

Value Addition to Red Sediment Placer Sillimanite Using Microwave Energy and in Depth Structural and Morphological Characterization of Mullite

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Received July 1, 2012; revised August 3, 2012; accepted August 13, 2012

ABSTRACT

This paper deals with the effect of microwave energy for mullite formation from placer sillimanite. A mullite formation is seen when 60 % SiC and 5% binder are used with the composite charge material, *i.e.* sillimanite (60%) and Al₂O₃ (40%). The maximum temperature of the microwave sintering furnace achieved is 1355°C at 2450 W microwave power. Addition of 10 % binder to the same charge material with 60% SiC, the furnace temperature achieved is 1384°C at microwave power 1900 W. Mullite is formed within 25 minutes from the sillimanite, under the above experimental conditions. Whereas under the similar additive conditions, the mullite formed from sillimanite in conventional furnace heating, it took 3 hours at 1300°C. XRD data show the mullite phase for both the products obtained from microwave sintering furnace and conventional furnace. FESEM image analysis shows the mullite formations, SiC fibrous cluster and alumina needles in microwave treated sample. Thus microwave heat source is much more effective for value addition to red sediment placer sillimanite to form mullite in compare to conventional furnace.

Keywords: Microwave Heat Energy; Sillimanite; Mullite; Value Addition

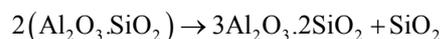
1. Introduction

This paper provides a simple theoretical model to investigate determinants of the vertical IIT based on Bertrand price competition. We find that the volume of trade is higher among countries where R&D investments are larger. In addition, the vertical IIT share increases with the similarity between two countries in terms of technology and per-capita income. Our theoretical findings are consistent with recent empirical findings.

2. Introduction

Red sediments in India are recent geological formations. These red sediments occur in badlands topography. These sediments essentially contain industrial placer heavy minerals such as ilmenite, sillimanite, rutile, zircon, monazite and other heavy minerals. Sillimanite (Al₂O₃. SiO₂) is mineral which has special property of undergoing conversion into mullite (3Al₂O₃.2SiO₂) and vitreous silica (cristobalite) on heating between 1350°C and 1500°C. Thus the placer minerals which contain considerable amount of sillimanite can be made use of mullite formation for industrial applications. The decomposition of sil-

limanite to mullite and silica is as follows



On heating the placer sillimanite between 1500°C and 1650°C with conventional heating process, it decomposes to mullite and silica [1] in such a way that their decompositions produce a mixture of the mullite 3:2 plus free silica. Due to presence of rejected silica phase, the impurities become segregated at the grain boundaries. However, it is logical to believe that incorporating alumina to react with the rejected silica to form a single-phase mullite structure can minimize this disadvantage. Use of conventional furnaces for preparation of mullite from sillimanite is a universally known process. Several publications and patents are available in the literature on this aspect. Literature pertaining on the preparation of mullite using microwave heat source is very much restricted. The available literature is on formation of mullite from kaolinite or kaolin clay. The literature reveals that Elias and Ruth [2] observed the mullite phase in XRD analysis for the sample treated by microwave carbothermal reduction of kaolin. Ebadzadeh, *et al.* [3] observed about mullite behavior from the reaction sintering of clay and alumina

heated in a microwave oven. According to them, alumina and clay exhibit low dielectric losses (0.1 ± 0.03 and <1 , respectively) and are difficult to heat in a microwave oven at room temperature, therefore SiC crucible with a high dielectric loss (300 ± 50) were used which behave as a susceptor. They also observed that after microwave processing, the minimum temperature required for the presence of mullite residual phase was 1250°C . However, so far no attempt is made to investigate the effect of microwave heat treatment on placer sillimanite for mullite formation in microwave sintering furnace, as all attempts have been made for mullite formation with conventional furnace on kaolin clay or fly ash [4] using microwave oven only. Hence it is felt necessary to study the effect of microwave heat on sillimanite for formation of mullite using microwave sintering furnace. The present study deals with the mullite formation from placer sillimanite using microwave sintering furnace.

