

MULLITE GLASS CERAMICS PRODUCTION FROM COAL ASH AND ALUMINA BY HIGH TEMPERATURE PLASMA

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The waste and highly hazardous coal ash from the power plants is proved to be a potential source for the production of low cost mullite glass ceramics when mixed with alumina at very high temperatures produced by plasma. In this present work, the coal ash and alumina are mixed at different weight percentages and treated with high temperature plasma produced by Transfer Arc Plasma Torch (TAP) of 10 kW power. The XRD patterns confirm that the complete single phase homogeneous mullitization occurs when 50% of coal ash is mixed with 50% of alumina. The SEM results also show that the formation of elongated needle - like mullite glass ceramics at very high temperatures. The TG – DTA analysis reveals that an endothermic phase transition and mullitization temperature occurs at 920^oC when equal weight % alumina mixed with equal weight % of coal ash. The sharpened strong endothermic peak at 920^oC reflects the homogeneity of formed mullite. The results show that the lowcost single phase mullite is obtained in a very short period of time (5 minutes) is found to be a key factor with required microstructure.

(Received October 3, 2009; after revision December 6, 2009; accepted December 19, 2009)

Key words: Glass-ceramics, Coal ash, Alumina, Mullite, Transfer Plasma Arc, Chemical Resistance.

1. Introduction:

Mullite is a stable intermediate compound ($3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$) formed with Al_2O_3 - SiO_2 system [1]. It has high melting point, low coefficient of thermal expansion, high chemical inertness, insoluble in hydrogen fluoride (HF), excellent high temperature creep resistance, good chemical resistance, infrared transparency, low dielectric constant, unique resistance to thermal shocks and high strength at high temperatures [2,3]. These extraordinary properties enable the material to be used in advanced structural applications. Mullite has an orthorhombic structure with lattice constant $a = 7.545 \text{ \AA}$, $b = 7.689 \text{ \AA}$ and $c = 2.884 \text{ \AA}$ (JCPDS card #15 – 776). It consists of edge shared AlO_6 octahedral chains aligned in the c – direction and cross shared (Si, Al) O_4 tetrahedra [4]. A lot of efforts have been made to prepare mullite ceramics using various starting materials such as industrial grade and chemical methods, all of which follow different mullitization routes on heating. The path ways can be classified into two types. (1) Mullite formation above 1200^oC through Al_2O_3 precursor. Mullite is observed in the mixture of Kaolinite and alumina sol mixtures and diphasic gels. (2) Direct formation of Aluminum (Al) rich mullite at about 900 – 1000 ^oC [5] is observed in monophasic gels and glasses. The occurrence of different mullitization routes is due to the different degrees of mixing of Al_2O_3 and SiO_2 with grains and on a molecular scale. In all these cases Mullitization occurs by nucleation growth mechanisms. However, there are different opinions on rate controlling step of mullitization.

Wei and Halloran [6] suggested that, either interface control or control of short range of diffusion near the interface occurs for mullitization of diphasic gels. Hulling and Messing [7] reported that the release of alumina from the initially formed γ - Al_2O_3 structure is the rate controlling step in diphasic gels. Sundaresan and Aksay [8] presented a similar rate limiting mechanism with mullitization of diphasic gels and suggested that the mullitization is limited by alumina release and its dissolution at low temperatures ($<1350^\circ\text{C}$) and diffusion at high temperature ($<1650^\circ\text{C}$). In the rate controlling step of mullitization with type 1, it is observed that the starting materials change at higher temperatures to diffusion - controlled process without being dominated by the transfer of Alumina from γ - Al_2O_3 to amorphous silica. In type 2 reactions, the starting materials proceed in 3 stages (i) nucleation (ii) nucleation growth and (iii) coalescence as the heating temperature increases [9]. The Mullite purity, homogeneity and Mullitization temperatures vary with synthesis methods [10, 11]. Mullitization temperature depends on the degree of mixing of alumina and silica in the precursors. Natural mullite precursors like Aluminum Silicate minerals are found to be advantageous for the production of mullite because Al_2O_3 and SiO_2 are mixed on a molecular scale [12]. Aluminum Silicate systems like pure clays and clay aluminum hydroxide (or) clay aluminum oxide mixtures have been studied to produce mullite ceramics along with Kaolin based mixtures [14 – 24] since, mullite is the common product of aluminium silicates at high temperatures [13].

The mullite rich products and other classes of high technology ceramics are produced by caolinite and caolin based mixtures [14, 15, 16, 19, 21].

1.1. Coal ash

In the present work, production of glass-ceramics by high temperature plasma using coal ash has been proposed as a useful choice to recycle coal ash from power plants. Coal ash consists of fine inorganic particles having SiO_2 and Al_2O_3 as the main components which are glass network formers. Hence, it is possible to use coal ash as a raw material to develop glass materials [25, 26, 27]. The reuse of silica rich coal ash for the production of glass ceramics is a promising development [26, 28, 29].

