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Synthesis and Characterization of Fused Mullite Nano Powder

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Abstract

Mullite powder has been prepared by using many techniques like sol gel, fusion of starting materials, high energy ball milling, spray pyrolysis etc. Bayer alumina, quartz sand, rock crystals and fused silica wax were used as starting materials to prepare fused mullite of stoichiometric composition $3Al_2O_3.2SiO_2$. The raw materials were melted in an electric furnace above 2000^oC and cooled in the molds, during which crystallization of mullite took place. The aluminum silicate melt was cast in molds and cooled to room temperature by air cooling. The quenching being rapid produced a higher Al_2O_3 content. The cast melts were later crushed to produce mullite powder. The fused mullite powder was subjected to ball milling technique at different time intervals such as 75, 100 and 150 hrs. Then the prepared mullite nanopowder was characterized using UV Visible, XRD, PSA, EDAX & AFM analysis. UV Visible study confirms the low absorption value of mullite nanopowder in which the transmission value is very high. XRD characterization studies confirm the crystalline nature of the powder and the presence of Al_2O_3 and SiO_2 phases. EDAX studies confirm the presence of aluminium, silicon and oxygen in mullite powder. Particle size analysis confirms the narrow size distribution and proves the efficiency of the ball milling method. AFM analysis of 2D and 3D images confirms the size and morphology of the nanopowder. 3D form confirmed most of the nanoparticles have needle shaped morphology.

Key words: *Fused nano mullite, Atomic Force Microscopy, Powder XRD, EDAX, PSA*

1.INTRODUCTION

Mullite is a suitable material for use in structural ceramic applications due to its high temperature strength and creep resistance. It has a high melting point of 1830^0C, good electrical resistance, good mechanical strength, low thermal expansion coefficient (4.5×10^{-1}), low electrical conductivity and low dielectric constant ($\varepsilon = 56.5$ at 1 MHz) and good chemical and thermal shock resistance properties. It is used in refractory applications, electronic applications, protective coatings, electrical insulators, for gas turbine components and optical fields. Due to its versatile properties, a cost effective and easy method of synthesis of mullite becomes necessary for bulk/mass production of engineering components. Generally the synthesis methods can be grouped into six categories, based on the starting materials used, 1) A mixture of solids such as oxides, hydroxides, salts and clay materials, 2) A mixture of sols, 3) A mixture of sols and salts, 4) A mixture of Si-alkoxide and Al-salt, 5) A mixture of Al-alkoxide and Si-alkoxide and 6) A mixture of other materials [1].

Many researchers have attempted to synthesize nano particles of mullite and the work done so far has been presented briefly below. The synthesis and characterizion of nanostructured spherical particles of mullite powders can be obtained using ultrasonic spray pyrolysis method [2]. In another study, the review is divided into four parts. In the first, classification and general issues of nanostructured ceramics are reported. The second provides basic structure–property relations, highlighting the grain-size dependence of the material on properties.

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The third describes the role of nano crystalline second-phase on the mechanical properties of ordinary grain sized ceramics. Finally, the fourth part revises mainly the used synthetic routes to produce nanocomposite ceramic powders, underlining the critical role of the synthesis method on the control of microstructure and properties of the sintered ceramics [3]. Nano scaled mullite ($3Al_2O_3.2SiO_2$) powders had been fabricated by an organic-inorganic solution technique using a polyvinyl alcohol (PVA) as an organic carrier. PVA polymer contributed to a soft and porous powder microstructure, and ball milling with the porous powder was effective in making nano-sized mullite powders [4]. In flame spray pyrolysis method an alcohol-soluble precursors allowed the synthesis of mullite-composition nano powders (average size of; 60–100 nm) that, when annealed carefully, provided processable nano-mullite powders [5]. Daniel and co workers made an attempt to synthesize nano mullite/mullite nanocomposite powder by spray pyrolysis [6].