2. Materials and Methods

2.1. Raw Materials

Placer sillimanite (Al_2SiO_5) recovered from the red sediments of badlands topography, near Nolia Nuagam Odisha, India. The recovery process and its chemical composition are described in the methodology. The location map for Nolia Nuagam, Odisha is shown in **Figure 1**.

The sample collection points (\rightarrow) of red sediments [(a) red sediment hillock and (b), (c) & (d) heavy mineral placer concentrations] at Nolia Nuagam, Odisha, India is shown in **Figure 2**. The 250 meshed SiC powder and alumina ($\alpha\text{-Al}_2\text{O}_3$, $d_{90} < 10 \text{ mm}$) were used in the present study.

2.2. Recovery of Sillimanite

The experimental plan for recovery of placer sillimanite mineral from red sediments of badlands topography is shown in **Figure 3**. The high grade placers having mineral



Figure 1. Location of the red sediment deposits of Nolia Nuagam, Odisha, India.

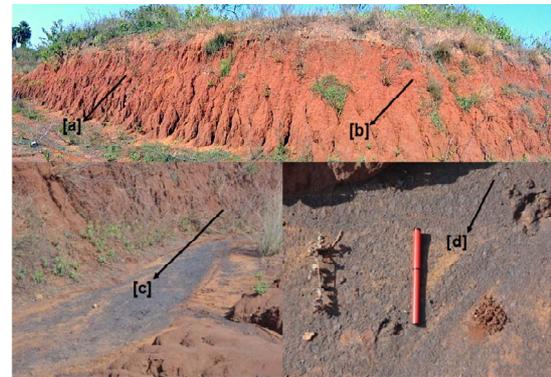


Figure 2. Sample collection points (\rightarrow) of red sediments at Nolia Nuagam, Odisha, India [(a): red sediment hillock, (b), (c) & (d): heavy mineral concentrations].

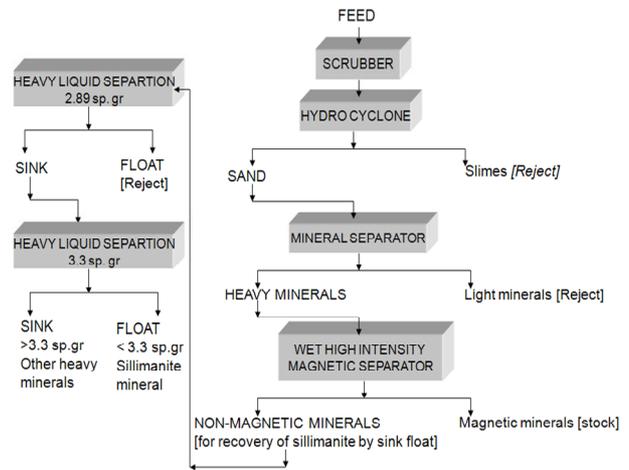


Figure 3. Experimental plan for recovery of sillimanite mineral from red sediments of badlands topography.

concentrate containing greater than 63% of total heavy minerals were scrubbed initially in an alkaline medium. The slimes were rejected. The sand was subjected to magnetic separation for recovery of non magnetic sillimanite and other associated heavy minerals. The non magnetic fraction was subjected to sink float tests using bromoform (2.89 sp.gr) and methylin iodide (3.3 sp.gr). The non magnetic methylin iodide float is sillimanite. The recovered sillimanite was used in the present investigations.

2.3. Effect of Microwave Treatment on Sillimanite

The recovered sillimanite from red sediments containing 56.67% Al_2O_3 was used in all the experiments. In all experiments 60% sillimanite was used as constant parameter. The samples in form of pellets were made with the combination of sillimanite (Al_2SiO_5), alumina (Al_2O_3) and additives of silicon carbide (SiC) powder in various ratios. These samples were then placed inside the microwave

sintering furnace separately in order to study the effect of microwave heating.