Coal ash is a waste residue obtained by combustion of pulverized coal collected by. The mixed samples are treated under high temperature produced by transfer arc plasma (TAP) torch. In the electrostatic precipitators in thermoelectric power plants. The emissions arising from lignite burning are coal ash particles, which cause local pollution. These particles are considered to be highly contaminating, because their high surface area gives rise to the enrichment of potentially toxic elements which condense during cooling of combustion gases. Epidemiologic studies have revealed that the short term increase in air borne particle mass concentrations is associated with increased mortality and morbidity from respiratory and cardiovascular diseases. Coal ash has been recycled through thermal treatment, which can be used as construction materials such as aggregates, bricks, tiles and eco cement [30, 31]. Coal ash particles are potential discontinuous disperoids used in metal matrix composites, since they are low cost and low density reinforcement available in large quantities as a waste byproduct from thermal power plants. The major chemical constituents of coal are SiO_2 , Al_2O_3 , Fe_2O_3 and CaO . The coal ash constitutes the aluminosilicate glasses containing Quartz, Mullite, Hematite, Magnetite, Spinal and Alumina. Incorporation of coal ash particles in Aluminum (Al) alloys improves the wear resistance, damping properties, hardness, and stiffness. Aluminum coal ash composites have variety of potential applications such as covers, pans, shrouds, casting, pulleys, manifolds, valve covers, brake rotors, engine blocks and in electrochemical industries [32]. Mullite based composites are attractive because of their inherent oxidation resistance at high temperatures, unique resistance to thermal shocks and damage tolerance properties. This paper presents the production of mullite from coal ash and alumina mixed at different weight percentages by ball milling TAP processes is better than conventional sintering and reaction sintering methods because mullite produced by the TAP process requires very short period of time and also cost effective compared to conventional sintering methods. There are various conventional technologies including energy saving, clean energy, waste management and material recycling. Ceramics technology is one of the promising technologies to establish the practical environmental technology for better global

environment[33]. TAP is one such a widely used technology for melting and vitrification of hazardous wastes due to their high temperatures and simplicity of their generation and control. The TAP is assumed to be stable, steady, axi-symmetric, optically thin and in a local thermodynamic equilibrium in an atmospheric pressure environment [34, 35]. The TAP process is characterized by extremely high temperatures (up to 20,000 - 30,000 °K), excellent arc stability and low environmental impact (low oxides emissions, low % of ultra fine powder). High density allows high production rate with evident time savings [36, 37, 38, 39].

2. Experimental (Methods and Materials)

Glass ceramics are prepared using coal ash and alumina mixtures as raw materials. Coal ash is a complex material, with a heterogeneous and variable compositions.. This fact is directly related to the heterogeneous composition of the lignite feed of the power plants. The investigated coal ash particles consist mainly of inorganic constituents. The inorganic constituents may be amorphous or crystalline. The raw material coal ash is taken from thermal power plant NLC [Neyveli Lignite Corporation], Tamilnadu, South India. Alumina is purchased from CUMI India (P) Ltd. The coal ash and alumina chemical composition are given in table 2a.

Table 2a. Chemical composition of raw materials

Oxides	Alumina	Coal
Al_2O_3	80.35	28.97
SiO_2	7.12	60.44
TiO_2	5.51	1.97
Fe_2O_3	3.31	4.49
MgO	1.55	1.03
K_2O	0.21	1.08
P_2O_5	0.33	0.37
CaO	0.59	0.77
Na_2O	0.29	0.27
Others	Balance	Balance

Table 2b. Operating parameters of TAP torch

Input power	10 kW
Plasma Gas and flow rate	Air; 10 lpm
Cooling water flow rate	10 lpm
Processing time	5 minute
Cooling time	20 minutes
Cooling medium	Air(open air rapid cooling)

Alumina is added to coal ash by 0, 25, 50 and 75 weight percentages and thoroughly mixed by planetary ball milling system (Insmart, India) for two hours. The ball to mixture weight ratio is kept at 10:1 and milled for 2 hours; the mixture is in powder form. The milled powders are melted by Transferred Arc plasma torch (Ion Arc Technologies, India) for 5 minutes at 10KW input power and the heated mixture is allowed to cool rapidly in open atmosphere for 20 minutes. The schematic diagram of the experimental setup is shown in Fig.1. The experimental set up consists of plasma torch, power supply, gas and water lines. The torch consists of a graphite bowl with 100mm depth and 50 mm inner diameter serves as an anode and melting bed. The cathode is made up of graphite rod of 250mm long and 50 mm diameter. Its end tapers to a conical shape for better electron emission. The cathode is enclosed in a hollow brass cylinder and provisions are made for water circulation for cooling and gas flow. The system has multiple inlets for plasma gas at the cathode end. The operating parameters of plasma torch are shown in Table 2b.

