Sol-gel synthesis of nanoparticulate mullite precursor with the highest solid content

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ABSTRACT

Mullite is an alumina silicate with the general formula $Al_2(Al_{(2+2x)}Si_{(2-2x)})O_{(10-x)}$. *Specifically, when x=0.25, mullite is represented as 3:2 (*$3Al_2O_3{\cdot}2SiO_2$*). In recent years, it has gained recognition as a critical raw material in the production of refractory materials and advanced engineering ceramics. To synthesize high-purity mullite at low temperatures with a uniform and homogeneous nanostructure, the sol-gel technique is a highly effective method. Achieving a mullite sol with a high solid content is also essential. This research aims to develop an innovative approach to produce a mullite precursor sol with the highest possible solid content using aluminum nitrate nonahydrate (*$Al(NO_3)_3{\cdot}9H_2O$*) and colloidal silica. The primary focus of the study is to investigate the effects of pH and the stoichiometric ratio of* Al_2O_3 *to* SiO_2 *on the solid content and the types of phases forming in the sol. At an acidic pH (3-4) with a 3:2 ratio, only mullite was formed after calcination at 1250°C. In contrast, at higher pH values, intermediate phases of alumina and cristobalite were also observed. By varying the stoichiometric ratio of Al2O3 to SiO2 and increasing the amount of silica (3:3, 3:4), the solid content of the mullite sol increased, with the highest solid content of 25.50% achieved in the 3:4 sample. X-ray diffraction (XRD) results of the powders synthesized at 1250°C show that the mullite phase is present in all three samples, although traces of intermediate phases of alumina are noted in the 3:3 and 3:4 samples. As the calcination temperature is raised to 1400°C, weak mullite peaks appear in all samples, indicating the penetration of alumina and silica due to the high heat treatment temperature. Thus, the mullite formation process is completed in all samples.*

Keywords: Mullite, Sol-Gel, Aluminum Nitrate, Colloidal Silica، Solid Content

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1. INTRODUCTION

Mullite ($3Al_2O_3.2SiO_2$) is a highly valued ceramic material due to its exceptional thermal stability, mechanical strength, and resistance to creep and corrosion [1]. These properties make mullite a preferred material for high-temperature applications, such as refractory linings, thermal barrier coatings, and advanced ceramic composites [2]. The sol-gel process is a versatile and widely used method for synthesizing mullite precursors, offering precise control over composition, homogeneity, and nanostructure [3]. In this method, aluminum and silicon precursors, such as alkoxides or salts, are hydrolyzed and condensed to form a gel with a uniform distribution of Al and Si [4]. The resulting nanogel exhibits a high surface area and nanoscale porosity, which are critical for achieving desirable properties in the final mullite ceramic [5]. Subsequent calcination of the nano gel at elevated temperatures leads to mullite crystallization, with controlled grain size and morphology [6]. This approach enables the synthesis of mullite with tailored properties for use in extreme environments, such as aerospace, energy, and industrial applications [1].

2. Materials And Methods

2.1 Precursors

The raw materials used in this study included aluminum nitrate nonahydrate ($Al(NO_3)_3.9H_2O$)[1], as a source of alumina and colloidal silica[2], ammonia solution(NH_4OH)[3], Acetic acid[4], and deionized water.

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[1]. purity > 98%, for analysis, Supelco company, Germany
[2]. Purity = 30%, Padideh Shams Iranian company, Iran
[3]. Purity = 25%, for analysis, Dr. Mojallali company, Iran
[4]. Purity> 99%, Extra Pure, Neutron company, Iran

2.2 Synthesis Procedure

The general flowchart for synthesizing mullite precursor sol in this work is shown in Figure 1:

