and 'goodness of fit' varied from 2.5 to 4.0 among different samples. Microstructure was studied by SEM analysis on powdered raw pyrophyllite as well as on some selected sintered samples using a LEO S-430i apparatus. For SEM studies on fired specimens, the specimens were polished to 1 μm finish with diamond paste after initial grinding with Silicon carbide powder/Cerium oxide powder and water. The polished surfaces of such samples were etched with 5% HF solution for 60 s duration at room temperature (35 °C), washed with distilled water and acetone followed by gold sputter coating (Edwards, Scancoat).

3. Results and discussion

The sample of pyrophyllite was obtained as grayish white hard massive lumps. There were occasional green and purple patches in the as received lumps. The specific gravity of the as received sample was 2.743. Dry linear shrinkage was 2.33% (±0.12).

The chemical analysis of the pyrophyllite sample has been presented in Table 1. The results indicate that the sample was rather low in SiO_2 (59.51%) and rich in Al_2O_3 (30.43%) in comparison to those of theoretical values (SiO_2 67% and Al_2O_3 28%). The presence of diaspore as indicated by other studies

Table 1
Chemical analysis of pyrophyllite sample.

Chemical analysis	I
Oxide constituents	wt%
SiO_2	59.51 (±0.030)
TiO_2	0.26 (±0.02)
Al_2O_3	30.43 (±0.020)
Fe_2O_3	0.86 (±0.03)
CaO	0.37 (±0.03)
MgO	0.78 (±0.02)
Na_2O	0.73 (±0.01)
K_2O	1.95 (±0.01)
L.O.I.	5.40 (±0.10)

(XRD analysis and DTA) might have contributed for this higher percentage of Al_2O_3. Total alkali content ($Na_2O + K_2O$) in the sample was 2.68% indicating the presence of *sericitic/muscovitic* minerals. The association of sericite in pyrophyllite is quite common and was reported by other researchers [30,31]. The sample contained a small amount of colouring oxides, Fe_2O_3 (0.86%) and TiO_2 (0.26%) respectively which is acceptable in whiteware industries. Alkaline earth oxide content (CaO and MgO) was also within limit (1.15%).

3.1. Study of thermal effect

The results of fired properties of the pyrophyllite sample are presented in Figs. 1–4. Colour of the fired specimens was observed visually and they were white/off-white irrespective of the firing temperatures (up to 1350 °C). Presence of ferruginous oxides ($Fe_2O_3 + TiO_2$) caused no significant problem. Results of fired linear shrinkage indicated that the specimens expanded initially up to 1150 °C and then shrank (Fig. 1). The expansion characteristics were due to the exfoliation of the alumino-silicate layer, causing a permanent linear expansion. Beyond 1150 °C, specimens of the pyrophyllite sample showed shrinkage up to the temperature of maximum firing (1350 °C). Water absorption values (Fig. 2) of the specimens showed gradual decrease with the rise in test temperatures up to 1350 °C. The water absorption value reached 1.65% only at 1350 °C. This might be attributable to the presence of higher proportion of alkali bearing minerals in the sample. Bulk density values of the samples (Fig. 3) of pyrophyllite increased with progressive increase in temperature and reached a maximum value (2.43 g/cm^3) as the point of vitrification was approached.

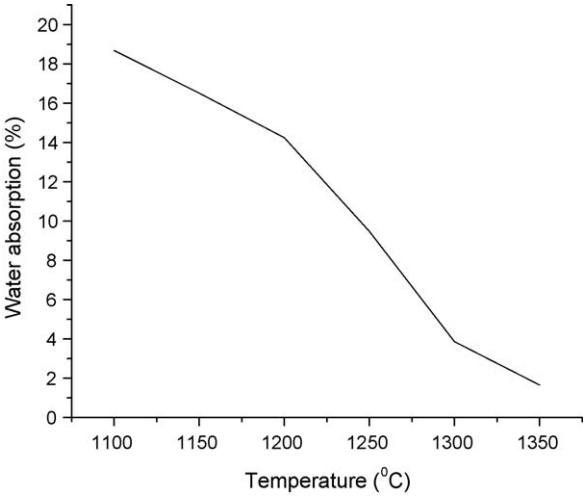

Fig. 2. Variation of water absorption with temperature.

The results of the thermal expansion characteristics studied up to 1000 °C of fired pyrophyllite specimens (1200 °C) are presented in Fig. 4. The percent thermal expansion of the sample showed uniformly higher values with progressive rise in temperature up to 1000 °C. A more or less linear curve was obtained indicating that thermal expansion is linearly dependent on rise in temperature.