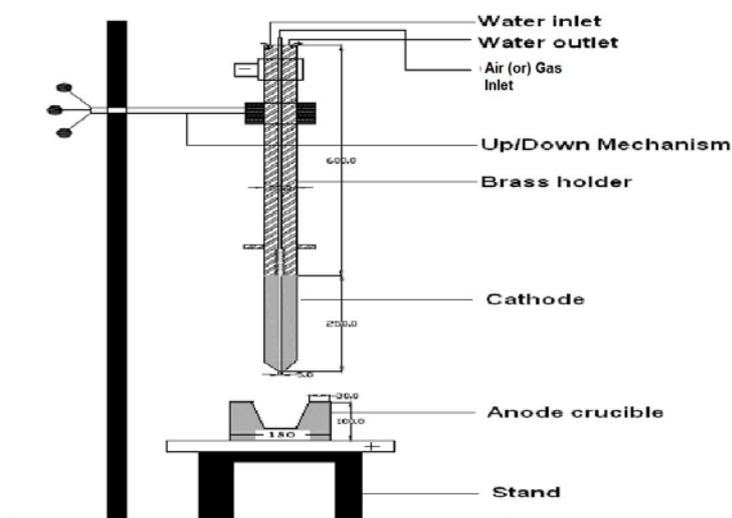


Fig.1. Schematic diagram of experimental setup.

The different compositions of coal ash – Alumina mixture are prepared with respect to the weight ratio of alumina (coal ash 100%, Alumina 100%, coal ash 75% + Alumina 25%, coal ash 50% + Alumina 50% and Coal ash 25% + Alumina 75%). For Scanning Electron Microscope investigations (SEM) the samples are polished first with a set of silicon carbide papers and then with diamond paste. Then, the samples are chemically etched using 30 wt% Hydrogen Fluoride (HF) solution for 30 seconds. The surface study of the raw materials and processed samples are carried out by SEM Philips XL30. The TAP processed samples are milled to a few micrometer size powders in an achate mortar prior to X-ray diffraction. The structural analysis is carried out by X – ray diffractometer (XRD) Philips PW 3710 with $K\alpha$ radiation. The XRD study is performed on pulverized Mullite specimen over 2θ values of $0 - 80^\circ$. The crystalline phases are identified by comparing the peak positions and intensities with data files (JCPDS). To determine exothermic crystallization temperatures and endothermic phase transition temperatures of raw samples and processed samples, a Thermo Gravimetric and Differential thermal analysis (TG–DTA) DuPont model 2000 apparatus is used to obtain TG – DTA patterns. Analysis is carried out with nitrogen at the furnace temperature. For holding samples, alumina crucibles are used and α – Alumina powder is used as the reference material. The samples are heated to 1600°C , held for 20min and then cooled. The heating and cooling rates are $20^\circ\text{C}/\text{min}$. The area under the peaks on the DTA is integrated to calculate the heat released by phase transition (or) chemical reactions.

3. Results and discussions

3.1. Structural, compositional, surface and thermal analysis of raw materials Coal ash and Alumina.

Figure 3.1a shows the coal ash XRD peaks. Quartz is the main phase present (JCPDS CARD #46-1045). In addition to that, minimum of calcium sodium aluminum iron silicon oxide, microcline (KAlSi_3O_8), Leucite (KAlSi_2O_6), Calcium Sodium Aluminum oxide ($\text{Ca}_{0.5}\text{Na}_{1.5}\text{Al}_2\text{O}_6$) and Micro perthite ($\text{K}_{0.96}\text{Na}_{0.04}\text{AlSi}_3\text{O}_8$) and other alkali and alkaline earth metal oxides are present. Fig.3.1b is the SEM photograph of raw coal ash heated at plasma temperature. The surface is found to be porous due to the evaporation of organic particles [40] and absorbed water.