The microwave sintering furnace used in the present investigation was G N Tech, 37.500 W, 2.45 GHz. An adequate argon pressure is maintained in microwave furnace in order to avoid any type of oxidation reaction. The susceptor SiC placed near to sample further to facilitate the microwave absorption and heating the sample in microwave sintering furnace [5]. The susceptor SiC is placed diagonally to the sample in microwave sintering furnace. Experiments were conducted in microwave furnace by changing ratio samples such as SiC powder and alumina (Al_2O_3) variables and at constant 60% sillimanite by weight. On taking consideration that the minimum temperature required to form the mullite is 1250°C , the different samples were heated separately either by varying the duration of time or by varying the power fed with respect to variation of SiC powder and alumina (Al_2O_3). Experiments were also carried out in conventional furnace to achieve the mullite phase. The resulting products were characterized by X-Ray diffraction, FESEM and EDAX.

2.4. Analytical Methods

The PANalytical X-Pert X-Ray powder diffractometer with Mo-K α radiation ($\lambda = 0.709\text{\AA}$) from 6° to 40° scanning angle at a scanning rate of $0.02^\circ/\text{sec}$ was used for phase analysis of present investigation. Morphological features of mullite were studied using the FESEM (model: Supra55; Zeiss, Germany). The FESEM has a resolution of 1 nm at 30 KV which is equipped with 20 mm². Oxford's Energy dispersive X-ray spectroscopy (EDS) detector for imaging of conducting as well as non-conducting samples without gold coating. SEM/EDAX studies were done by using Hitachi VP-SEM S-3400N. It has high SE resolution of 10 nm at 3KV. The magnification of the instrument is 5X - 300.000X; alternating voltage is 0.3 - 30 KV. The grains were mounted on a SEM brass stub. The mounted grains were coated with gold in a vacuum evaporator while the mullite sample was being slowly rotated. Mullite and silicon carbide materials were analyzed to know the weight % of various constituents of atoms using EDAX.

3. Results and Discussion

3.1. Characterization of Raw Material

The chemical analysis of red sediment placer sillimanite given in **Table 1** indicate that the sample contain 56.67% Al_2O_3 , 25.21% SiO_2 , 0.51% TiO_2 and 0.23% Fe_2O_3 . The modal analysis of red sediment feed sample is shown in **Figure 4**. The data indicate that the deslimed feed sample contain 7% sillimanite, 51 % ilmenite, 1% zircon, 25% quartz, 2% rutile, 12 % slimes and 2 % others. The

XRD pattern of deslimed feed shown in **Figure 5** indicates that the sample contain ilmenite, quartz, sillimanite are abundant minerals followed by rutile, zircon, hematite.

3.2. Studies on Formation of Mullite from Sillimanite Using Microwave Sintering Furnace

It is a known fact that microwave sintering furnace has a wide range of applications in mineral and material technology. In microwave heating of minerals, the materials which couple to microwave radiation contain dipoles [5,6]. These dipoles align themselves in an applied elec-

Table 1. Complete chemical analysis of the sillimanite concentrate.

Compound Name	Conc. (%)
Al_2O_3	56.67
SiO_2	40.21
TiO_2	0.51
Fe_2O_3	0.23
CaO	0.42
MgO	0.31

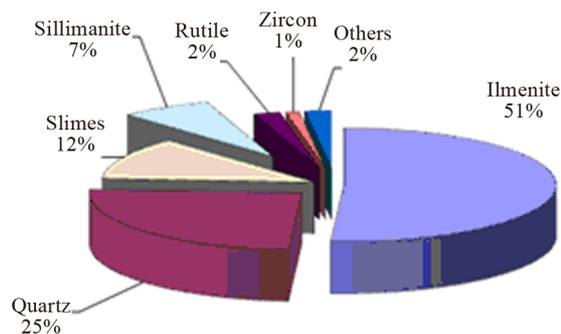


Figure 4. Modal analysis of red sediment feed sample.

