

Comparison of α -Al₂O₃ Synthesized by Sol-Gel Process using AlCl₃ and Al(NO₃)₃ as Precursors

Syed Nasimul Alam, Lailesh Kumar, Aishwarya Rani Sahoo

Metallurgical and Materials Engineering Department, National Institute of Technology Rourkela, Orissa, Pin-769008, India

Abstract

The present study deals with the synthesis and characterization of Al₂O₃ using two precursors. In the first method inorganic aluminum chloride (AlCl₃) was used whereas in the second method aluminium nitrate (Al(NO₃)₃), malic acid (C₄H₆O₅) and polyvinylpyrrolidone, PVP ((C₆H₉NO)_n) was used. Owing to the difficulty of synthesis of nanosized α -Al₂O₃ powder due to grain growth at high temperatures involved during calcinations, Al₂O₃ was prepared by two different sol gel processes. In the first method AlCl₃, ethanol and 28 % NH₃ was used to form a gel followed by calcinations at 1200°C for 2 h. In the second process aluminium nitrate, malic acid and PVP in the mass ratio of 10:3:1.5 was used to form a gel followed by heating the gel at 60°C for 24 h in an oven and then by heat treating at 1250°C for 2 h to form α -Al₂O₃. The α -Al₂O₃ formed was analyzed by x-ray diffraction (XRD) and particle size analyzer to characterize the powders in terms of their crystallinity and particle size. Microstructural characterization was performed using SEM and TEM. The thermal stability of particles was analyzed using DSC/TGA.

Keywords- Alumina, Sol-gel method, FTIR, SEM, FESEM

Introduction

Alumina or aluminum oxide (Al₂O₃) is a very widely used ceramic material and is a major engineering material. Alumina is the only oxide of aluminum. It has a combination of good mechanical and electrical properties which leads to a wide range of applications. It has a very high hardness (15 to 19 GPa) and low density (3.75 to 3.95 g/cm³). This is why it is very often used as a reinforcement in several composites. Due to its high hardness alumina is used as an abrasive material. It has a very high compressive strength (2,000 to 4,000 MPa) and moderate to extremely high mechanical strength (300 to 630 MPa). Its elastic modulus is 200 to 300 GPa. Apart from this it is a very good electrical insulator (1x10¹⁴ to 1x10¹⁵ Ωcm). Alumina is also an inert biomaterial and is biodegradable. Its operating temperatures could be as high as 1000 to 1500°C without mechanical load. The high melting point of alumina (2072°C) makes it useful as a refractory and as linings of furnaces. It has high corrosion and wear resistance. Alumina has been used in a wide range of applications like medical prostheses, laser tubes, electrical insulator, wear components, seal rings and several others. Nanosized alumina (Al₂O₃) is very attractive due to their unique combination of excellent mechanical properties and high thermal stability. The combination of structure, topology and dimensions create a horde of physical properties like high hardness and resistance to crack propagation in these materials thereby making them an ideal reinforcing agent for high strength composites. Aluminium oxide nanoparticles has high stability, hardness and is widely used in a variety of plastics, metals, rubber, ceramics and refractory products as reinforcement. The applications emanating from the remarkable properties of nanosized alumina include optical devices and high temperature materials, in biomedical engineering, as coatings against corrosion and abrasion and in electrical engineering for the fabrication of fuel cells, sensors, piezoelectric devices etc. Alumina nanoparticles can be widely used in high temperature applications. Here Al₂O₃ nanoparticles was synthesized by using an aqueous sol-gel method. The sol-gel method is known to be an alternative route for the synthesis of ceramic powders [1-5].