Hussein Alaajaber found a new route for synthesizing high purity submicron size mullite ($3Al_2O_3.2SiO_2$) powder at relatively low temperature was attempted. Mullite precursor has been prepared by mixing precipitated silica powder with solution of aluminum nitrate nonahydrate ($Al(NO_3)_3.9H_2O$) through sol-gel process, in order to obtain composite powder [7]. Lucia tellez jurado and their coworkers found mullite ceramics were created by the sol-gel method, using silicotetraetilorto silicate (TEOS) mixed with aluminum tri-sec-butoxide (TSBAI) or aluminum chloride. The quantities used of each substance were those that led to obtain stoichiometric mullite ($3Al_2O_3.2SiO_2$). The experimental methodology used for obtaining mullite consisted of sol-gel synthesis of precursor materials, isothermal treatment of those materials, and characterization of resulting materials [8]. Do Nascimento Jurado *et al* proposes the production of mullite powders by the Pechini method, which is today one of the most viable methods and successful technique used in the preparation of nano sized materials. The aim was to achieve better structural and morphological properties [9]. Enrico Bernardo and co workers carried out the heating in air of a selected mixture of a silicone resin and alumina nanoparticles in the temperature range 1200°–1500°C yielded dense, crack-free mullite samples [10]. Tong *et al* which have successfully synthesized mullite nano composite powders from pretreated coal gangue via hydrothermal crystallization process [11]. Shumaila Islamet *et al* found thermally stable aluminum-silicate i.e. mullite is doped with erbium for optical device applications. The matrix is synthesized and doped with 0.1 M of Er^{3+} by the sol-gel precursor method at room temperature [12]. The preparation of nano mullite powders has been achieved from calcined kaolin via open hydrothermal process [13]. L.B.Kong *et al* found High-energy ball milling had a great influence on phase formation and morphology development of mullite derived from oxide precursors. Mullite phase was formed at 1300°C in an oxide mixture of Al_2O_3 and quartz without high-energy ball milling and the mullitization was not complete up to 1500°C. After milling for 5 h, the mullitization temperature was reduced by about 200°C, at the same time, mullite whiskers were obtained [14]. Effects of attrition milling on the decomposition of kyanite (Al_2SiO_5) and its reaction with α-alumina (Al_2O_3) to form stoichiometric mullite ($3Al_2O_3.2SiO_2$) are reported by Aguilar-santillan and their co workers. In this work the Kyanite-alumina mix was attrition milled for times from 1 h to 12 h [15].

The present study focuses on the synthesis of mullite of nano meter size by using the top down approach of ball milling the factory product. A simple and cost effective method suitable for up scaling to manufacturing has been studied in this paper for the synthesis and characterization of mullite nanopowder and understand its physical and chemical properties.

2.Experimental

Mullite Powder Synthesis

Raw materials for fused mullite ceramics and refractories such as high purity Bayer alumina, pure quartz sand, rock crystals and fused silica wax were used as starting materials to prepare fused mullite of stoichiometric composition $3Al_2O_3.2SiO_2$. The materials were supplied by M/s Carborundum Universal, Kalamaserry, India.

The raw materials were fused and melted in a tilting type electric furnace above 2000^0C and subsequently cast into ingot moulds and cooled to room temperature by air cooling, during which crystallization of mullite took place. Controlled cooling of the molten mass ensures a high degree of mullitization characterized by well-defined columnar crystals. The grits formed were of macro size. Referring to the phase

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diagram of mullite, Figure- 2, crystal growth begins at 1890^0C. The impurity level of the raw materials was kept low to avoid formation of secondary phases. The quenching being rapid produced a higher Al_2O_3 content. The cooled crude is further crushed, cleaned of magnetic impurities in high intensity magnetic separators and classified into desired size fractions. Fused mullite is one of the main raw materials used by the refractory industry for applications requiring thermal shock resistance and corrosion resistance. A photo of the mullite powder is shown in figure 1.before ball milling. The phase diagram of mullite is shown in figure 2.

Ball Milling

The mullite powder prepared was ball milled in a Planetary Ball Mill PM 400, Type Reitzh, Germany for durations of 75 hours, 100 hours and 150 hours and later sieving was done to separate the different powder sizes. Three different particle sizes were obtained. The samples were dried in an oven before testing to remove the moisture content if any.