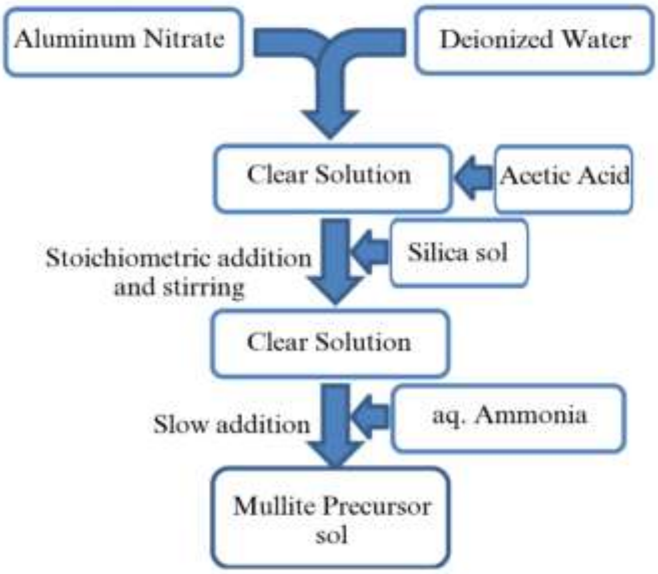

Fig. 1. *Mullite sol-making process*

To start, aluminum nitrate was vigorously stirred with deionized water using a magnetic stirrer set to 70°C. Next, acetic acid was added as a catalyst in amounts ranging from 0.1 to 0.3 wt%. Once the aluminum nitrate had dissolved entirely, silica sol was gradually incorporated into the solution, which was stirred at high speed for one hour. Following this, ammonium hydroxide was slowly added to adjust the pH and viscosity of the mixture. The suspension was then stirred for approximately 5 to 6 hours to achieve a clear and stable mullite precursor sol. Finally, the resulting sol is aged 24-48 hours at room temperature, followed by drying at 100-120°C to remove residual water. The dried gel is calcined at temperatures ranging from 1250 to 1400°C for 2-4 hours to promote phase transformation and crystallization of mullite. The effect of pH, stoichiometric ratio of Al_2O_3:SiO_2, and synthesis temperature on the properties of the precursor sol, such as the amount of solid content and the type of constituent phases, were evaluated.

2.3 Characterization Methods

pH measurement

The pH of the synthesized sol was measured using a digital pH meter due to its high accuracy and reliability. Before the measurements, the pH meter was calibrated using standard buffer solutions with known pH values. After calibration, the electrode was immersed directly into the sol, and the pH value was recorded from the digital display. This process ensured precise monitoring of the sol's acidity or alkalinity during synthesis and pH adjustment.

Measurement of Solid Content of Sol

The solid content of the synthesized sol was determined using the thermal gravimetric method[1]. A known weight of the sol (W_2) was placed in an alumina crucible and heat-treated at 1000°C for 2 hours in a furnace to remove all volatile components. After cooling to room temperature, the weight of the remaining solid residue (W_1) was measured using a high-precision analytical balance with an accuracy of 0.001 g. The solid content of the sol was then calculated using the following formula:

$$\text{Solid Content (\%)} = (W_1/W_2) \times 100$$

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[1] . Loss on ignition method (LOI)

Where:

- W_1 = Weight of the sintered sol after heat treatment at 1000°C
- W_2 = Initial weight of the synthesized sol

Phase Analysis of Synthesized Using X-Ray Diffraction

X-ray diffraction (XRD) analysis was performed to identify the crystalline phases present in the synthesized powders by using an X-ray diffractometer at the Central Laboratory of Tabriz University[1]. The resulting diffraction patterns were analyzed using HighScore Plus software with the X'Pert platform.

3. Results and Discussion

3.1. Assessing the effect of pH

Table 1 summarizes the characteristics of the synthesized sol under different pH conditions

***Table 1**. Characteristics of Synthesized Sols at Variable pH*

pH	3	5.5	10
Appearance	Nearly transparent	Opaque	Opaque
(Al_2O_3: SiO_2)	3:2	3:2	3:2
Temperature (°C)	70	70	70
Solid Content (%)	6.9	7.3	7.5
Phase Analysis at 1250°C	Mullite	Mullite, Alumina, and Cristobalite	Mullite, Alumina, and Cristobalite

In silica sol, water molecules form hydrogen bonds (H-bonds) with the silanol groups (Si-OH) present on the surface of silica (Reaction 1), leading to the formation of a layer that covers each silica particle. This bond creates a short-range repulsive force that overcomes van der Waals forces, preventing particle coagulation [7, 8].