This paper reports the synthesis of nanosized alumina by using sol-gel techniques and its characterization. Alumina being a biodegradable, high temperature ceramic with good mechanical properties finds a lot of applications in a large number of areas. Owing to the difficulty of synthesis of nanosized α -Al₂O₃ powder due to grain growth at high temperatures involved during calcinations, Al₂O₃ was prepared by sol-gel process. The sol-gel process is a method popularly

known as chemical solution deposition and has wide range of applications. The process consists of the (a) stable sol formation using precursors (b) formation of a gel by adding suitable reagent (c) allowing the gel to mature and age into a solid mass (d) removal of any remaining liquid phases by drying the gel and (e) calcination of the mass formed in a furnace at a high temperature for some time. Sol-gel technique is a continuous and simple process involving low cost and high yield. In this paper nanosized alumina was synthesized by two processes. The first one was using AlCl_3 , ethanol and 28 % NH_3 followed by calcinations at 1200°C for 2 hours in a furnace. The second process involved aluminium nitrate ($\text{Al}(\text{NO}_3)_3$), malic acid ($\text{C}_4\text{H}_6\text{O}_5$) and PVP ($(\text{C}_6\text{H}_9\text{NO})_n$) in the mass ratio of 10:3:1.5. The gel was heated at 60°C for 24 hours in an oven followed by heat treatment at 1250°C for 2 h to form $\alpha\text{-Al}_2\text{O}_3$ [6-10].

Experimental

The precursor used for the synthesis of $\alpha\text{-Al}_2\text{O}_3$ is aluminium chloride (AlCl_3) in an alcoholic medium (ethanol). The other reagent used in this process is NH_3 . Here we have tried to synthesize $\alpha\text{-Al}_2\text{O}_3$ by the sol-gel process using AlCl_3 . A 0.1 molar AlCl_3 ethanolic solution was prepared by adding ethanol to AlCl_3 . Magnetic stirring for around 30 minutes was done in order to dissolve AlCl_3 in the ethanol. Subsequently around 28% NH_3 solution was added into the mixture under continuous stirring at a consistent feed rate which resulted in the formation of a gel. The gel was allowed to mature at room temperature for 30 h. Later the gel was dried at 100°C for 24 h in an oven. Finally the gel was calcined at 1200°C for 2 h in a furnace. The calcined sample was then milled in a planetary ball mill for 30h to further reduce the crystallite size range. $\alpha\text{-Al}_2\text{O}_3$ was also synthesized by using a different precursor. The precursor for the synthesis of alumina by this method are aluminium nitrate, malic acid and poly vinyl pyrrolidone (PVP). It is a water soluble polymer made from the monomer N-vinylpyrrolidone. In this process the precursor sol was prepared by sol-gel technique using aluminium nitrate ($\text{Al}(\text{NO}_3)_3$) and malic acid ($\text{C}_4\text{H}_6\text{O}_5$). The gel was synthesized by mixing aluminium nitrate, malic acid and PVP ($(\text{C}_6\text{H}_9\text{NO})_n$) in the mass ratio of 10:3:1.5. The gel was heated at 60°C for 24 h in an oven. The alumina synthesized was heat treated at 1250°C for 2 h. The phase structure was identified by x-ray diffraction using $\text{Cu K}\alpha$ ($\lambda = 1.5406 \text{ \AA}$) radiation. A Phillips Pananalytical PW 3040/00 x-ray diffractometer was used. The alumina formed by the two sol gel techniques were analysed by x-ray diffraction (XRD) to characterize the powders in terms of their degree of crystallinity and crystallite size. The microstructure of the $\alpha\text{-Al}_2\text{O}_3$ obtained were characterized using a JEOL JSM-6480LV scanning electron microscope (SEM). A FEI NOVA NANO SEM 450 (FEG) field-emission scanning electron microscope (FESEM) was also used for microstructural characterization. A JEM-2100 JEOL HRTEM with point to point resolution of 0.194 nm was used for analyzing the structure of the alumina. Spectroscopic analysis like Fourier transform infrared spectroscopy (FTIR) was also done using a Shimadzu IR Prestige 21 FTIR. Besides, thermal analysis of the powder was also carried out using a differential scanning calorimeter (DSC) to find out the phase transformations that takes place during heating. The dry powder was heated up to 1200°C , with a heating rate of $10^\circ\text{C}/\text{minute}$. Thermogravimetric analysis (TGA) was also performed. A MALVERN particle size analyzer was used to find out the distribution of particle size in the powder.