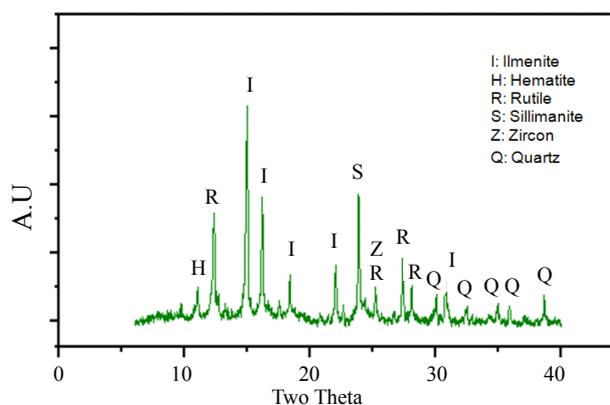
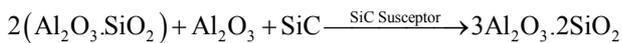


Figure 5. XRD pattern of deslimed feed.

tric field and will flip around in an alternating electric field. As a consequence, the material will be heated as the stored internal energy [5-7] is lost to friction. This energy mode conversion has the advantage of being selective to individual mineral phases within a mass by which the mullite is formed from sillimanite.

The results of microwave power on mullite formation from sillimanite using SiC as susceptors are given in **Table 2**. It may be noted here the role of SiC in the microwave sintering furnace is as a heating agent because it couples quickly with electromagnetic radiation, creating heating owing to the Joule effect. The decomposition of sillimanite with addition of Al₂O₃ and SiC may be expected as



It is also an important fact to express at this point that the desired temperature for decomposition of sillimanite to mullite and silica is in the temperature range of 1300°C - 1700°C. It is observed from **Table 2** that mullite is not formed with the charge sample containing sillimanite (60%) and Al₂O₃ (40%) alone. This is due to the fact that maximum temperature of the microwave sintering furnace achieved is 805°C only. This effect can clearly be seen in **Figure 6** where the effect of different variables such as SiC as additive and binder on the achievement of temperature (°C) with microwave power fed (Watt) is expressed. It is further seen that from **Figure 6** that the temperature of the microwave sintering furnace is not increasing beyond 805°C even with increasing of microwave power beyond 2850 Watt.

An increase in microwave power led to an increase in the heating rate of the samples with the combination of sillimanite, alumina, silicon carbide shows an affinity for microwave radiation, *i.e.*, it heats effectively with increase of the applied power and as a consequence the temperature of the sample inside the furnace rises (measured by infrared pyrometer).

The transfer of energy does not rely on diffusion of heat from the surfaces and it is possible to achieve rapid and uniform heating of sample volumetrically [6-8].

Table 2. Results of microwave energy on mullite formation from sillimanite using SiC susceptor.

Charge Sample [Sillimanite + Al ₂ O ₃]	SiC as Additive (%)	Binder (%)	Microwave Power (W)	Max Temp reached (°C)	Findings (Mullite formed)
60% + 40%	Nil	0	2850	805	No
60% + 40%	5	5	3000	1050	No
60% + 40%	40	5	2950	1080	No
60% + 40%	60	5	2372	1355	Yes
60% + 40%	60	10	1900	1384	Yes

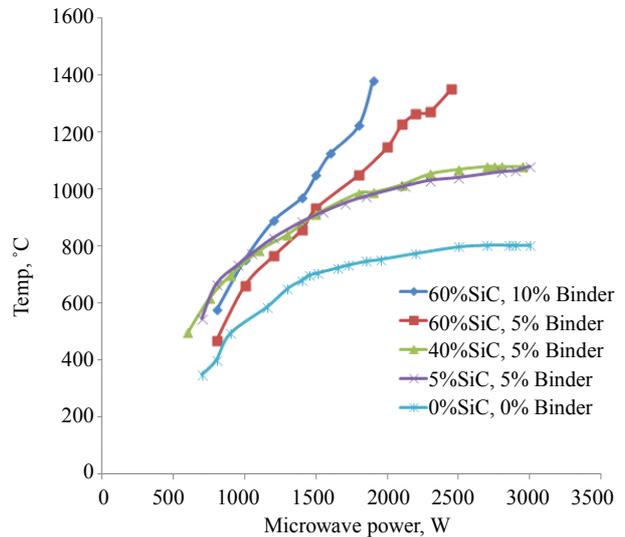


Figure 6. Effect of different variables on achievement of temperature with microwave power fed.

The results seen in **Table 2** on the effect of different variables such as 5% SiC and 40% SiC with 5% binder to achieve the desired temperature around 1300°C for mullite formation from sillimanite is not seen and hence mullite has not been formed in both the conditions.