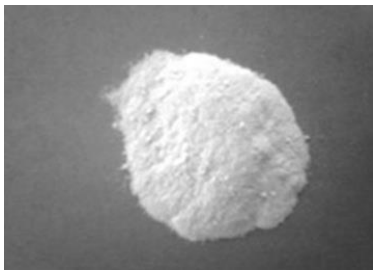

Figure 1.Mullite Powder before Ball Milling

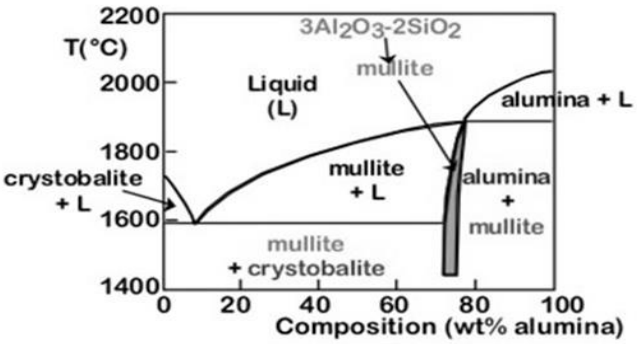

Figure 2.Multiphase Diagram of Mullite Powder

3. Characterization

The optical properties of nanoparticles of various sizes were determined in a UV-Vis spectrophotometer, UV - Analytik Jena Specord 210 Plus of Germany. The instrument covers the range from high-performance real double-beam instruments with Cooled Double Detection (CCD) to high power diode-array systems for simultaneous high speed measurement and spectrophotometer using Split- Beam-Technology (SBT). The samples were tested in a particle size analyser Horiba nanopartica SZ 100 of USA. The evolution of phases of milled powders was followed by X-ray diffraction (XRD) using Panalytical Xpert Pro Powder Diffraction unit with Kα radiation of Cu and collimator of 1 mm, scanning from 10 to 80 degrees in 2θ at 2degrees/minute, with 2θ increments of 0.03 degrees. Particle size analysis was studied using particle size analyzer Horiba nanopartica SZ 100 of USA. The composition of the powder is found out from Energy-dispersive X-ray spectroscopy (EDS or EDX) studies observed in Jeol JSM T100 SEM/EDS equipment. The particle morphology and size details are seen with AFM - APE Research A100 SPM scanning system, of

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APE Research, Italy s.r.l. with X-Y scan size :100 x 100 µm (high voltage mode); Z scan size:10 µm (high voltage mode). Particle size is measured using dynamic light scattering (DLS) principle. Depending on the physical properties of the sample, the dynamic range is 0.3 nm – 8 µm.

4. Results and Discussion

UV Visible Spectroscopy

The UV Visible spectra recorded are shown in figures 3 a, b & c at different ball mill duration at 75,100 & 150 hrs. Absorption peaks were observed at 700 nm, 300 nm and 1000 nm respectively for the three samples. The absorption values are very low which means the transmittance is very high. The material transmits almost all the UV light and is hence nearly transparent. For the first sample, the absorbance A is 0.385 and the transmittance T is 41.69%, for the second, A= 0.130, T= 74.13 %. For the third sample, A= 0.070 and T = 85.11 %. Note that as the particle size decreases, the absorbance decreases and the transmittance increases. The material can be used for applications where translucence is required.

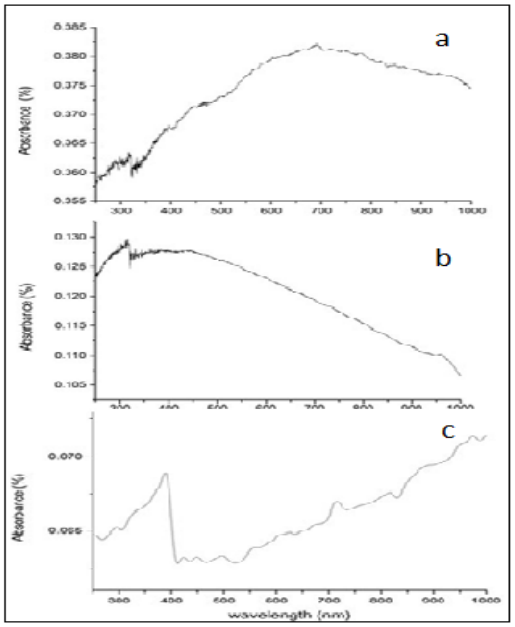

Figure 3. UV Spectrometer Plot for Sample a, b & c at Different Ball Milling Intervals (75,100,150 hrs) from Top to Bottom