Results and Discussions

Aluminum chloride (AlCl_3) in an alcoholic medium (ethanol) was used as a precursor for the synthesis of $\alpha\text{-Al}_2\text{O}_3$. The other reagent used in this process is NH_3 . A 0.1 molar AlCl_3 ethanolic solution was prepared by adding ethanol to AlCl_3 . Magnetic stirring was done in order to dissolve AlCl_3 in the ethanol. Subsequently around 28% NH_3 solution was added into the mixture under continuous stirring at a consistent feed rate in order to form a gel. The gel was allowed to mature at room temperature for a period of 30 h which was subsequently dried at 100°C for 24. Finally the gel was calcined at 1200°C for 2 h. The SEM images in Figs. 1(a,b) show that the particle size of Al_2O_3 obtained after calcining at 1250°C for 2 h. The SEM images of the 30h milled sample in Fig. 2(a-c) show finer particles as compared to the unmilled alumina powder. The SEM images of the

30 h milled alumina shows the presence of agglomerates of different geometries. The EDX analysis of the 30 h milled powder in Fig. 2(d) shows Al (37.61 at. %) and O (62.39 at. %). The EDX analysis of the 30 h milled powder suggests that the composition of the powder is very close to the stoichiometric composition of Al_2O_3 . Due to the brittle nature of Al_2O_3 it could be broken down to very fine size by milling. Particle size of less than $1\mu\text{m}$ could be seen in the SEM image in Fig. 2(d) of the 30 h milled Al_2O_3 powder prepared from AlCl_3 as precursor. TEM micrographs of $\alpha\text{-Al}_2\text{O}_3$ powder in Fig.3 (a, b) obtained from AlCl_3 as precursor which was subsequently milled for 30 h confirms the nanometric dimension of the particles. The spot pattern in the SAD image in Fig. 3(c) of the 30 h milled $\alpha\text{-Al}_2\text{O}_3$ powder confirms the high degree of crystallinity of $\alpha\text{-Al}_2\text{O}_3$. X-ray diffraction of the Al_2O_3 synthesized by sol-gel method and the subsequent milling of the Al_2O_3 powder for 30 h is shown in Fig. 4. Crystallite size and r.m.s. strain was calculated from the x-ray diffraction plot of $\alpha\text{-Al}_2\text{O}_3$ obtained using AlCl_3 as the precursor using the Voigt's method. The crystallite size of the powder was found to be 199 nm and the r.m.s. strain was found to be 0.182%. Further the crystallite size of Al_2O_3 obtained after milling the $\alpha\text{-Al}_2\text{O}_3$ obtained using AlCl_3 as precursor for 30 h was found to be 26 nm and the r.m.s. strain was found as 0.002%. 30 h milling of the $\alpha\text{-Al}_2\text{O}_3$ has led to considerable broadening of the peaks suggesting the decrease in crystallite size [11-14].

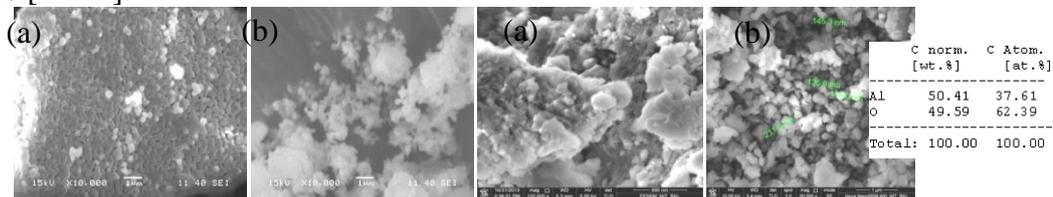


Fig.1 (a,b) SEM of sample after calcining at 1200°C for 2 h

Fig.2. (a, b) SEM of $\alpha\text{-Al}_2\text{O}_3$ powder obtained from AlCl_3 as precursor after calcining at 1200°C for 2 h and milled for 30 h along with XEDX analysis

The particle size analysis of the 30 h milled $\alpha\text{-Al}_2\text{O}_3$ powder is shown in Fig.5. The particle size distribution is found to be Gaussian with average size, $D(v, 0.5)$, of the particle as $5.57\mu\text{m}$. The particle size distribution suggests that there is a significant vol. % of particles less than the average as well as above the average particle size. When AlCl_3 was used as a precursor, the dried gel is $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$. Thermal treatment of the gel leads to decomposition of $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ and results in the formation of a mixture of $\gamma\text{-Al}_2\text{O}_3$ and $\alpha\text{-Al}_2\text{O}_3$. Increasing the temperature of heat treatment up to 1200°C for two hours results in the formation of only $\alpha\text{-Al}_2\text{O}_3$.