It is seen from the experiments that the temperature occurred for given microwave power to form mullite is increasing with addition of SiC. The SiC is one of the reducing agents, which heat rapidly in presence of applied electric field. They conduct energy into the bulk sample so that electrons in non-dielectric materials can become more mobile. Due to this extra mobility, there is the formation of dipoles [5,9] in the microwave field and the material can heat on its own. It is an established fact that microwave energy has potential for the speedy and efficient heating of minerals and in a commercial context may provide savings in both time and energy. The role of SiC powder of 250 mesh in the present investigation is not only behave as reducing agent but also as heating agent owing to it couples with microwaves creating heating, essential to proceed reactions [9,10]. Also as mentioned earlier that on increasing the microwave power led to an increase in the heating rate of the samples shows an affinity for microwave radiation, *i.e.*, it heats effectively with increase of the applied power and as a consequence the temperature of the sample inside the furnace rises which is measured by infrared pyrometer.

Thus a mullite formation is seen when 60% SiC and 5% binder are used with the composite charge material *i.e.* sillimanite (60%) and Al₂O₃ (40%). The maximum temperature of the microwave sintering furnace achieved is 1355°C at 2450 W microwave power. Addition of 10% binder to the same charge material with 60% SiC, the furnace temperature achieved is 1384°C at microwave

power 1900 W. Hence when the sillimanite is exposed for 25 minutes, a mullite is formed under these experimental conditions. During microwave processing, the potential energy exists to reduce processing time and enhance product quality as microwaves can transfer energy throughout the sample volumetrically.

3.3. Studies on Formation of Mullite from Sillimanite Using Conventional Furnace

The experimental results on the formation of mullite from sillimanite using conventional furnace with the charge sample containing sillimanite (60%) and Al_2O_3 (40%) and additives with 40% SiC and 10% binder reveals that it took three hours to form a mullite at 1300°C .

It is important to mention here the observations once again on the tests carried out with conventional furnace and microwave furnace that a mullite formation is seen at 25 minutes of experimental duration with microwave furnace and where as the formation of mullite is not seen with conventional furnace during 25 minutes under optimum material variables. It has taken three hours of time at 1300°C furnace temperature for formation mullite using conventional furnace.

The heating mechanism through microwaves furnace are distinctly different form that in the conventional furnace. Typical **Figure 7** shows a schematic illustration of the process steps and effect of the heating mechanism in the carbothermal reduction reaction for microwaves furnace and conventional furnace with the charge material kaolin clay [2].

In the microwaves furnace, the heating with microwaves started in the central region of the pellets, resulted in two distinct zones: darker central core completely surrounded by lighter zone. It is also observed that the outer zone for MWCR as shown in **Figure 7** is primarily mullite with a small percentage of Al_2O_3 and much less SiC than in the central zone with primarily SiC and small percentages of mullite and Al_2O_3 . Both CO and SiO gases must diffuse out of the pellets. However, during conventional heating as shown in **Figure 7**, the carbothermal reaction began outer the pellets and then progressed into

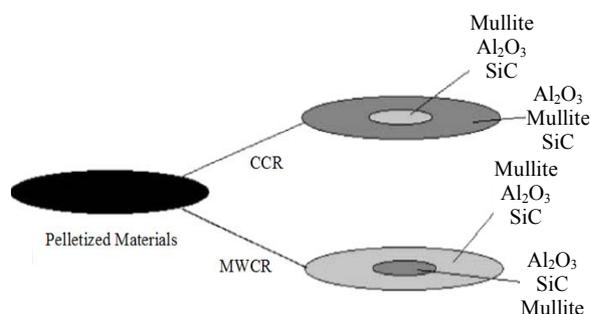


Figure 7. Effect of heating mechanism for the carbothermal reduction for both CCR and MWCR.

the central core. The pellet showed two distinct zones: lighter central region completely surrounded by a darker zone. It was also observed that the outer zone was primarily mullite with small percentages of SiC, whereas the inner region was primarily mullite with a small percentage of SiO_2 and much less SiC than in the outer zone.