XRD Analysis

The XRD plots are shown in figures 4 a, b & c at different ball mill duration. Considering the XRD plot in figure 4a, peaks of higher intensity generally refer to mullite with peaks at 35, 37, 43, 52 and 68, 2Θ (rounded off) values referring to Corundum phase (Al_2O_3) and 26,58,67,68 and 78, 2Θ (rounded off) values referring to the Quartz phase (SiO_2) as per JCPDS reports for mullite, Corundum and Quartz. A similar inference can be made for the other two (4b & 4c) XRD plots shown. Almost all the peaks refer to mullite phase and the differences in intensities for the three samples are noted. The reason for this variation is the particle size and the volume content of the samples. The intensity is lower in the third sample (4c) due to lower particle size (125 nm). The sharp narrow diffraction peaks seen in the XRD plot imply the good crystalline nature of the as-synthesized mullite powder with little (note the hump in the plots for the 10 to 20 degrees 2 Θ range) or no amorphous content. Similar type of XRD spectrum is observed in available literature [16].The diffraction intensities were recorded from 10 to 80 degrees 2 Θ angles. The spectra were recorded in a Panalytical Xpert Pro Diffractometer (Cu Kαradiation, λ_1 = 1.540; λ_2 = 1.544) running at 40 kV and 30 mA.

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The average crystalline size (D) of the nano-sized mullite particles was estimated to be about 21.39, 20.445 and 24.022 A^0 according to the Debye-Scherrer equation: $D = K \lambda / \beta \cos\Theta$, Where, D = crystalline size, Å, K = crystalline-shape factor, λ = X-ray wavelength, θ = observed peak angle, degree, β = X-ray diffraction broadening, radian.

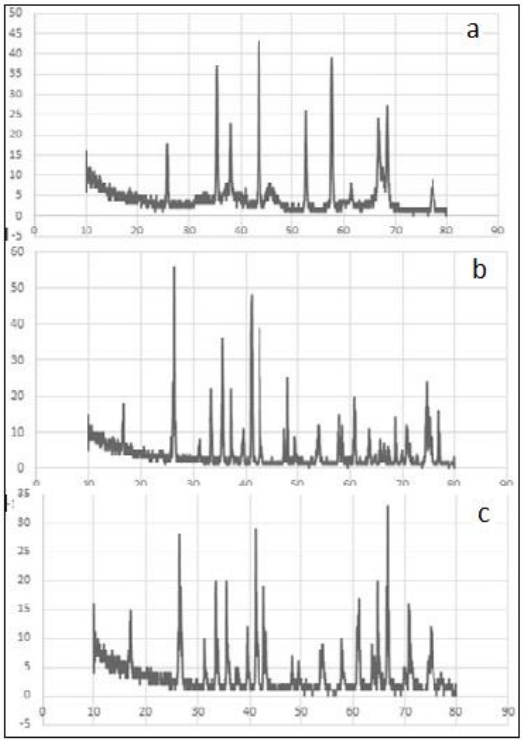

Figure 4. XRD Spectrum for Sample a, b & c at Different Ball Milling Intervals (75,100,150 hrs) from Top to Bottom

Particle Size Analysis

Figures 5 a, b and c show the particle size analysis of three samples at different (75,100,150 hrs) ball mill duration. The particle sizes measured for sample 'a' is 278 nm, 'b'- 240 nm, 'c'- 124.6 nm in diameter. These powders show a Gaussian particle size distribution. The powder milled in the attrition mill reaches an average size of around 278 nm, but has a very narrow size distribution ranging from 200 nm up to 400 nm for the first sample (5a). For the second sample (5b), the average size is around 240 nm and the size ranges from 200 to 300 nm and for the third sample (5c), it is of the order of 125 nm, with the size ranging from 100 to 180 nm. The narrow size distribution in the samples proves the efficacy of the ball milling method.