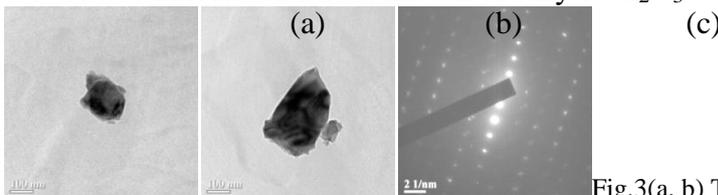


Fig.3(a, b) TEM (c) SAD pattern of $\alpha\text{-Al}_2\text{O}_3$ powder

obtained from AlCl_3 as precursor milled for 30h

Fig. 6 below shows the FTIR spectra of α -alumina that was synthesized from AlCl_3 as precursor. The IR absorption bands observed in the range $1600\text{-}1650\text{ cm}^{-1}$ and $3000\text{-}3700\text{ cm}^{-1}$ could be assigned to the OH vibrational mode. It shows a broad O-H stretching band at the wavenumber around 3400 cm^{-1} which corresponds to OH stretching of Al_2O_3 surface. The shoulder region seen at around 1600 cm^{-1} is also O-H vibrational mode possibly due to the structural water or moisture absorbed in the sample. The FTIR spectrum of the solid shows mainly the absorption bands corresponding to O-H at $3000\text{ to }3700\text{ cm}^{-1}$ and 1655 cm^{-1} . These bands are assigned to the bending vibration and stretching vibration of the O-H bond due to the absorbed water suggesting that there is residual structural OH. The broad absorption peaks exhibited by this solid indicates that the formation of an amorphous hydrated alumina. The bands around 450 cm^{-1} and 525 cm^{-1} are due to the Al-O stretching. The absorption bands at around 950 cm^{-1} possibly corresponds to the bending

of Al-OH group. The peaks at 2950 and 2860 cm^{-1} is possibly due to C-H aliphatic stretch. The C-H bonds are possibly from the PVP (polyvinylpyrrolidone) used during the synthesis of Al_2O_3 from AlCl_3 as precursor. The band at 1360 cm^{-1} is due to the C-O stretching mode. The IR absorption band at 2250 cm^{-1} is possibly due to the $-\text{C}\equiv\text{N}$ stretching. These bonds have been possibly formed due to the reaction of ethanol and NH_3 . It has been reported that the $-\text{C}\equiv\text{N}$ stretching bands of the majority of nitriles fall in the 2300-2200 cm^{-1} . The positions of the peaks associated to the -OH group of alumina at 2090 cm^{-1} can be used as fingerprints of the boehmite structure (AlOOH). The broad absorption in the 950-1200 cm^{-1} range, indicates the formation of Al-O-Al bonds. Bands due to alumina are present at 1400, 1034 and 563 cm^{-1} . The DSC result for 30 h milled $\alpha\text{-Al}_2\text{O}_3$ powder obtained by sol-gel method from AlCl_3 is shown in Fig.7. It was observed that up to the temperature of 220 $^\circ\text{C}$ there is a weight gain of around 0.73%. In the region between 220 to 700 $^\circ\text{C}$ there is a total weight gain of 13.11% in the case of the 30 h milled sample of Al_2O_3 . Weight loss of the material is less than 0.19 % which takes place between 800 to 1200 $^\circ\text{C}$. In this region we also see a lot of fluctuation in temperature. An exothermic peak at 440.9 $^\circ\text{C}$ is observed which can be attributed to the pseudomorphic phase transformation of bohemite ($\gamma\text{-Al(O)OH}$) to $\gamma\text{-Al}_2\text{O}_3$. It should be noted that during thermal treatment stable $\alpha\text{-Al}_2\text{O}_3$ phase is obtained through the phase transformations, hydrous alumina \rightarrow bohemite ($\gamma\text{-Al(O)OH}$) \rightarrow γ \rightarrow δ \rightarrow θ \rightarrow α . The weight gain of the sample takes place simultaneously with the exothermic reaction [15-18].