Thus it is concluded that during microwave processing, the potential energy exists to reduce processing time and enhance product quality as microwaves can transfer energy throughout the sample volumetrically. Hence microwave heat source is much effective for value addition to red sediment placer sillimanite to form mullite in compare to conventional furnace.

3.4. Structural and Morphological Characterization of Mullite

The XRD patterns of charge materials and additives such as sillimanite, alumina, silicon carbide and composite charge material (raw mullite) are shown in **Figure 8**. The XRD patterns of mullite formation in both microwave furnace and conventional furnace are also shown in **Figure 9**.

The XRD data indicate that the mullite formation in both microwave furnace and conventional furnace are almost similar with reference to mullite phase concern. The results evidenced that microwave is more efficient to produce Al_2O_3 /mullite/SiC composite at 25 min than conventional furnace at $1300^\circ\text{C}/3$ h duration.

The FESEM images for mullite formation from red sediment placer sillimanite using microwave heat treated is shown in **Figure 10**. It can clearly be seen that SiC (massive form), and mullite in cluster structure, are observed in the morphological features of mullite formed from red sediment placer sillimanite using microwave furnace.

It may be noted here that as the metal melts at high temperatures, it attracts Si and C atoms from the vapor to the catalyst to form whiskers. When saturation of these atoms occurred in the liquid catalyst, the growth is side branched type, resulting in formation of fibrous structure [11]. Apart from this, the alumina needles are also found and seen in the SEM image. This alumina phase is very helpful in microwave heating because it helps to isolate silica from silicon carbide during mullite formation.

Typical SEM EDAX data and image mapping for Al, Si, C and O of microwave mullite are shown in **Figures 11 and 12** respectively.

The image mapping for Al, Si, carbon and oxygen for typical mullite sample prepared from red sediment placer sillimanite using microwave sintering furnace reveals that the sample contain both mullite and SiC materials. Thus the data obtained from XRD, SEM EDAX confirm the findings on the presence of mullite and silicon carbide

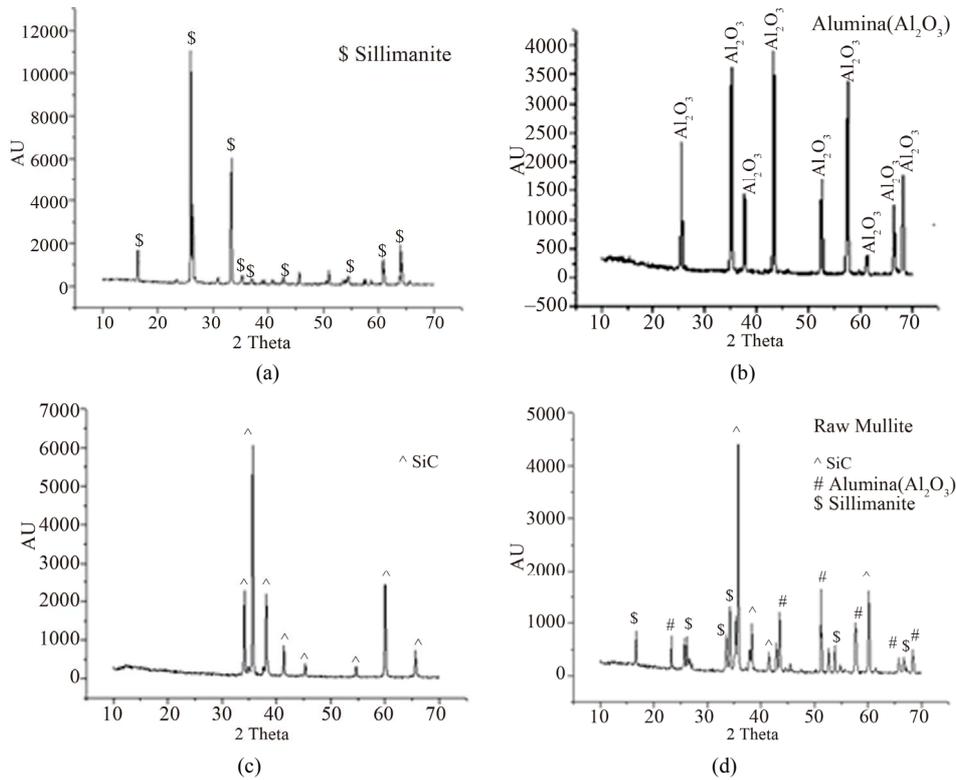


Figure 8. XRD patterns (Cu target) of (a) sillimanite (b) alumina (c) SiC and (d) raw mullite.