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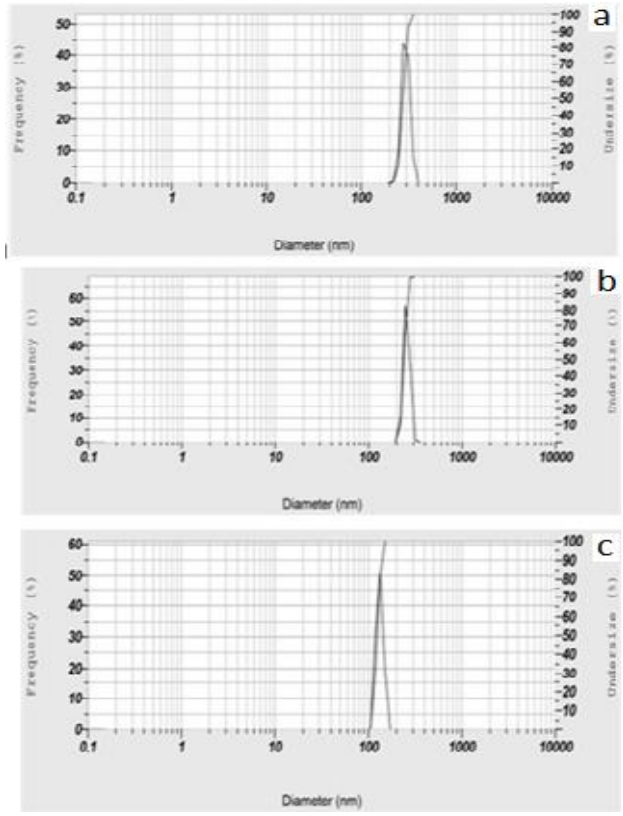

Figure 5. Particle Size Analyzer Sample a, b & c at Different Ball Milling Intervals (75,100,150 hrs) from Top to Bottom

Energy Dispersive Spectroscopy (EDAX) Studies

Figure 6 shows the EDAX spectrum of mullite nanopowder. The quantitative chemical analysis by EDS confirmed the presence of all elements in the mullite powder - aluminum, silicon, oxygen and traces of nickel and chromium.

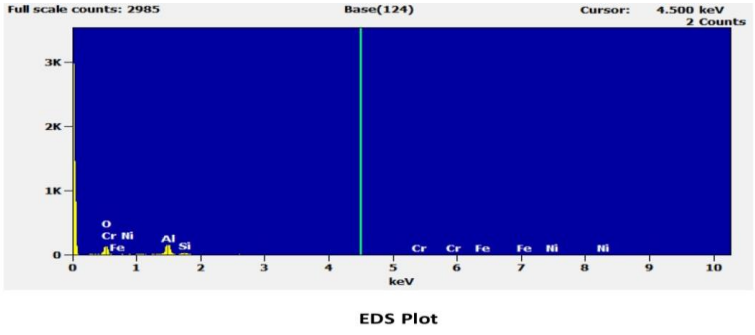

Figure 6.EDAX Spectrum of Mullite Nano Powder

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AFM studies

AFM images shown in figures 7 a, b and c depict agglomeration of particles of different sizes, with less spreading. This normally happens for particles of nano size. The 2-D image and the height scale are shown adjacent to each other in each figure. The height information is displayed in Z – scale and the 2-D image shows the top view. The scale area can be noted from the 3-D image. Since the scanned area is small, only lumps of powder are seen with little or no spreading. The height information is actually displayed in a color scheme, but shown in black here. Typically the z scale is shown with exaggerated zoom. Fig.7a & b the morphology of the powders obtained is needle like, with a particle size of nano metric order as demonstrated through the analysis made by AFM and from the size distribution measurement of the powder particles.

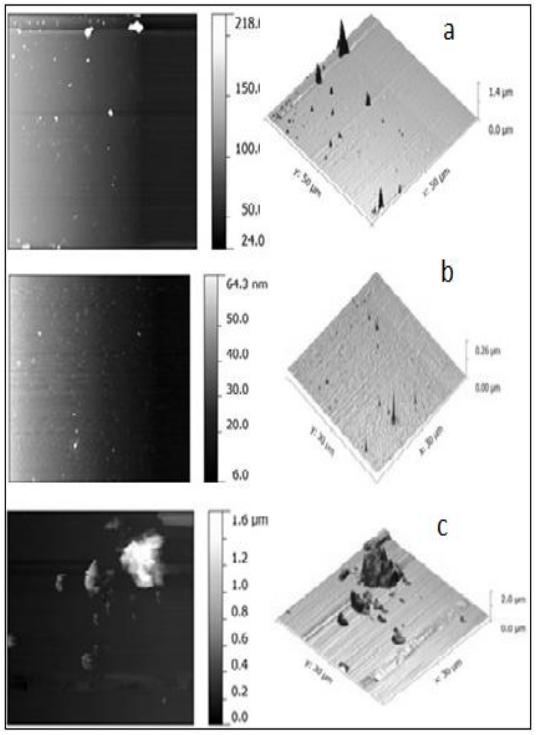

Figure7. AFM 2D & 3D Image of Sample a, b & c at Different Ball Milling Intervals (75,100,150 hrs) from Top to Bottom