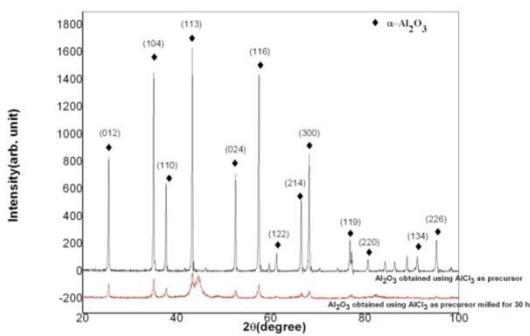


Fig.4 XRD of $\alpha\text{-Al}_2\text{O}_3$ obtained using AlCl_3 as precursor

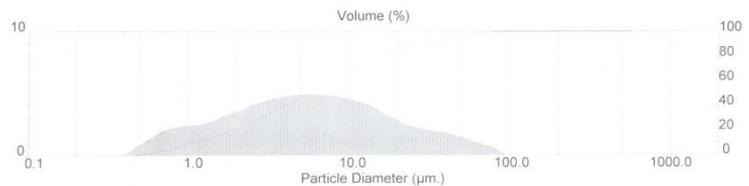


Fig.5 Particle size analysis of 30 h milled $\alpha\text{-Al}_2\text{O}_3$ powder

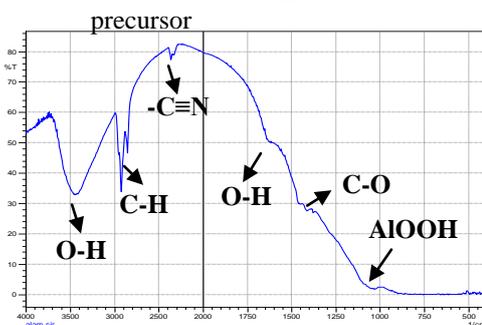


Fig. 6 FTIR spectra of $\alpha\text{-Al}_2\text{O}_3$ from AlCl_3 as precursor

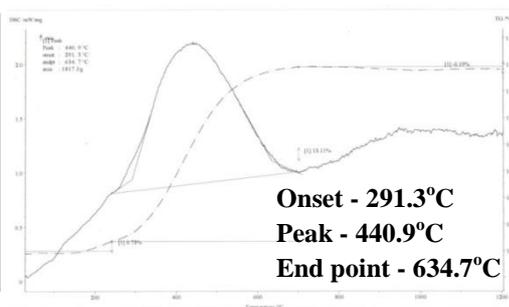


Fig. 7 Thermal analysis of milled $\alpha\text{-Al}_2\text{O}_3$ powder obtained by sol-gel method from AlCl_3

In another process the precursor sol was prepared by sol-gel technique using aluminium nitrate ($\text{Al}(\text{NO}_3)_3$) and malic acid ($\text{C}_4\text{H}_6\text{O}_5$). The gel was synthesized by mixing aluminium nitrate, malic acid and PVP ($(\text{C}_6\text{H}_9\text{NO})_n$) in the mass ratio of 10:3:1.5. The gel was heated at 60 $^\circ\text{C}$ for 24 h in an oven. The alumina synthesized was heat treated at 1250 $^\circ\text{C}$ for 2 h. Fig.8(a-e) shows the FESEM of the $\alpha\text{-Al}_2\text{O}_3$ powders obtained from $\text{Al}(\text{NO}_3)_3$ as precursor. The alumina synthesized by from $\text{Al}(\text{NO}_3)_3$ as precursor is fibrous and was found to have a higher aspect ratio as compared to the alumina synthesized from AlCl_3 . They are plate like instead of particles which were seen in the previous process. With the increase in aspect ratio, various properties of the material improves thereby leading to a unique combination of excellent mechanical, electrical and magnetic properties as well making them an ideal reinforcing agent for high strength composites. Fig. 8(f) is

the EDX analysis of the Al_2O_3 synthesized using $\text{Al}(\text{NO}_3)_3$ was used as the precursor. The EDX analysis suggests that the Al_2O_3 is highly stoichiometric where the at. % of Al is 40.40 and the at. % of O is 59.60[19-21].