The thermal expansion values of the raw pyrophyllite sample have been presented in Fig. 5. It has been observed that the expansion values were higher than that of the respective samples in the fired form (Fig. 4) at all temperatures. For example, the percent expansion of raw specimen at 1000 °C was 1.865% whereas the same in fired form and at the same temperature recorded expansion of 0.39% only. This is a characteristic phenomenon for the mineral pyrophyllite and may be used as a tool for identification of the same. One observation is that there

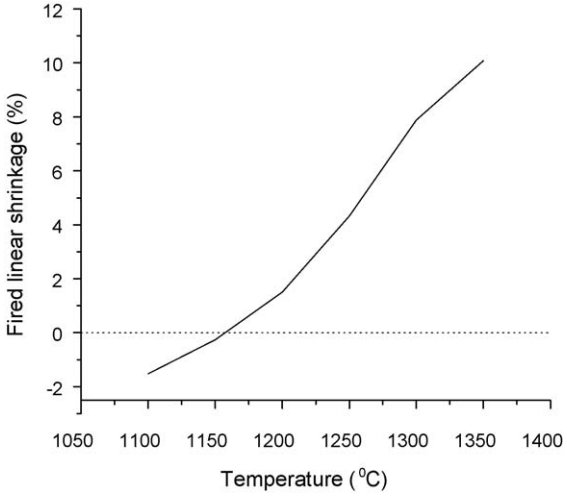

Fig. 1. Variation of fired linear shrinkage with temperature.

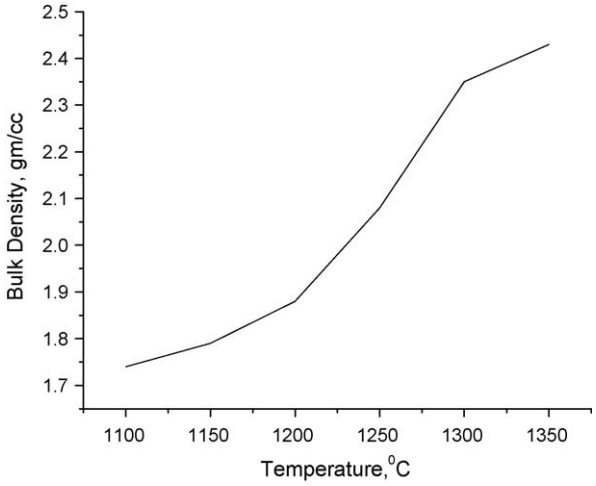

Fig. 3. Variation of bulk density with temperature.

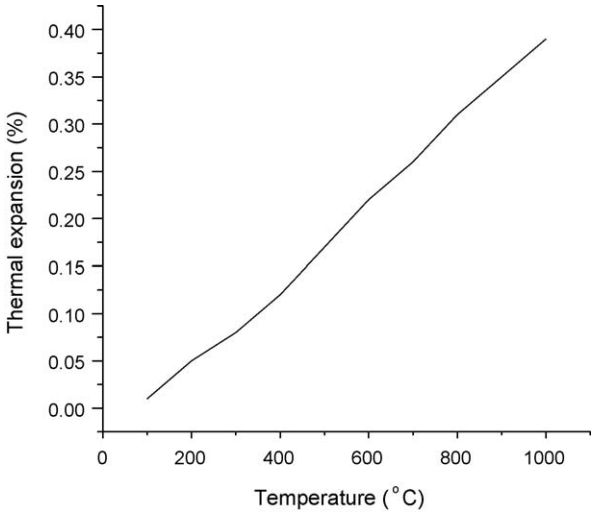

Fig. 4. Variation of thermal expansion of fired specimen of pyrophyllite (1200 °C) with temperature.

was a sudden rise in percent thermal expansion value from 0.96% to 1.72% when temperature was raised from 600 °C to 700 °C. This may be due to the fact that the raw pyrophyllite lost water of constitution between 600 °C and 800 °C and alumino-silicate layers separated out which eventually gave a permanent linear expansion. Similar observation was made by Parmelee and Barrett [31] as well as by Kersey and Jerner [19] beyond 700 °C while studying the pyro-chemical properties of pyrophyllite from two different sources in USA. On the other hand, in fired specimen the expansion due to dehydroxylation and exfoliation of alumino-silicate layers had already occurred during the first firing of the sample and the observed values were due to the presence of different constituents or phases formed during firing such as quartz, mullite, glass, etc. in the microstructure.

3.2. XRD analysis

XRD analysis result confirmed the presence of pyrophyllite and sericite in the raw pyrophyllite sample. The results confirm

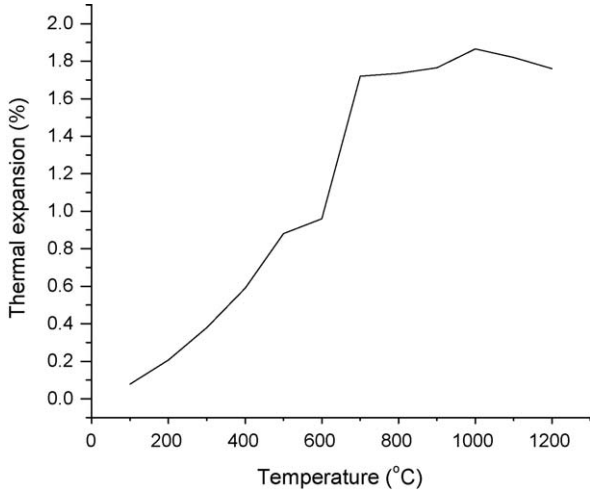

Fig. 5. Variation of thermal expansion of raw specimen of pyrophyllite with temperature.