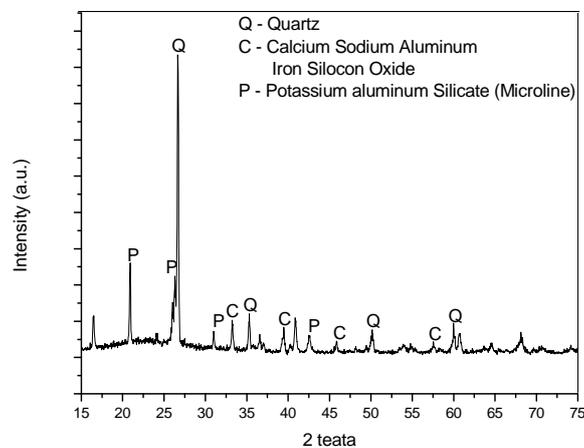


Fig. 3.1a. XRD pattern of 100% Coal Ash (Q:JCPDS CARD #46-1045),

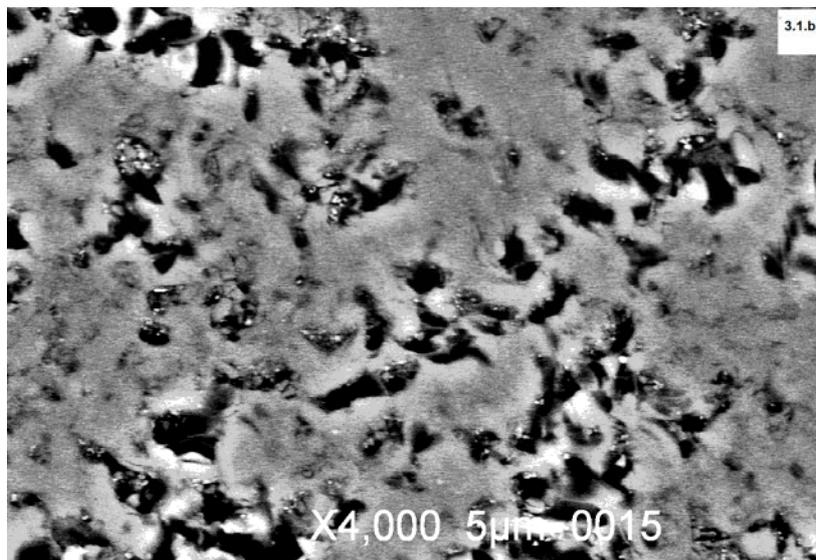


Fig. 3.1b SEM pattern of 100% Coal Ash

Fig. 3.1.c reveals the TG – DTA patterns of raw coal ash heated to a temperature 1600°C. The TG curve shows that during heating the mass loss is negligibly small (about only 1%) and no specific exothermic peaks are noticed in DTA curve. Endothermic heat absorption is utilized in evaporating organic particles [40] and absorbed water present in coal ash Fig 3.1b.

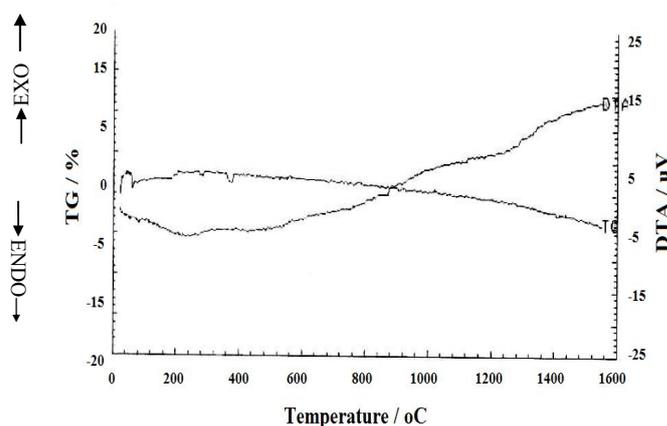


Fig. 3.1.c. TG - DTA pattern of 100% coal ash

Fig 3.1.d shows the XRD peaks of Alumina. Aluminum oxide (Al_2O_3) is the major phase (JCPDS CARD #10-173) of the alumina and it is combined with small quantities of Sillimanite (Al_2SiO_5) (S: JCPDS CARD #22-18) and Cristobalite (C: JCPDS CARD #11-695). The alumina is mainly composed of alumina oxide (80.35 wt %) and small amount of SiO_2 (7.12 wt %), Titania (5.51 wt %), Fe_2O_3 (3.31 wt %), other alkali and alkaline-earth metal oxides such as Na_2O , K_2O , MgO and CaO also exist.

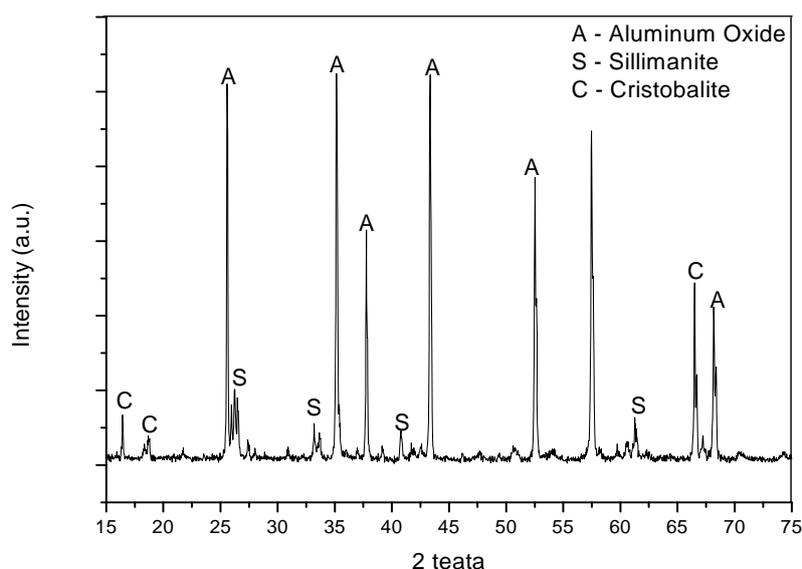


Fig.3.1.d. XRD pattern of 100% Alumina
(A: JCPDS CARD #10-173, S: JCPDS CARD #22-18, C: JCPDS CARD #11-695)

Fig 3.1.d The surface structure of alumina shown by SEM analysis. It is found that the surface is embedded in a high fraction of residual glassy phase.