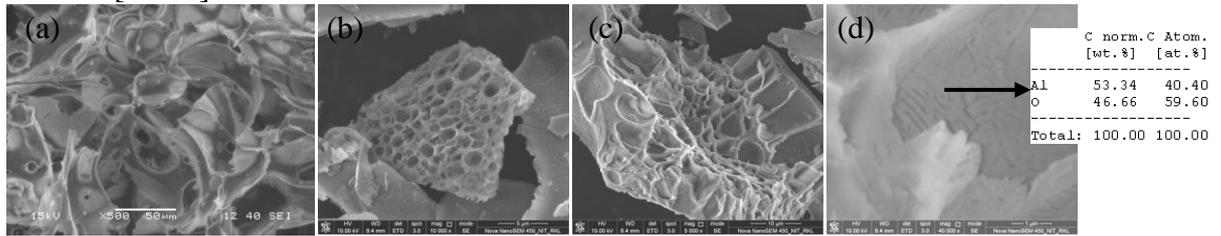


Fig.8(a-d) FESEM (e) EDX analysis of $\alpha\text{-Al}_2\text{O}_3$ powder obtained from $\text{Al}(\text{NO}_3)_3$ as precursor

Fig. 9(a) is the XRD plot of $\alpha\text{-Al}_2\text{O}_3$ obtained using $\text{Al}(\text{NO}_3)_3$ as precursor. The alumina synthesized by using AlCl_3 and $\text{Al}(\text{NO}_3)_3$ as precursor show identical peak positions in the XRD plots as was seen in the case of $\alpha\text{-Al}_2\text{O}_3$ obtained using AlCl_3 as precursor. Crystallite size was calculated from the XRD peak using the Voigt's method. $\alpha\text{-Al}_2\text{O}_3$ synthesized using $\text{Al}(\text{NO}_3)_3$ as precursor had crystallite size of 114 nm as compared to the crystallite size of $\alpha\text{-Al}_2\text{O}_3$ obtained by using AlCl_3 as the precursor where the crystallite size was found to be 199 nm. Fig. 9(b) shows the particle size analysis of $\alpha\text{-Al}_2\text{O}_3$ obtained using $\text{Al}(\text{NO}_3)_3$ as precursor. The average particle size is found to be around 0.7418 μm . The Al_2O_3 synthesized using $\text{Al}(\text{NO}_3)_3$ as precursor gives a much smaller particle size as compared to Al_2O_3 synthesized using AlCl_3 as precursor (5.57 μm). Fig.10 shows the FTIR spectra of $\alpha\text{-Al}_2\text{O}_3$ synthesized from $\text{Al}(\text{NO}_3)_3$ as precursor after calcining at 1250 $^\circ\text{C}$ for 2 h. This process has led to $\alpha\text{-Al}_2\text{O}_3$ having crystallite size smaller than the previous technique. The $\alpha\text{-Al}_2\text{O}_3$ synthesized had crystallite size of 114 nm as compared to the crystallite size of $\alpha\text{-Al}_2\text{O}_3$ obtained by the previous method where the crystallite size was found to be 199 nm. Smaller particles which have size similar to that of the wavelength of the light waves interact with the light waves and therefore lead to a broader peaks and slanted baselines in the FTIR plot of this sample. The broadening is due to the lower crystallite size. Broader peaks indicate increase in interaction with the light wave. There is no considerable change in transmission peak positions. The broad IR peak at around 3400 cm^{-1} is due to the O-H group. The absorption band observed around 1650 cm^{-1} could also be assigned to the O-H vibration mode possibly due to the moisture absorbed in the sample. The peaks at 2950 and 2860 is possibly due to C-H aliphatic stretch. The peak between 1350-1400 cm^{-1} is possibly due to the N-O group which possibly came from the precursor $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ which was used as precursor in this process. Reaction of the precursor materials also lead to the formation of HNO_3 which later decomposes to give NO_3 . Both the FTIR analysis in Fig. 6 and Fig. 10 for $\alpha\text{-Al}_2\text{O}_3$ synthesized from AlCl_3 and from $\text{Al}(\text{NO}_3)_3$ as precursor respectively show similar peaks but the FTIR spectra of $\alpha\text{-Al}_2\text{O}_3$ obtained from $\text{Al}(\text{NO}_3)_3$ as precursor after calcining at 1250 $^\circ\text{C}$ for 2 h shows a strong peak due to N-O group. In the second process $\text{Al}(\text{NO}_3)_3$ was used as precursor. The thermal treatment also leads to the formation of an ($\alpha + \gamma$) - Al_2O_3 mixture which on further increase in temperature to 1250 $^\circ\text{C}$ results in the formation of $\alpha\text{-Al}_2\text{O}_3$ with very small crystallite size and higher aspect ratio. Fig. 11 shows the thermal analysis of $\alpha\text{-Al}_2\text{O}_3$ powder obtained by sol-gel method from $\text{Al}(\text{NO}_3)_3$ as precursor. Here we do not see any exothermic or endothermic reaction taking place as the temperature is raised from room temperature to 1200 $^\circ\text{C}$. The plot shows that there is a slight loss in weight of the sample due to evaporation of adsorbed water. Weight loss of the charged material is found to be less than 1%. There is no sign of exothermic or endothermic reaction in the sample [22].