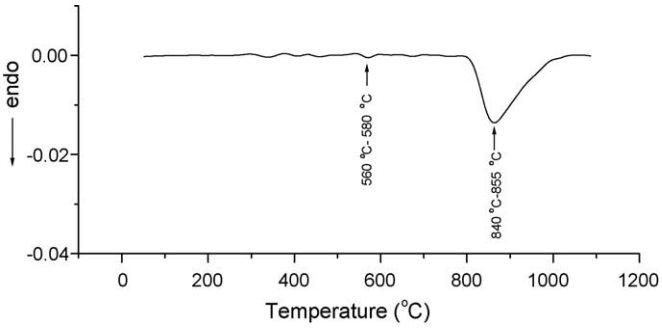

Fig. 6. DTA curve of raw pyrophyllite.

that in the sample the major phase is a double-layer monoclinic pyrophyllite with additional mineral phases of sericite, quartz and diaspore in minor quantity. Presence of peak values at *d* (Å) 3.978, 2.316 and 2.077 may be an indicative of the presence of diaspore. Similarly the peak values at *d* (Å) 3.665, 3.327, 2.382, 2.16 and 2.020 indicate the presence of sericite/muscovite. Thus, the X-ray powder diffraction of the mineral (Fig. 7) shows that the agreement between the observed *d*-values and the published values for pyrophyllite-2M1 (JCPDS 12-0203) is very good. Characterization of raw pyrophyllite by XRD analysis was also done by others [32,33].

XRD analysis of pyrophyllite sample calcined at 1250° and also at 1350 °C (Figs. 8 and 9) indicated the presence of mullite as major crystalline phase. Quantitative phase analysis results indicate around 11.5% mullite phase along with 2% quartz when the pyrophyllite sample was calcined at 1250 °C and the mullite phase increased to 14% when the calcination temperature was raised to 1350 °C. At the same time, glassy/amorphous phase in substantial quantity (around 85%) is produced, as the background of X-ray diagram suggests. However, mullite crystals were not well resolved possibly due the presence of too high proportion of highly viscous amorphous phase. It may be noted that simultaneously with mullite formation from dehydroxylated pyrophyllite large amount of amorphous silica is discarded which will definitely

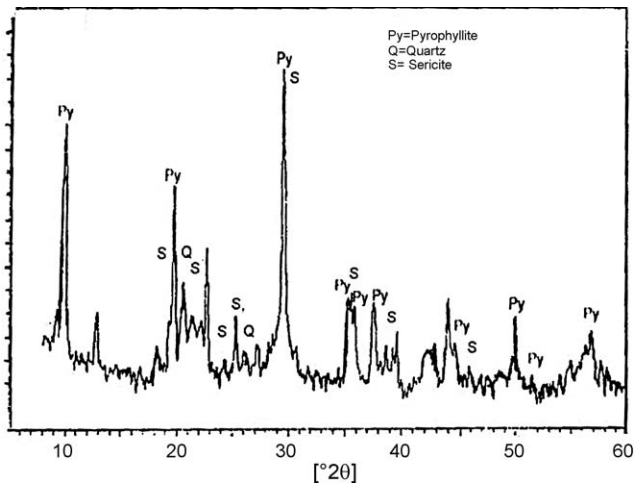

Fig. 7. XRD pattern of raw pyrophyllite.

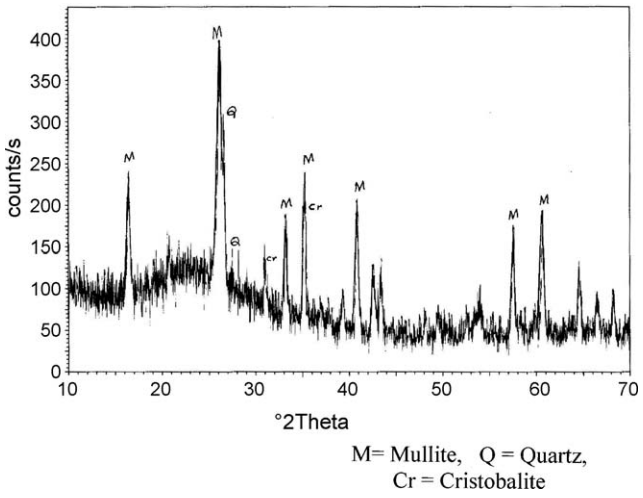

Fig. 8. XRD pattern of pyrophyllite calcined at 1250 °C.

go into solution forming SiO_2-rich glassy phase at the firing temperature [23]. Minor quantity of quartz phase was detected and the quantity of the same varied from 2% to 3.5% as the firing temperature was raised from 1250 °C to 1350 °C. Crystallization of cristobalite could not be conclusively proved although indication of the presence of this phase was noticed at 1350 °C.