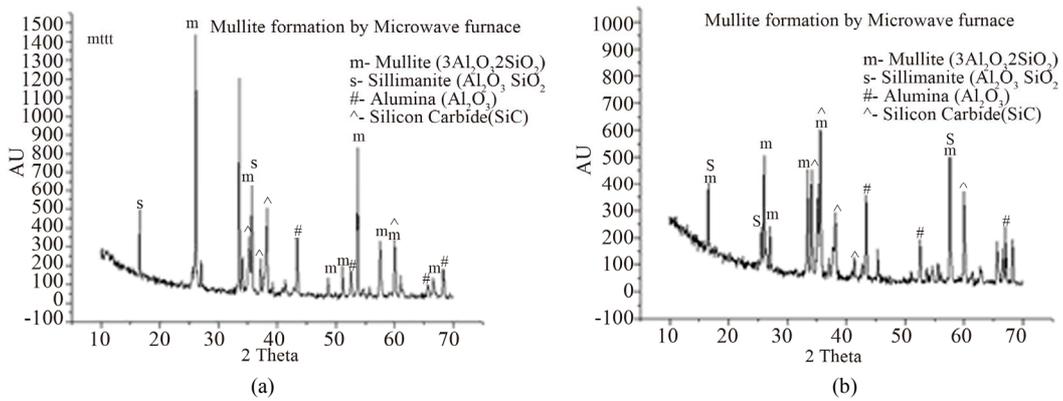


Figure 9. XRD patterns of mullite formation (Cu Target) in (a) microwave furnace (a) and (b) conventional furnace.

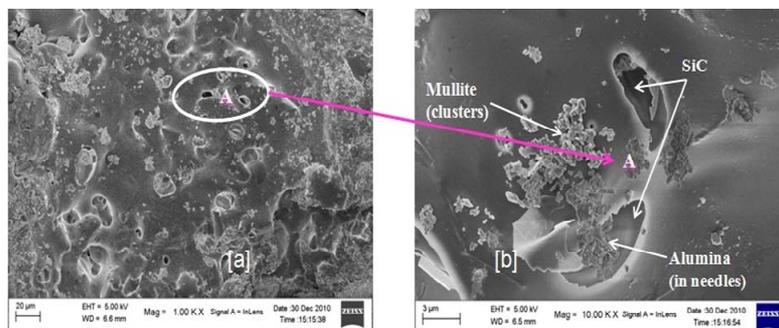


Figure 10. Morphological features of mullite (cluster), alumina (needle shape) and silicon carbide (massive structure) at one location. Figure 10(a). shows the image with 1K mag. image; Figure 10(b). shows the image of spot A of Figure 10(a), which is enlarged to 10 K mag.