$$SiOH + H^+ \leftrightarrow SiOH_2^+ \qquad (1)$$

When this sol is mixed with an aluminum nitrate solution, the solution becomes acidic, with a pH of approximately 2. At this pH, the surface of the silica particles carries a positive charge. Upon the addition of ammonium hydroxide, the pH increases, leading to the formation of aluminum hydroxide ($Al(OH)_3$) and silicic acid ($Si(OH)_4$). As a result, the formed sol exhibits a biphasic nature [9, 10]. At higher pH levels, silica dissolves as silicate. The hydrated silica particles now carry a negative charge, causing them to repel each other, which inhibits the polymerization of hydrolyzed silica and the evolution of water [11]. This phenomenon likely contributes to the lower weight loss observed for powders prepared at higher pH levels, where the solid content of the sol reaches 7.5% at pH 10. On the other hand, due to the condensation of Al^{3+} ions at pH levels between 8 and 10, through the mechanisms of olation (Reaction 2) and oxolation (Reaction 3) (in olation, low-valency cations lead to the formation of polycations and hydroxide precipitation, while in oxolation, high-valency cations result in the formation of polyanions and oxides), a polynuclear hydroxide is formed [7, 12, 13].

$$[Al(H_2O)_6]^{3+} \leftrightarrow [Al(H_2O)_5OH]^{2+} + H^+ \qquad (2)$$

$$[(H_2O)_5Al{-}OH{-}Al(H_2O)_5]^{5+} \qquad (3)$$

Under acidic conditions, the equilibrium of Equation 2 shifts to the left, thereby preventing multiple condensation. Phase investigations, as shown in Figure 2, revealed that at a stoichiometric ratio of Al_2O_3: SiO_2 = 3:2 and a pH of approximately 3, only the mullite phase forms after synthesis at 1250°C. However, with increasing pH, phases related to alumina and silica also appear. In fact, at pH 3, aluminum nitrate and silica sol form a hydrated aluminosilicate, which transforms into mullite at 1250°C according to Reaction (4) [9]. At higher pH levels, due to the separation of silica caused by repulsive forces, the polynuclear aluminum

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[1] TD-3700 X-Ray Diffractometer, made in China, Cu lamp, λ = 1.5406 Å.

hydroxide becomes highly condensed and tends to flocculate. Consequently, after synthesis at 1250°C, it transforms into alumina and cristobalite.

$$3\delta\text{-}Al_2O_3 + 2\,SiO_2\text{-amorphous} \rightarrow 3Al_2O_3\cdot 2SiO_2 \qquad (4)$$