3.3. Infrared (IR) spectroscopy study

To support the XRD results by studying absorption frequencies corresponding to characteristic vibrations of different bonds in the molecules present, the IR spectra were recorded. The Infrared spectrogram of raw pyrophyllite mineral is shown in Fig. 10. Similar to the observations of Khandal and Gangopadhyay [34] in the IR spectra of clays, the peak observed at 3669 cm^{-1} may be assigned to the O–H vibration of the Al–OH linkage, while the peak at wave number 3446 cm^{-1} may be due to O–H stretching of the surface water, and the peak at 1646 cm^{-1} may be assigned to bending of the surface O–H

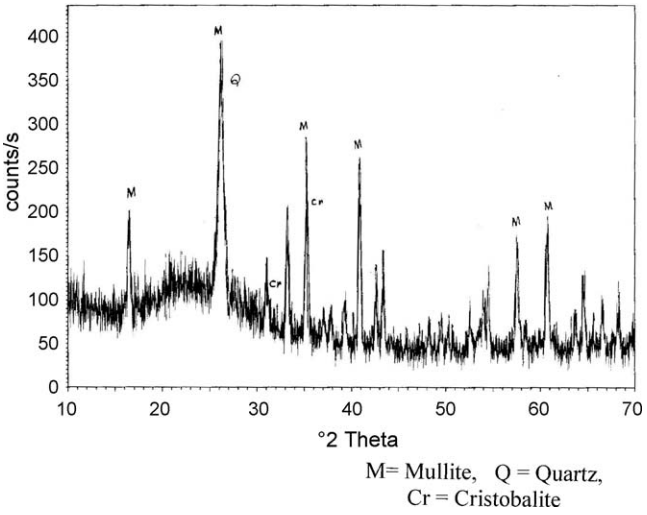

Fig. 9. XRD pattern of pyrophyllite calcined at 1350 °C.

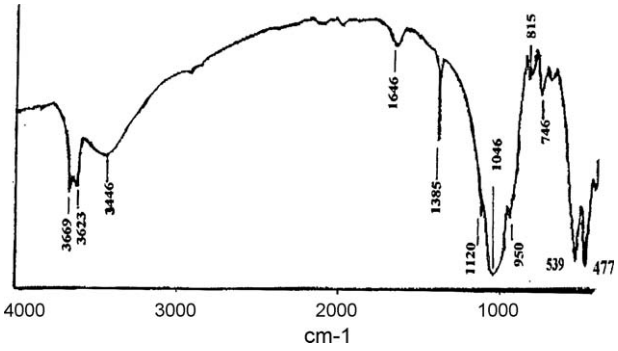

Fig. 10. Infrared spectrogram of raw pyrophyllite.

group. Similar types of peaks were also observed (3673 cm^{-1}, 3461 cm^{-1} and 1633 cm^{-1}) by Amritphale et al. [35]. The peak at 1120 cm^{-1} is assigned to Al–OH vibration following Miller [36]. The peak at 1046 cm^{-1} corresponds to the intense Si–O and Si–O–Al stretching frequencies, characteristic of aluminosilicates [37,38]. This band is formed by the vibrations of oxygen common to tetrahedron and octahedron, and the Si–O vibration that is perpendicular to the silicate layers [39,40]. The peak at 950 cm^{-1} may be attributed to Al–(OH) vibrations [41,42]. The position and sharpness of the perpendicular vibration vary with the physical state and degree of substitution [37]. Illite and muscovite may be characterized by the OH-stretching around 3620 cm^{-1}, accompanied by the broad absorption at 3400 cm^{-1} [38,43]. The peaks in the range 815 cm^{-1} and 746 cm^{-1} indicates the presence of Si–O–Al where Al is in tetrahedral co-ordination supporting the earlier observation of the possible presence of sericite/muscovite minerals. The peaks in the range 539 cm^{-1} and 477 cm^{-1} is due to octahedral AlO_6 sheet vibrations [42,44].

3.4. SEM study

The original sample of pyrophyllite (Fig. 11) showed large flat crystals with occasional book like stacked structure. Some flaky structured materials appeared to be micaceous minerals were also found occasionally as is evident from Fig. 12. Similar observations were made by Huö and Nam [45] in their study of sericite minerals from different sources. SEM examination of

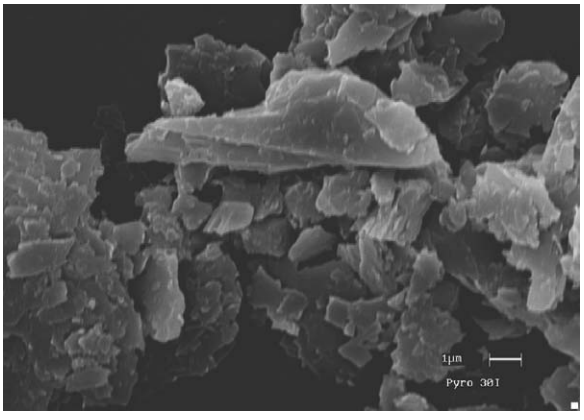

Fig. 11. SEM of raw pyrophyllite showing flat crystals.