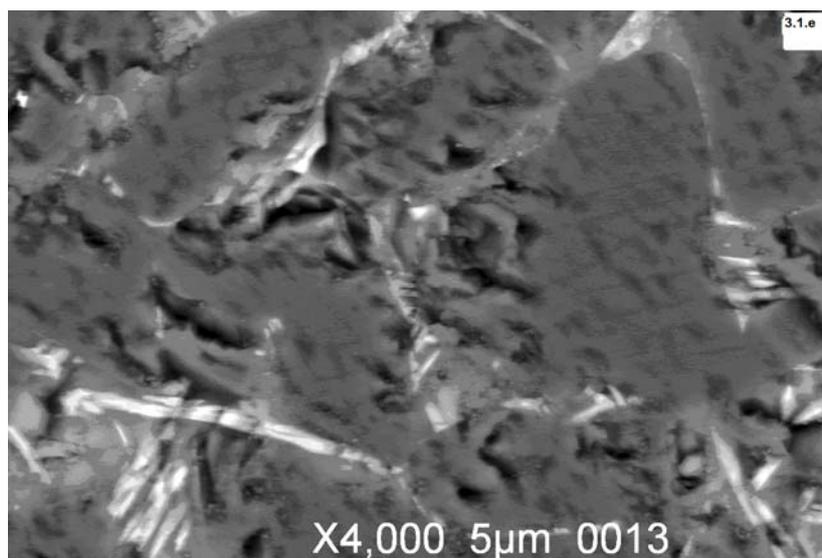


Fig. 3.1.e. SEM pattern of 100% Alumina

Fig 3.1f shows the TG – DTA patterns of heated alumina. The TG graph exhibits that there is no loss of mass of alumina during heating. A small endothermic peak occurs at around 320°C due to the evaporation of organic materials [40] and absorbed water. An exothermic solidification peak occurs at a phase transition temperature of 700°C for pure alumina. It is confirmed by the presence of glassy phase in the SEM photograph of alumina as shown in Fig 3.1.e. Another broad endothermic peak occurs due to the absorption of heat at 1200°C. These exothermic and endothermic peaks are due to the formation of silimanite and cristobalite due to the decomposition of Alumina at such higher temperatures.

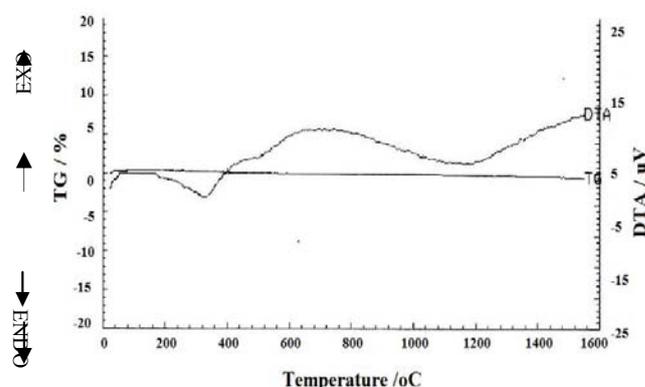


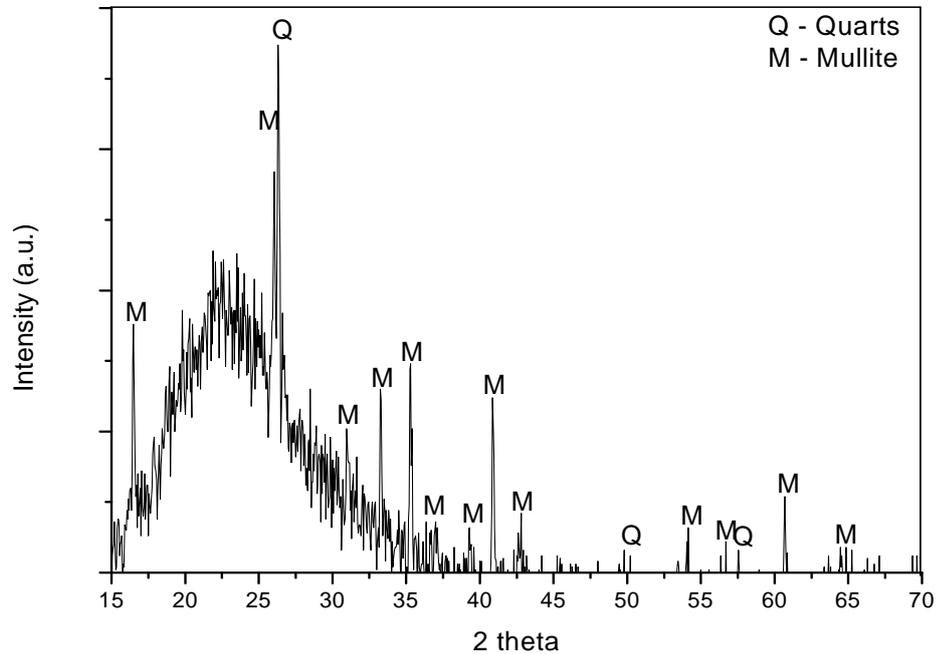
Fig. 3.1.f. TG - DTA pattern of 100% Alumina

Structure, compositional, surface and thermal analysis of alumina mixed with coal ash at 4 different weight percentages:

4.1 75% coal ash + 25% Alumina

Fig 4.1a gives the XRD pattern of 75% of coal ash mixed with 25% of alumina and heated to plasma temperature. Major phase of Mullite is formed. Another phase of Quartz is also obtained. The structure is found to be polycrystalline and heterogeneous since the mixing of the Al_2O_3 and SiO_2 in the processed samples is not on the molecular scale, but occurs at the level of grains. Further, the inter diffusion of Al_2O_3 and SiO_2 does not occur even at a very short distance of diffusion for the formation of complete mullite nuclei in the sample [9].