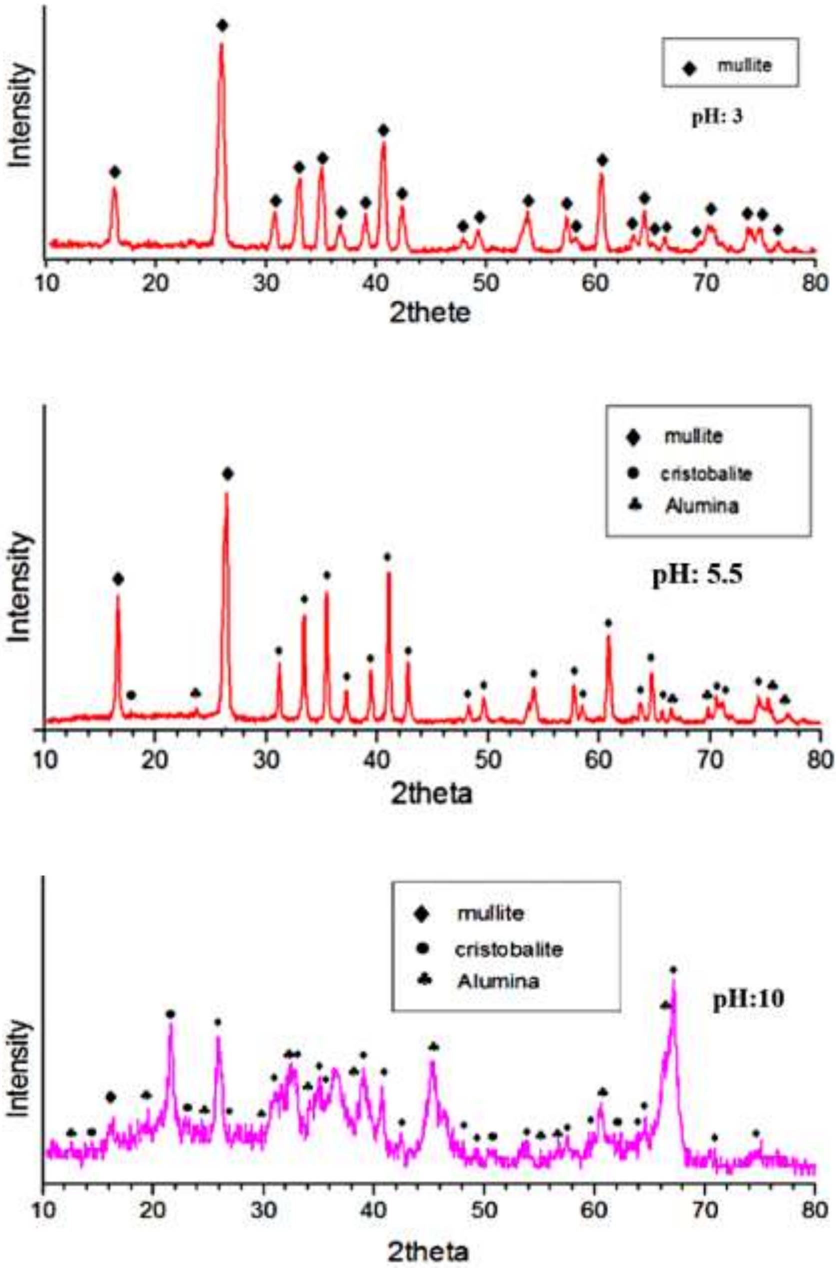


Fig. 2. *XRD patterns of mullite precursor sols synthesized at 1250 °C with a stoichiometric ratio of 3:2 at pH levels of 3, 5.5, and 10.*

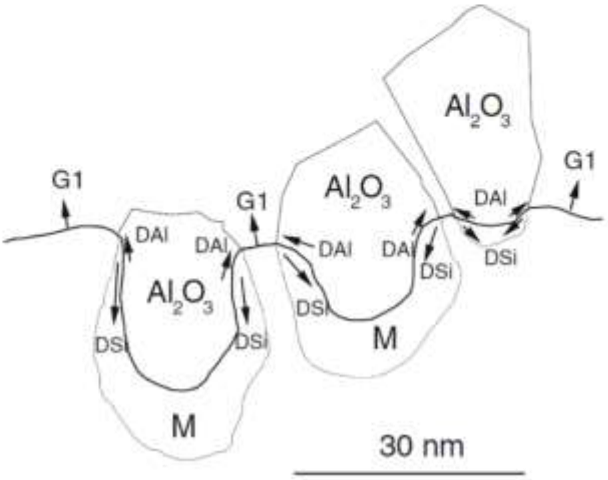


Fig. 3. *Diffusion of silicon and aluminum in mullite*

Figure 3 illustrates the crystallization process of mullite from alumina and silica grains. The growth mechanism is influenced by the diffusion of silicon and aluminum in this area.

3.2. Assessing the effect of the stoichiometric ratio of Al_2O_3:SiO_2

The characteristics of the sols synthesized by changing the stoichiometric ratio of Al_2O_3:SiO_2 are given in Table 2:

Table 2*. Characteristics of sols synthesized with different ratios of* Al_2O_3 *to* SiO_2

(Al_2O_3:SiO_2)	3:2	3:3	3:4
Appearance	Transparent	Semi-transparent	Semi-transparent
pH	3-4	3-4	3-4
Temperature (°C)	70	70	70
Solid content (%)	20.71	22.24	25.50
Phase analysis at 1250°C	Mullite	Mullite, (δ,θ)-alumina	Mullite and θ-alumina
Phase analysis at 1400°C	Mullite	Mullite	Mullite

According to Table 2, as the Al_2O_3:SiO_2 ratio increases, the solid content of the mullite sol also increases. The highest solid content, recorded at 25.50%, was achieved in the sample with a ratio of 3:4. The XRD patterns of the powders synthesized at temperatures of 1250°C and 1400°C are shown in Figures 4 and 5, respectively. At 1250°C, as seen in pattern 4, the mullite phase (M) is present in all three samples. However, in samples b and c, which have Al_2O_3:SiO_2 ratios of 3:3 and 3:4, respectively, traces of intermediate alumina phases are also detected. It is essential to note that the peaks associated with alumina and mullite are quite similar at certain angles, which may result in some overlap. When the synthesis temperature is raised to 1400°C, weak mullite peaks emerge in all samples, as illustrated in Figure 5. The appearance of these weak mullite peaks suggests that increased temperatures facilitate the infiltration of alumina and silica, which becomes significantly more pronounced at this stage.