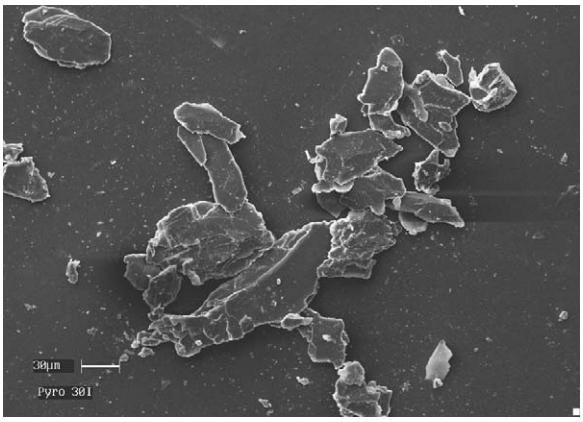

Fig. 12. SEM of raw pyrophyllite showing possible presence of mica.

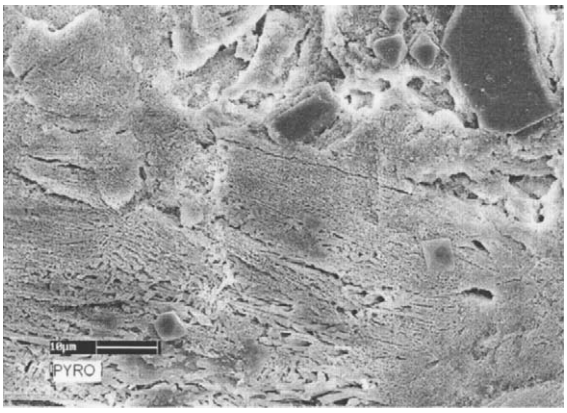

Fig. 14. SEM of pyrophyllite calcined at 1250 °C.

sample heated up to 1150 °C (Fig. 13) showing the retention of same shape of stacks indicated no differences compared with the original raw pyrophyllite (Fig. 11). No visible change in the structures caused by the heat treatment is apparent and thus supporting the observations of Sanchez-Soto et al. [21]. However, some crystallites appeared to be distributed on the plates leading to slight roughing of the surfaces. According to Wardle and Brindley [48], pyrophyllite dehydroxylate is produced after total dehydroxylation. This phase retains a well-organized structure similar to hydroxylate and is stable over a wide range of temperatures. Heller [17] and Schomburg [46] indicated that pyrophyllite dehydroxylate is stable up to 1150 °C, Mackenzie et al. [47] reported similar observations up to 1100 °C and Sanchez-Soto et al. [21] indicated that the shape of the heated sample is retained up to 1200 °C although XRD patterns change very rapidly from 1150 °C to 1200 °C. All the above facts support present observations as described. Upon further heating at 1250 °C, SEM micrograph (Fig. 14) shows a greater development of mullite crystals but flat forms are also still present. Presence of quartz crystals, both small and big, was also conspicuous. At 1350 °C, mullite crystals appeared distributed over the region (Fig. 15) and no additional information about the microstructural changes could be noted. Rod shaped mullite crystals with low aspect ratio were found distributed in the microstructure. However, presence of glassy phase and recrystallization of fine needle shaped interlocking secondary mullite were also quite obvious in the microstructure (Fig. 16).

3.5. DTA–TG analysis

The DTA curve of Maharashtra pyrophyllite (Fig. 6) showed one small endothermic depression between 560 °C and 580 °C followed by another wide endothermic peak (broad and shallow in nature) between 840 °C and 855 °C. The small endothermic depression between 560 °C and 580 °C may be due the dehydroxylation of diaspore which is also supported by XRD analysis. The broad and shallow endothermic peak between 840 °C and 855 °C may be an indicative of the presence of pyrophyllite corresponding to dehydroxylation and structural break down of the mineral. The general inferences of the present work are in agreement with those of other researchers [2,21,47]. The formation of mullite from pyrophyllite involves a small energy change and as expected no sharp and large exothermic peak was observed which is in conformity with the observation of earlier workers [16,17]. The endothermic peak due to loss of structural water is also not very prominent as there is only one molecule of water in the structure.

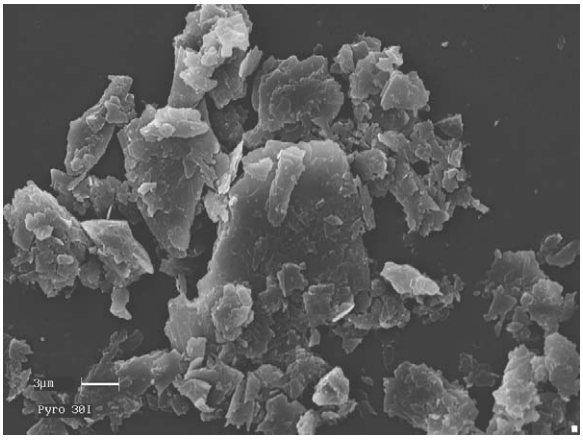

Fig. 13. SEM of pyrophyllite after thermal treatment at 1150 °C.