The samples 7a and c have clearly a continuous structure of agglomerates while the sample 7b exhibits the fragmentation of agglomerates and the separation of particles to some extent. Note that the height of the particles in sample 7b is lower, maybe due to smaller than average particles scanned. The general trend is agglomeration of the particles. The peak height of the particles can be noticed and varies from sample size to size. High surface area to volume ratio of nano particles provides a very high surface energy. To minimize its surface energy the nanoparticles get agglomerated. Uncontrolled agglomeration of nanoparticles also occurs due to attractive Vander Waals forces between particles. As the particles are loose, surface morphology or force measurements cannot be made as normally done on bulk solid surfaces.

5. Conclusion

Mullite ceramic powder was successfully prepared in the factory using raw materials by the fusion method. The powder was later ball milled, sieved and 3 samples of different sizes were taken up for the characterization study. The method is a low cost method, by which bulk quantities of mullite ceramic powder of

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micro and nano sizes can be produced. Subsequent ball milling can still reduce the powder size to lower levels. Characterization studies have yielded good results as to the particle size, UV spectral data and crystalline nature of the powder.

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6. REFERENCES

[1] Juliana Anggono, Mullite Ceramics: Its Properties, Structure, and Synthesis, Jurnal Teknik Mesin 7, (2005), 1-10

[2] Dj. Janackovic, V. Jokanovic, Lj. Kostic-Gvozdenovic, D. Uskokovic, Synthesis of mullite nanostructured spherical powder by ultrasonic spray pyrolysis, Nanostruct. Mater., 10, (1998), 341-348.

[3] Paola Palmero, Structural Ceramic Nano composites: A Review of Properties and Powders' Synthesis Methods, Nanomaterials, 5, (2015), 656-696

[4] S. J. Lee, C. H. Jung, Characterization of Nano Scaled Mullite Powders Prepared by Organic- Inorganic Solution Technique, SSP, 119, (2007), 43-46

[5] Rita Baranwal, Maria P. Villar, Rafael Garcia, Richard M. Laine, Flame Spray Pyrolysis of Precursors as a Route to Nano-mullite Powder: Powder Characterization and Sintering Behavior, J. Am. Ceram. Soc., 5, (2001), 951–61

[6] Daniel M. Dabbs, Nan Yao and Ilhan A. Aksay, Nano composite mullite/mullite powders by spray pyrolysis, J. Nanopart. Res.1 (1999), 127–130

[7] Hussein AlaaJaber, Synthesis of Mullite Powder from Aluminum Nitrate and Precipitated Silica using Sol-Gel Process, Eng. & Tech. Journal, 34, (2016), 8

[8] Lucia Téllez Jurado, et.al, Sol-Gel Synthesis of Mullite Starting from Different Inorganic Precursors, Journal of Powder Technol., 268070, 2013, 7

[9] do Nascimento Simões, et.al, Synthesis of Mullite by the Pechini Method, Mater. Sci. Forum, 820, (2015), 107

[10] Enrico Bernardo, et.al, Novel Mullite Synthesis Based on Alumina Nano particles and a Preceramic Polymer, J. Am. Ceram. Soc 89, (2006), 1577-1583

[11] L. X. Tong, J. H. Li, F. Liu, Preparation of Mullite Nano composites Powders by the Hydrothermal Crystallization Method from Coal Gangue, Key Eng. Mater., 512-515, (2012), 49-53

[12] Shumaila Islamet.al, Low temperature sol-gel based erbium doped mullite nanoparticles: Structural and optical properties, J. Taiwan Inst. Chem. Eng.70 2017,-366–373

[13] Jinhong Li, Lingxin Tong, Xiang Wang, Preparation and mechanism of nano mullite powders from kaolin via open hydrothermal process, J. Nanosci. Nanotechnol., 14(5) (2014), 3876-9

[14] L.B. Kong, et.al, Micro structural composite mullite derived from oxides via a high-energy ball milling process, http://doi.org/10.1016/j.ceramint.2003.12.022.

[15] Aguilar-Santillan, Joaquin, Heberto Balmori-Ramirez, Richard C. Bradt Dense mullite from attrition milled kyanite and alpha-Alumina, JCPR,8 (2007), 1

[16] B.Viswanath,V.Vijayaragavan,https://sg.inflibnet.ac.in

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