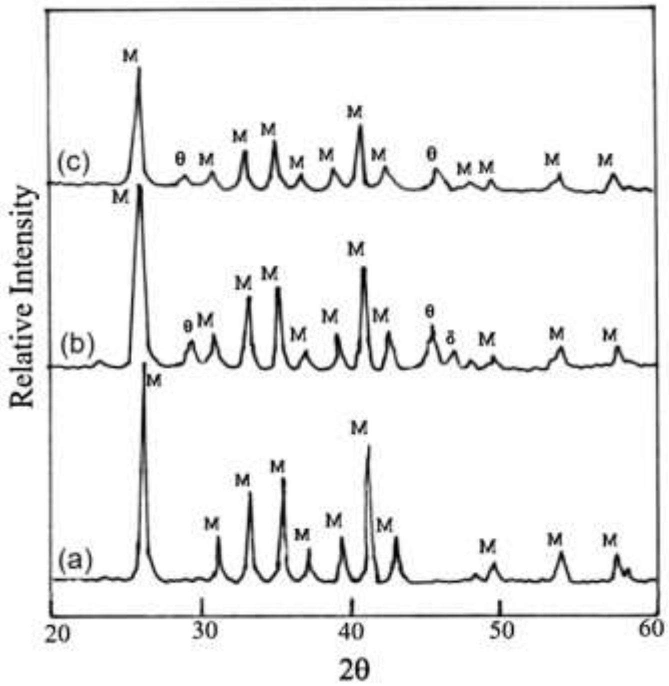


Fig. 4. *shows the XRD patterns for mullite precursor sols synthesized at 1250℃ with different Al_2O_3:SiO_2 ratios: (a) 3:2, (b) 3:3, and (c) 3:4.*

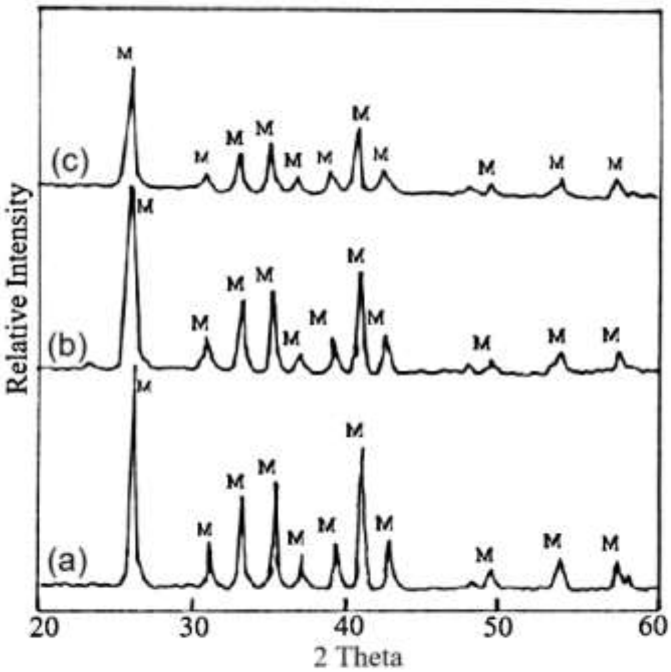
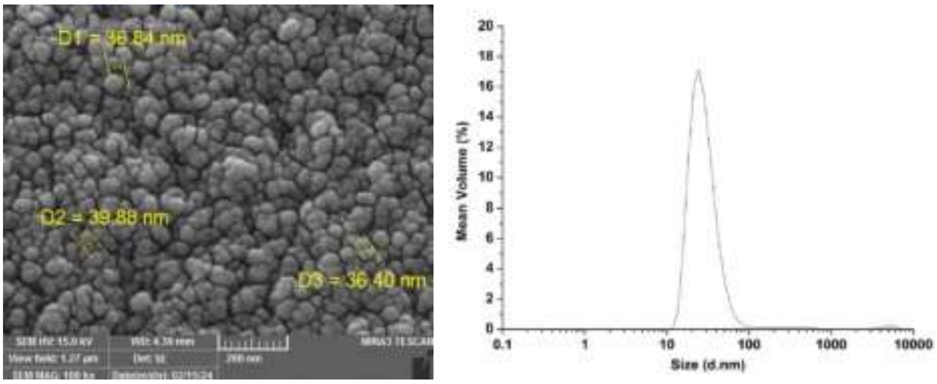


Fig. 5. *shows the XRD patterns for mullite precursor sols synthesized at 1400℃ with different Al_2O_3:SiO_2 ratios: (a) 3:2, (b) 3:3, and (c) 3:4.*

The particle size distribution plot in Figure 6 indicates that all sol particles fall within the size range of 10–100 nm, with the majority being smaller than 40 nm.