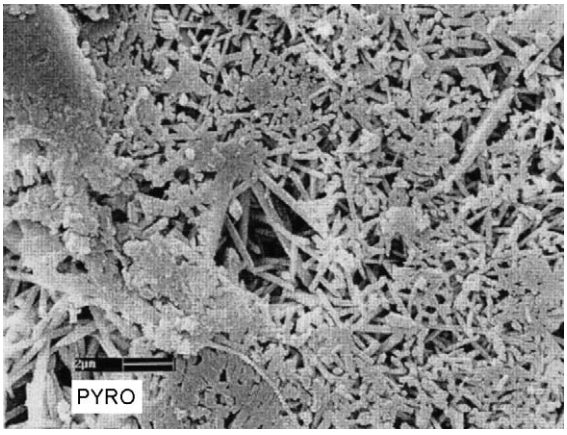

Fig. 15. Rod shaped mullite crystals with low aspect ratio are shown. SEM of pyrophyllite calcined at 1350 °C.

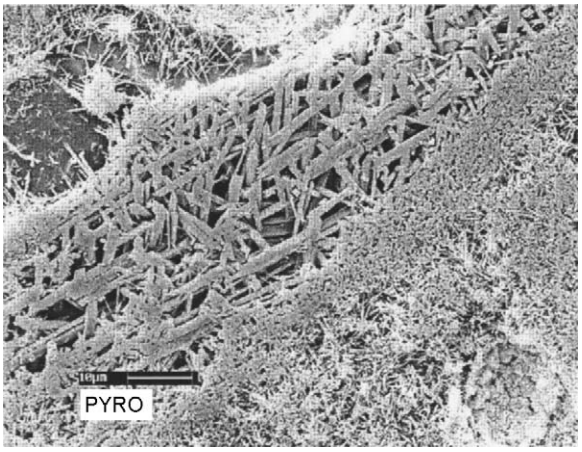

Fig. 16. Recrystallization of fine needle shaped mullite from the glassy phase are shown. SEM of pyrophyllite calcined at 1350 °C.

From the foregoing discussion we may conclude that different pyro-chemical properties of pyrophyllite may be advantageously utilized in formulation of porcelain compositions. Unlike kaolinite, pyrophyllite is non-plastic in nature. The specimen of pyrophyllite expanded initially up to 1150 °C and then shrank. The shrinkage up to 1250 °C is only 4.33%. Incorporation of this alumino-silicate mineral as a replacement of china clay and quartz is expected to reduce the fired linear shrinkage which would favourably influence the final output by reducing the losses due to deformation or cracking of the wares. This was actually observed [24] when china clay and quartz in the ratio of 1:2 was progressively replaced by pyrophyllite. Compared to kaolinite, pyrophyllite contains low alumina and high silica. In spite of this, percentage of mullite content was found to increase in the fired specimens when kaolinite was progressively replaced by pyrophyllite [23]. Moroz [49] and Pashenko [50] suggested that the compositions containing pyrophyllite were more favourable for mullite crystallization in comparison to those with kaolinite as referred in [8]. On heating, pyrophyllite mainly forms mullite and amorphous silica. The silica in turn generates large amount of liquid at the maturing temperature of ceramic articles. In our earlier work [23,24], it was observed that pyrophyllite incorporated compositions favoured the formation of mullite which eventually improved the thermo-mechanical properties of the specimens. Crystallization of mullite from pyrophyllite is rather facilitated than that from kaolinite. In case of kaolinite the system is required to cross higher energy barrier to transform to mullite as compared to that from pyrophyllite. A possible explanation for the same has been put forward in our earlier communication [23]. Therefore, pyrophyllite may be utilized in such compositions where mullite is a desirable phase and partial replacement of china clay by pyrophyllite is a viable alternative. However, beyond the optimum proportion of pyrophyllite addition, there occurred large volume of glass formation. Presence of large volume of glassy phase as well as formation of large pores of various shapes resulted in deterioration in ceramic properties [24]. Amorphous silica produced in the reaction system may act as an in situ produced filler material that reduces the use of quartz. Linear thermal expansion of matured specimens was found to decrease gradually as more and more pyrophyllite was incorporated as a replacement of quartz in the triaxial porcelain composition [22]. A reduction in thermal expansion of the pyrophyllite incorporated compositions is expected to enhance the thermal shock resistance of the products made thereof.

4. Conclusions

The pyrophyllite sample was characterized by chemical analysis, DTA, FTIR, XRD and scanning electron microscopy. The specimen confirmed the presence of double-layer monoclinic pyrophyllite as major phase with additional mineral phases of sericite, quartz and diaspore in minor quantity.

XRD analysis of pyrophyllite sample calcined at 1250 °C and also at 1350 °C indicated the presence of mullite as major crystalline phase and at the same time, amorphous phase in substantial quantity (around 85%) was produced. SEM examination of sample heated up to 1150 °C indicated no differences compared with the original raw pyrophyllite showing the retention of same shape of stacks. Mullite crystals were conspicuous above 1200 °C and at 1350 °C, mullite crystals appear distributed over the region. Rod shaped mullite crystals with low aspect ratio as well as fine needle shaped interlocking secondary mullite crystals were found distributed in the microstructure.