Since in this sample the weight % of coal ash exceeds the alumina the mullite formation corresponds to the nucleation growth region. The micro structure forms a particulate structure containing particles of SiO₂ rich composition dispersed in Mullite [9].



*Fig.4.1a. XRD pattern of Coal ash 75% + Alumina 25%
(Q: JCPDS CARD # 46-1045, M: JCPDS CARD #15-776)*

The SEM photograph Fig 4.1b also confirms the growth of heterogeneous Mullite structure and unreacted silica and other particles are distributed over the surface.

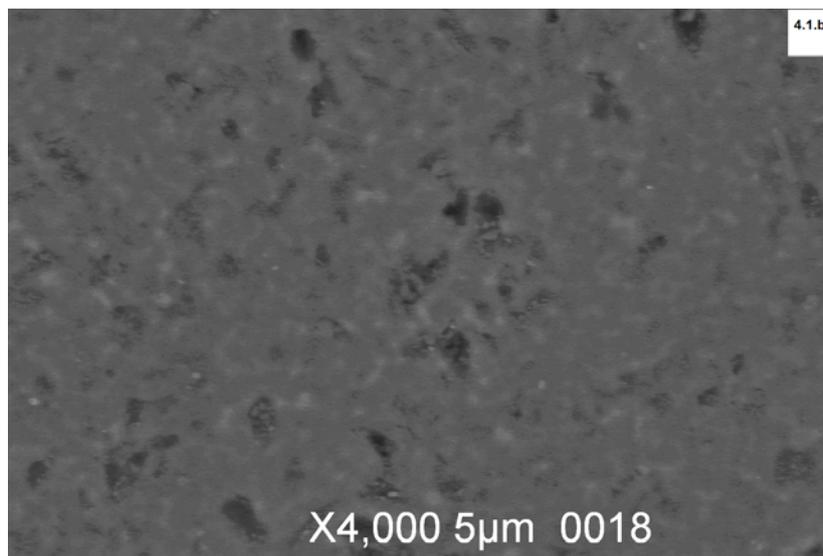


Fig.4.1b. SEM pattern of Coal ash 75% + Alumina 25%

The TG – DTA curve Fig 4.1c shows that two endothermic phase transition temperature occurs at around 920°C and 950°C for mullite and quartz [41] respectively. The peak obtained is not so sharp representing presence of two different phases of Mullite and Quartz. The Mullite obtained is polycrystalline and heterogeneous.

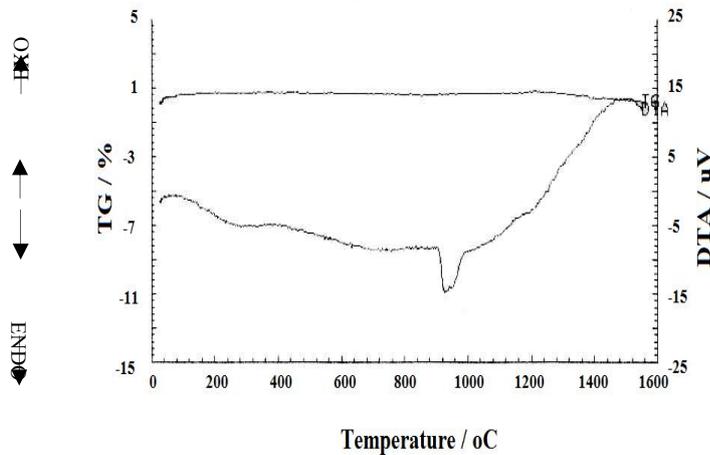


Fig.4.1c. TG - DTA pattern of Coal ash 75% + Alumina 25%

4.2 50% coal ash + 50% Alumina

When 50% Coal ash +50% Alumina are mixed the XRD pattern Fig 4.2 a. shows a complete Mullite formation. Homogeneous crystalline Mullite phase alone is present. The additional phase of Quartz appeared in the previous case (75% coal ash +25% alumina) disappears, since the coal ash and alumina are mixed perfectly on a molecular scale. This result may be the effect of interfaces introduced by phase separation occurring prior to crystallization [41]. The SEM photograph Fig 4.2 b also confirms the complete formation of homogeneous Mullite ceramic glasses in the form of elongated needles.