(a) *(b)*

Fig. 6. *(a): Microstructure of powder obtained by Calcination of mullite precursor sol at 1000 °C*
(b): PSD curve for mullite precursor sol.

Figure 7 shows that a mullite sol with a pH between 3 and 4 appears almost transparent and remains stable at room temperature. This means that the electrostatic stability of the particles is strong enough to counteract the adsorption potential energy (V_A), preventing the particles from settling and maintaining a homogeneous mixture. However, when exposed to temperatures above 100°C, the sol tends to gel, and the particles do not settle and remain homogeneous [1] and tend to gel when exposed to temperatures above 100℃.

(a) *(b)*

Fig. 7. *(a): Stable solution of the mullite precursor and, (b): gel formation at 110 ºC.*

4. Conclusions

In the present study, the mullite precursor sol was synthesized by a wet chemical (inorganic) method, which has a two-phase nature and is stable at room temperature. Phase analysis of the synthesized sol shows that the formation of a mixed oxide ceramic (pure mullite) strongly depends on pH, temperature and initial stoichiometric conditions, such that: at a stoichiometric ratio (Al_2O_3:SiO_2) of 3:2 when the pH is about 3 after synthesis at 1250°C, the only phase formed is mullite; with increasing pH, phases related to alumina and silica were also observed. At a synthesis temperature of 1250°C, intermediate phases of alumina were also formed in addition to the mullite phase. With increasing temperature to 1400°C, mullite is the only main and pure phase in all samples. In this study, a mullite precursor sol was synthesized using a wet chemical (inorganic) method.

REFERENCES

[1] Schneider, H., Schreuer, J., & Hildmann, B. (2008). "Structure and Properties of Mullite—A Review." Journal of the European Ceramic Society, 28(2), 329-344.

[2] Somiya, S., & Akiba, T. (1999). Mullite and Mullite Matrix Composites. Ceramic Transactions Series, Vol. 96, American Ceramic Society.

[3] Brinker, C. J., & Scherer, G. W. (1990). Sol-Gel Science: The Physics and Chemistry of Sol-Gel Processing. Academic Press.

[4] Li, D., & Thomson, W. J. (1990). "Mullite Formation Kinetics of a Single-Phase Gel." Journal of the American Ceramic Society, 73(4), 964-969.

[5] Rahaman, M. N. (2003). Ceramic Processing and Sintering. CRC Press.

[6] Pask, J. A., & Tomsia, A. P. (1991). Formation of Mullite from Sol-Gel Mixtures and Its Applications.

[7] Sunipa Bhattacharyya, T.K. Mukhopadhyay, Kausik Dana, Sankar Ghatak, "Pressure less reaction sintering of yttrium aluminum garnet (YAG) from powder precursor in the hydroxy hydrogel form", Ceramics International 37 (8), pp. 3463- 3468, 2011.

[8] S.R. Raghavan, H.J. Walls, S.A. Khan, "Rheology of silica dispersion in organic liquids: new evidence for solvation forces dictated by hydrogen bonding", Langmuir 16, pp. 7920-7930, 2000.

[9] Wei W-C, Halloran JW, "Transformation kinetics of diphasic aluminosilicate gels", J Am Ceram Soc 71, pp. 581–587, 1988.

[10] Zhang, D., et al., "Influence of powder characteristics of reactive alumina on properties of alumina-spinel castables", Ceramics International. 44(8), pp. 9984-9990, 2018.

[11] Jagannath Roy, Narayan Bandyopadhyay, Santanu Das, Saikat Maitra, "Studies on the Formation of Mullite from Diphasic Al_2O_3-SiO_2 Gel by Fourier Transform Infrared Spectroscopy", Iran. J. Chem. Chem. Eng, Vol. 30, No. 1, pp. 65-71, 2011.

[12] U. Paik, J. P. Kim, Y. S. Jung, Y. G. Jung, T. Katoh and J. G. Park, V. A. Hackley, "The effect of Si dissolution on the stability of silica particles and its influence on chemical mechanical polishing for interlayer dielectrics", Journal of the Korean Physical Society 39, S201-S204, 2001.

[13] Carla C. Osawa and Celso A. Bertran, "Mullite formation from mixtures of alumina and silica sols: mechanism and pH effect", J. Braz. Chem. Soc 16 (2), pp. 251-258, 2005.