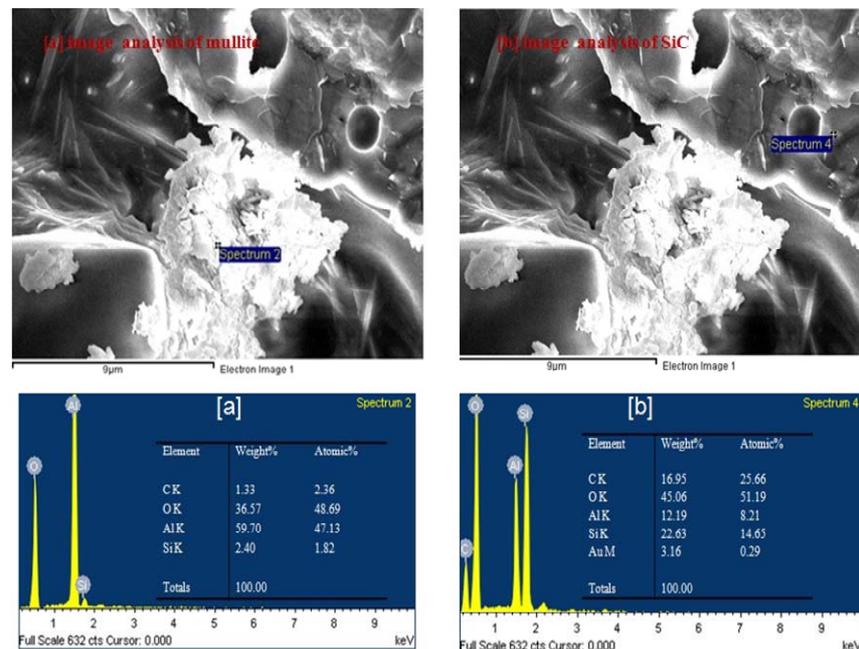


Figure 11. SEM-EDAX data of mullite and SiC. (a). image and spectrum analysis of mullite; (b). image and spectrum analysis of SiC.

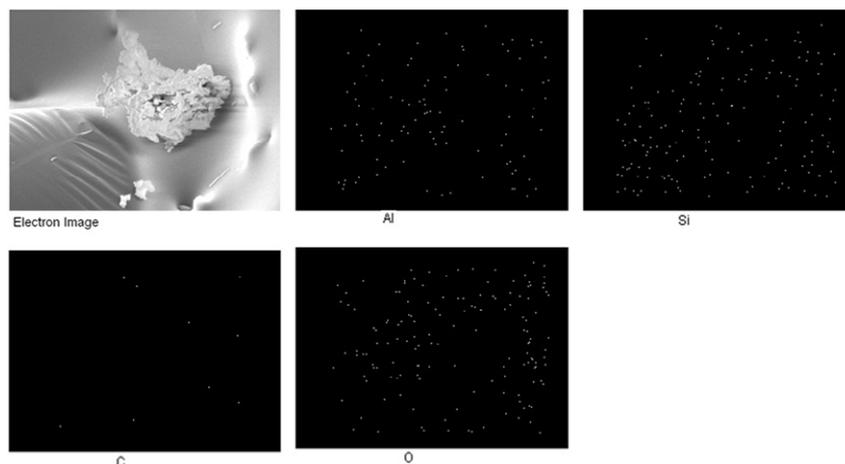


Figure 12. Image mapping of Al, Si, C and O for typical mullite sample prepared from red sediment placer sillimanite.

prepared from the red sediment placer sillimanite as a value addition.

4. Conclusions

The following conclusions are drawn from the study on value addition to red sediment placer sillimanite using microwave energy and in depth structural and morphological characterisation of mullite.

- A mullite formation is seen when 60% SiC and 5% binder are used with the composite charge material *i.e.* sillimanite (60%) and Al₂O₃ (40%). The maximum temperature of the microwave sintering furnace achieved is 1355°C at 2450 W microwave power.
- Addition of 10% binder to the same charge material

with 60% SiC, the furnace temperature achieved is 1384°C at microwave power 1900 W.

- A mullite is formed within 25 minutes from the sillimanite, under the above experimental conditions.
- Whereas under the similar additive conditions, the mullite formed from sillimanite in conventional furnace heating, it took more than 3 hours at 1300°C.
- The XRD data is shows mullite phase which relatively distinct from the formation mullite using microwave furnace than conventional furnace.
- FESEM image analysis shows the mullite and silicon carbide in microwave treated sample.
- The SEM EDAX and image mapping data also confirm the findings of mullite and silicon carbide.

- Thus microwave heat source is much effective for value addition to red sediment placer sillimanite to form mullite in compare to conventional furnace.

5. Acknowledgements

Er. Satya Sai Srikant is very much thankful to the Prof. B. K. Mishra, Director, CSIR-Institute of Minerals and Materials Technology, Bhubaneswar for giving permission to utilize infrastructural facilities of CSIR-IMMT and for his encouragements to do Ph.D. (Registered at SOA University; Bhubaneswar, Odisha, India) and publication of papers.

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