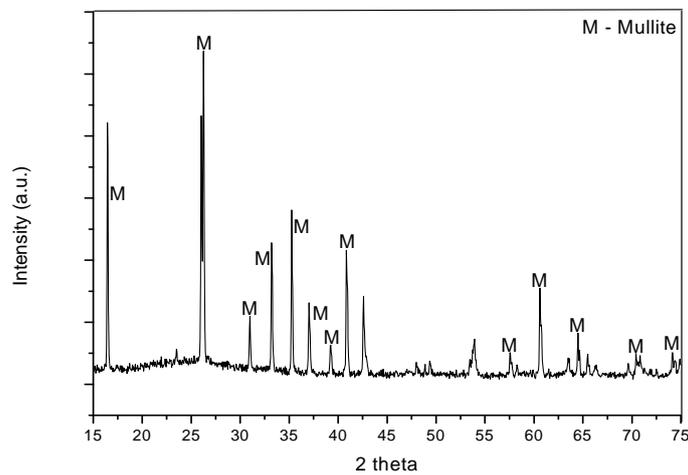


Fig.4.2 a.. XRD pattern of Coal ash 50% + Alumina 50%

(M : JCPDS CARD # 15-776)

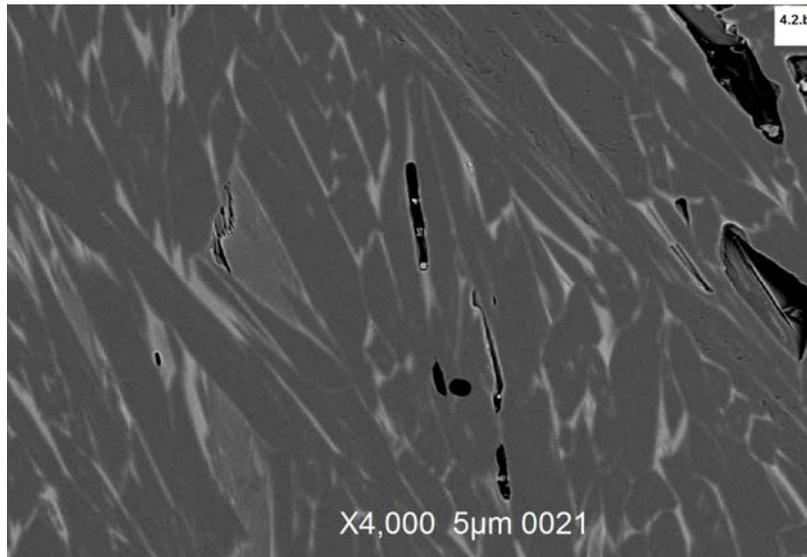


Fig.4.2 b.. SEM pattern of coal ash 50% + Alumina 50%

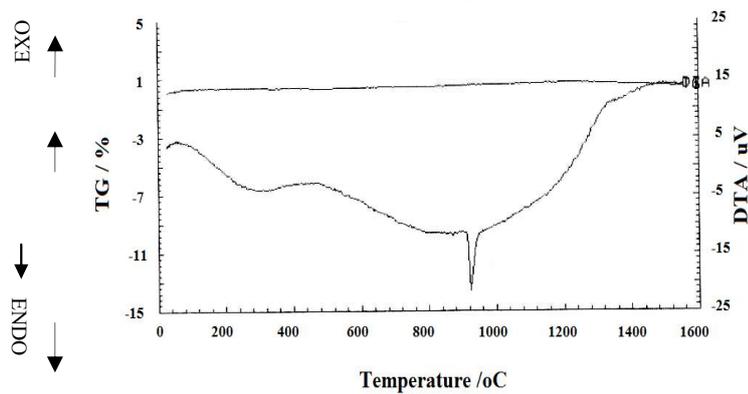


Fig.4.2 c.. TG – DTA pattern of Coal ash 50% + Alumina 50%

In Fig 4.2.c the TG – DTA the endothermic phase transition temperature is sharp at 920°C representing homogeneous single phase composition of mullite glasses. The heterogeneous structure gradually changes into single phase Mullite crystals indicating that equal weight % mixture of coal ash and alumina is necessary for single phase homogeneous Mullite glass formation. The occurrence and intensity of this endothermic peak is closely related to the intimacy and homogeneity of the Al-Si components in the sample [42]. A sharpened strong 920°C endothermic peak indicates a better homogeneity in the degree of mixing of the Al and Si components in the sample. The mullitization temperature at 920°C is considered to be an important criterion in the assessment of the mixing scale of the Al and Si components in the mixture. It is pointed out that temperatures in the range of $1600\text{--}1700\pm\text{C}$ are required to achieve mullitization when alumina and silica particles are mixed in the micrometer size range. If the mixing scale is at the molecular level, mullitization temperatures of $1000\text{--}1100\pm\text{C}$ can be achieved.[43].

4.3 25% Coal ash + 75% Alumina

Fig 4.3.a. shows the XRD patterns of 25% Coal ash + 75% Alumina. The weight % of alumina exceeds coal ash; hence in addition to Mullite phase another phase of alumina is present. The heterogeneous

crystalline mullite formation corresponds to the nucleation growth region. The microstructure forms a particulate structure containing particles of Alumina (Al) rich composition dispersed in mullite [9].