On heating, pyrophyllite mainly forms mullite and amorphous silica. Pyrophyllite may be utilized in such compositions where mullite is a desirable phase. Thus, partial replacement of china clay by pyrophyllite is a viable alternative. Amorphous silica produced in the reaction system acts as an in situ produced filler material that reduces the use of quartz. Therefore, it is suggested that pyrophyllite may be used in certain ceramic compositions to partially replace both china clay and quartz to enhance the product quality and reduce the cost. However, incorporation of pyrophyllite in a composition is restricted to a limit beyond which the ceramic properties deteriorate.

Acknowledgements

The authors wish to acknowledge the assistance received from XRD, SEM, IR and Analytical chemistry sections for characterizing the samples.

References

[1] S. Krishnaswamy, Indian Mineral Resources, 2nd edition, Oxford and IBH Publishing Co., New Delhi, 1979, pp. 470.
[2] S.K. Guha, Ceramic Raw Materials of India – A Directory, Indian Institute of Ceramics, Calcutta, 1982, pp. 110–111.
[3] M.L. Sykes, J.B. Moody, Pyrophyllite and metamorphism in the Carolina Slate Belt, Am. Miner. 63 (1–2) (1978) 96–108.
[4] L.D. Swindale, I.R. Hughes, Hydrothermal association of pyrophyllite, kaolinite, diaspore, dickite and quartz in the Coromandel area, New Zealand, N.Z. J. Geol. Geophys. 11 (5) (1968) 1163–1183.
[5] L. Wang, Metallogeny of pyrophyllite in the coastal region of Southeast China and pyrophyllite's thermal stability, PhD Thesis, Changsha Institute of Geotectonics, Chinese Academy of Sciences (in Chinese).