Conclusions

$\alpha\text{-Al}_2\text{O}_3$ powders of nanometric size were successfully synthesized by sol-gel method using two different precursors, aluminium chloride (AlCl_3) and aluminium nitrate ($\text{Al}(\text{NO}_3)_3$). The high temperatures used for heat treatment resulted in the formation of single phase $\alpha\text{-Al}_2\text{O}_3$. Much finer particle size of $\alpha\text{-Al}_2\text{O}_3$

could be achieved when $\text{Al}(\text{NO}_3)_3$ was used as a precursor. The decrease in size accompanied by an increase in aspect ratio makes it an ideal reinforcing agent for high strength composites.

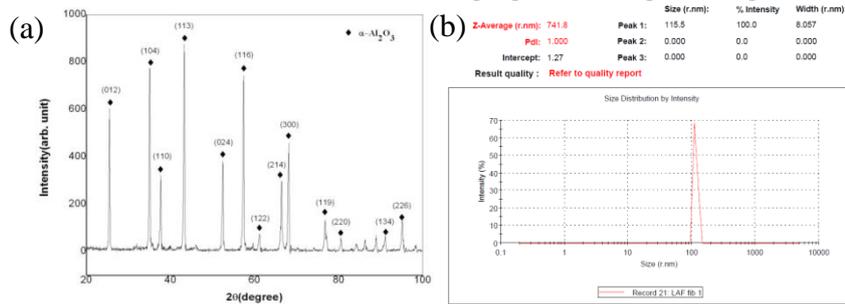


Fig.9(a) XRD(b) particle size analysis of $\alpha\text{-Al}_2\text{O}_3$ obtained using $\text{Al}(\text{NO}_3)_3$ as precursor

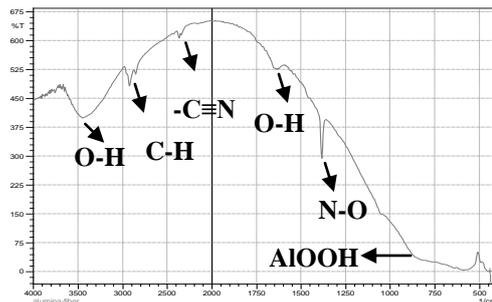


Fig. 10. FTIR spectra of $\alpha\text{-Al}_2\text{O}_3$ from $\text{Al}(\text{NO}_3)_3$ as precursor

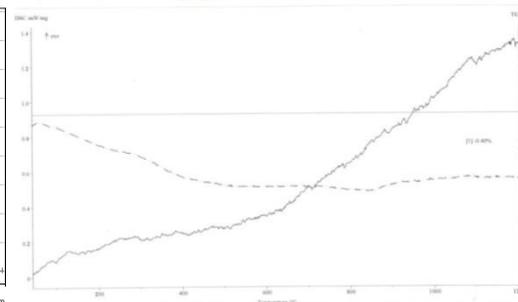


Fig. 11 Thermal analysis of $\alpha\text{-Al}_2\text{O}_3$ powder obtained by sol-gel method from $\text{Al}(\text{NO}_3)_3$ as precursor

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