Fig 4.3.b. conforms the alumina phase dispersed over Mullite phase. The presence of glassy phase is also seen with SEM photograph similar to SEM photograph of alumina (Fig 3.1.e). The TG – DTA (Fig 4.3.c.) also confirms the different phase compositions with heterogeneous mullite. The endothermic peak is not sharp representing the presence of different phases. The endothermic peak transition temperature also decreases to 800°C due to the heterogeneity and the presence of excess alumina. This result is attributed to the heterogeneity in the mixing scale of the Al-Si components in the sample [44].

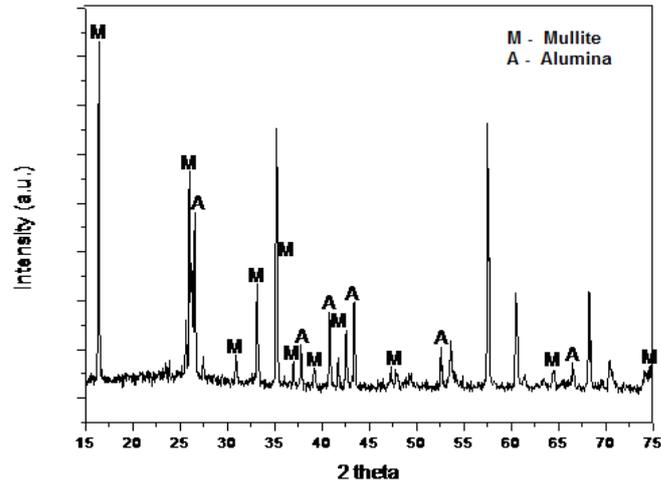


Fig.4.3.a. XRD pattern of Coal ash 25% + Alumina 75%

(M: JCPDS CARD # 15-776, A: JCPDS CARD # 10-173)

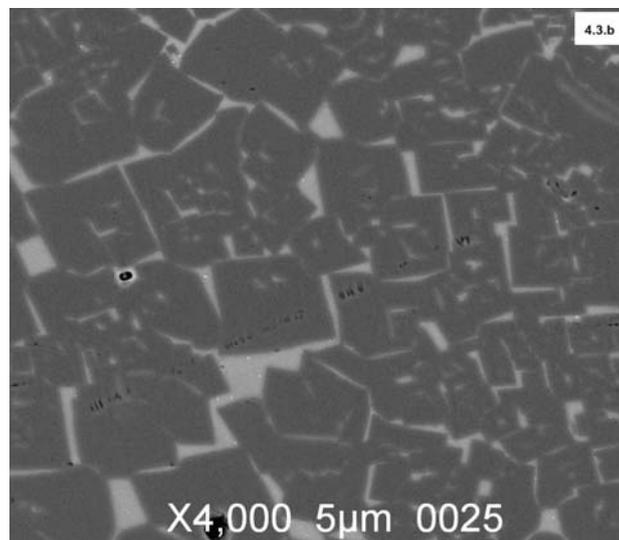


Fig.4.3.b. SEM pattern of Coal ash 25% + Alumina 75%

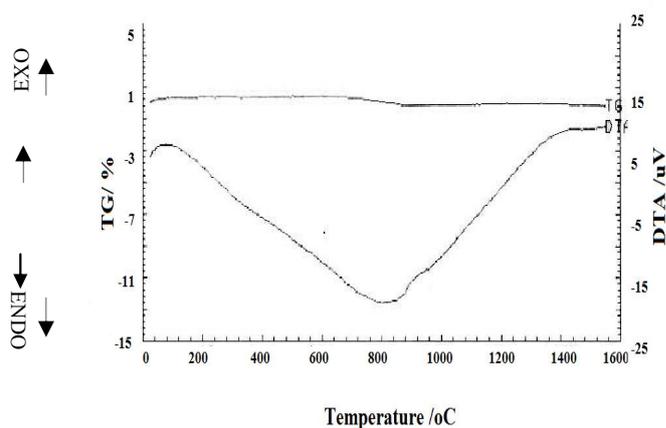


Fig.4.3.c. TG - DTA pattern of coal ash 25% + Alumina 75%

5. Conclusions

Low cost homogeneous single phase growth of Mullite is obtained by directly mixing alumina and coal ash and heating at very high plasma temperatures produced by TAP torch of low power (10 kW). Equal weight percentages of alumina and coal ash (50% Coal ash + 50% Alumina) are necessary for a complete homogeneous and single phase growth of Mullite. The phase transition temperature for single phase Mullitization occurs at about 920°C. A sharpened strong 920°C endothermic peak indicates a better homogeneity in the degree of mixing of the Al and Si components in the sample. In other weight percentages of alumina and coal ash, in addition to Mullite phase, Quartz (or) Alumina is formed. The problems encountered in the conventional sintering methods in the form of low bulk, grain boundary diffusion of mullite and very long processing time (>2 hrs) are eliminated in TAP plasma process. Low cost raw materials are used (coal ash and alumina) hence, the cost of production of mullite is reduced and these raw materials are found to be an alternative source for high cost industrial grades and chemicals for the production of mullite. The results show that the plasma (TAP) processing method can be very competitive compared to conventional sintering methods as the processing time period is 40 times less than conventional methods.

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