[6] M.L. Mishra, V.G. Upadhyay, Pyrophyllite from Hamirpur in whiteware bodies, Trans. Ind. Ceram. Soc. 19 (1) (1960) 25–31.
[7] E.W. Emrich, Use of high sericite pyrophyllite in vitreous bodies, J. Am. Ceram. Soc. 24 (4) (1941) 141–144.
[8] D.I. Alimdzhanova, A.A. Ismatov, M.M. Ganieva, The effect of quartz-pyrophyllite raw material on porcelain structure formation, Glass Ceram. 56 (1–2) (1999) 61–63 (Translated from Steklo i Keramika, 2 (February) (1999) 24–26).
[9] R.E. Tucker, Pyrophyllite does great things for sanitaryware, Ceram. Ind. 74 (4) (1960) 114–117, 141.
[10] E.H. Lintz, Use of talc and pyrophyllite in semi-vitreous dinnerware bodies, J. Am. Ceram. Soc. Abstr. 21 (1938) 229–237.
[11] I.E. Sproat, Use of pyrophyllite in wall tile bodies, J. Am. Ceram. Soc. 19 (5) (1936) 135–142.
[12] E. Tauber, H.J. Pepplinkhouse, M.J. Murry, Stoneware bodies based on pyrophyllite, J. Aust. Ceram. Soc. (1973) 47–51.
[13] C.S. Prasad, K.N. Maiti, R. Venugopal, Replacement of quartz and potash feldspar with sericitic pyrophyllite in whiteware compositions, Interceramics 40 (2) (1991) 94–98.
[14] S. Bhasin, S.S. Amritphale, N. Chandra, Effect of pyrophyllite additions on sintering characteristics of fly ash based ceramic wall tiles, Br. Ceram. Trans. 102 (2) (2003) 83–86.
[15] K. Dana, S. Ghosh, T.K. Mukhopadhyay, S.K. Das, Feldspathic and pyrophyllitic porcelain evolution during fast firing, Am. Ceram. Soc. Bull. 85 (12) (2006) 9201–9203.
[16] W.F. Bradley, R.E. Grim, High temperature thermal effects of clay and related minerals, Am. Miner. 36 (3–4) (1951) 182–201.
[17] L. Heller, The thermal transformation of pyrophyllite to mullite, Am. Mineral. 47 (1–2) (1962) 156–157.
[18] M. Nakahira, T. Kato, Thermal transformations of pyrophyllite and talc as revealed by X-ray and electron diffraction studies, in: W.F. Bradley (Ed.), Proceedings of the 12th National Conference of Clays and Clay Minerals, Pergamon Press, New York, 1964, pp. 21–27.
[19] B. Joe, R.C. Kersey, Jerner, The effect of firing temperature on properties of natural steatite and pyrophyllite, J. Mater. Sci. 7 (1972) 621–626.
[20] P.J. Sanchez-Soto, A. Justo, J.L. Perez-Rodriguez, Formation of mullite from pyrophyllite by mechanical and thermal treatments, J. Am. Ceram. Soc. 72 (1) (1989) 154–157.
[21] P.J. Sanchez-Soto, J.L. Perez-Rodriguez, SEM study of pyrophyllite high temperature transformation, J. Mater. Sci. 24 (1989) 3774–3778.
[22] T.K. Mukhopadhyay, S. Ghosh, S. Ghatak, H.S. Maiti, Effect of pyrophyllite on vitrification and on physical properties of triaxial porcelain, Ceram. Int. 32 (2006) 871–876.
[23] T.K. Mukhopadhyay, S. Ghatak, H.S. Maiti, Effect of pyrophyllite on the mullitization in triaxial porcelain system, in: Ceramics International, available online paper no. CERI 3109, 2009.
[24] T.K. Mukhopadhyay, S. Ghatak, H.S. Maiti, Effect of pyrophyllite incorporation in porcelain composition on mechanical properties and microstructure, in: Ceramics International, available on line paper no. CERI 3211, 2009.
[25] Indian Standard Specifications for Light Kaolin, IS: 505, 1995.
[26] Indian Standard Specification for vitreous sanitary appliances (vitreous china) Part I: General requirements, IS: 2556 (Part I), 1974.
[27] Indian Standard Specification for chemical analysis of high silica refractory materials, IS: 1527, 1972, Reaffirmed 1995.
[28] S. Dasgupta, S.K. Roy, Chemical Analysis of Ceramic and Allied Materials, Indian Institute of Ceramics, Calcutta, 1985, pp. 58–59.
[29] M. Thomson, J.N. Walsh, A Handbook of Inductively Coupled Plasma Spectrometry, Blackie, Glasgow/London, 1983, p. 83.
[30] J.L. Stucky, The dehydration temperature of pyrophyllite and sericite, J. Am. Ceram. Soc. 07 (10) (1924) 735–737.
[31] C.W. Parmelee, L.R. Barrett, Some pyrochemical properties of pyrophyllite, J. Am. Ceram. Soc. 21 (11) (1938) 388–393.
[32] T. Kogure, M. Jige, J. Kameda, A. Yamagishi, R. Miyawaki, R. Kitagawa, Stacking structures in pyrophyllite revealed by high-resolution transmission electron microscopy (HRTEM), Am. Miner. 91 (8–9) (2006) 1293–1299.
[33] D. Feldman, S.A. Mikhail, G. Denes, D. Banu, A preliminary study and laboratory characterization of the carpentier pyrophyllite mineral, J. Can. Ceram. Soc. 62 (2) (1993) 121–126.
[34] R.K. Khandal, P.K. Gangopadhyay, Characterisation and leaching studies on two Indian clays, Indian Ceram. 28 (9) (1985) 195–199.
[35] S.S. Amritphale, N. Chandra, R. Kumar, Sintering behaviour of pyrophyllite mineral: effect of some alkali and alkaline earth metal carbonates, J. Mater. Sci. 27 (1992) 4797–4804.
[36] J.G. Miller, An Infrared spectroscopic study of the isothermal dehydroxylation of kaolinite at 470 °C, J. Phys. Chem. 65 (5) (1961) 800–804.
[37] S. Raman, T.K. Dan, Physico chemical analysis of a raw brick clay of Bhopal (M.P.), Indian Ceram. 29 (2) (1986) 25–27.
[38] A.E. Lavat, M.C. Grasselli, J.E. Tasca, Phase changes of ceramic whiteware slip-casting bodies studied by XRD and FTIR, Ceram. Int. 33 (6) (2007) 1111–1117.
[39] M. Erdemoglu, M. Sarikaya, The effect of grinding on pyrophyllite floation, Min. Eng. 15 (10) (2002) 723–725.
[40] P.J. Sanchez-Soto, A. Justo, J.L. Perez-Rodriguez, Structural alteration of pyrophyllite by dry grinding as studied by IR spectroscopy, J. Mater. Sci. Lett. 13 (1904) 915–918.
[41] S.S. Amritphale, M. Patel, J. Silicate Ind. 3–4 (1987) 31.
[42] K. Ramaswamy, M. Kamalakkan, Infrared study of some South Indian clays, Indian J. Pure Appl. Phys. 25 (4) (1987) 284–286.
[43] J.L. Post, L. Borer, Physical properties of selected illites, beidellites and mixed layer illite–beidellites from Southwestern Idaho, and their infrared spectra, Appl. Clay Sci. 22 (2002) 77–91.
[44] S Bhattacharyya, S. Ghatak, Synthesis and characterization of YAG precursor powder in the hydroxygel form, Ceram. Int. 35 (1) (2009) 29–34.
[45] T.T. Huö, K.Q. Nam, Sericite mineralization in Viöt Nam and its economic significance, www.idm.gov.vn/Nguon_luc/Xuat_ban/Tapchi2004/22/t61.htm.
[46] J. Schomburg, Thermal investigations of pyrophyllites, Thermochim. Acta 93 (September) (1985) 521–524.
[47] K.J.D. Mackenzie, I.W.M. Brown, R.H. Meinhold, M.E. Bowden, Thermal reactions of pyrophyllite studied by high-resolution solid state ^{27}Al and ^{29}Si nuclear magnetic resonance spectroscopy, J. Am. Ceram. Soc. 68 (5) (1985) 266–272.
[48] R. Wardle, G.W. Brindley, The crystal structure of pyrophyllite, 1 Tc, and its dehydroxylate, Am. Miner. 57 (1972) 732–750.
[49] I.I. Moroz, Technology of Porcelain and Faience Products, Stroiizdat, Moscow, 1984 [in Russian].
[50] A.A. Pashenko, Physical chemistry of silicates, Vysshaya Shkola, Moscow, 1986 [in Russian].