# EFFECT OF CRYOGENIC TREATMENT ON ALUMINA NANOPOROUS MATERIAL

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## Abstract

*Alumina is one of the important ceramic material having high melting point, thermal conductivity , hardness etc. Their demand in nanodimension is very high due to wider application in the field of electronics, optoelectronics , mechanical and reinforcement composites etc. Alpha phase alumina is highly stable ceramic material, that undergoes agglomeration when treated at higher temperature ( > 800$^0$ Celsius ) during synthesis process .In present work successful effort was made to minimize agglomeration besides forming stable 1-D Nanorod alpha ( α) phase alumina structures by cryogenic treatment . The experimentation starts with the formation of alumina by sol –gel synthesis route while dissolving aluminium chloride hexahydrate ( $AlCl_3$ .$6H_2O$ ) into aqueous hydrochloric acid ( HCl ) . Thereafter it was subjected to mechanical grinding and calcination at 1050$^0$ Celsius for 6-7 hours . The repetition of whole process of grinding and calcinations for 8-10 times , gave alpha (α) phase nanoporous alumina in agglomerated state . After that it was given bath in cryogenic Liquid Nitrogen ( -196$^0$ Celsius ) for 6-7 hours and left at normal temperature for 3-4 hours before further processing . Their characterization study were done using BET ( BEL belsorp ) , XRD( Panalytical.s X.Pert Pro ) and FE SEM ( SU8010 ) . BET shows the formation of porous alumina structure with mean diameter 26.126 nm , whereas the formation of alpha (α) phase crystalline alumina was confirmed by XRD and lastly formation of highly stable 1-D Nanorods were confirmed by FE- SEM images.*

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## 1. INTRODUCTION

Alumina nanoporous material with pore like structure having larger surface area [1] induced wider interest in exploring various applications of this material . Their varied applications as magnetic storage [2] , solar cells[3] , optoelectronics [4] ,catalyst [5] , nanowire [6 ] , nanobelt [7 ] etc. In order to efficiently utilize the porous nanostructure of this material its synthesization process is given due importance . In majority of methods thermal treatment at higher temperature around 1230$^0$ Celsius [8] is important precondition in order to obtain stable alpha phase alumina nanoporous structure . But , this step was associated with unwanted agglomeration with large number of secondary particles [9] which poses problem during fabrication of nanoparticles derived application devices. Jing Yu et al [10] used supercritical carbon dioxide ( $CO_2$ ) for assembly of gamma ( ɣ ) Alumina Nanorods .They utilize supercritical carbon dioxide at 31.10$^0$Celsius as solvent for preparation of above alumina nanostructure . The aim of this paper is to utilize deep cryogenic treatment at -196$^0$Celsius with liquid nitrogen to reduce agglomeration in stable alpha (α) phase alumina nanomaterial besides forming 1-D nanostructures.

## 2. METHODOLOGY

The experimentation starts with the synthesis of alumina nanoparticles . It was formed by wet chemical route i.e sol-gel synthesis method in which reactant aluminium chloride hexahydrate ( $AlCl_3$. $6H_2O$ ) was dissolved into aqueous hydrochloric acid ( HCl ) [10(1) ]. After dissolving , solution was stirred continuously for 48 hours at room temperature and dried in hot air oven at 80$^0$Celsius for 48 hours such that it results in fine gray color powder . Thereafter , powder was given mechanical and thermal processing alternatively at 1050$^0$Celsius for 6-7 hours . The process was repeated until no further change in size of alumina particles was observed . Thereafter , alumina nanoparticles were put in a long glass tube and subjected to deep cryogenic treatment with liquid nitrogen at -196$^0$Celsius for approximately 6 hours . This experiment was carried out at room temperature . Characterization study regarding size of alumina nanoparticles and their associated porosity were carried out by XRD ( Panalytical X.Pert Pro ) and BET ( BEL Belsorp , Japan ) respectively . XRD analysis were done using powder X-ray diffractometer having minimum step size 0.001 in continous scanning mode with Cu Anode material Kα ( 1.54060 ) . Sample preparation was done with 2 mg of alumina, such that it was loaded into goniometer section and exposed to X-ray at different ( 2θ$^0$ ) angle for about 15 minutes . Thus diffraction patteren so obtained provide information about crystallinity , phase of material and nanocrystallite domain size of alumina particles . BET surface and porosity measurement was done with multipoint $N_2$ physiosorption process in which 52 milligram ( mg ) of alumina sample was preheated at 200$^0$ Celsius for 5 hours and then placed in a closed apparatus with liquid nitrogen for 12-14 hours . The process of continous adsorption and desorption provide information about the porosity of nanomaterial . Now this nanoporous alumina material after 3 hours of cryogenic treatment was characterized with FE –SEM ( Hitachi Model ( SU8010 ) ) . In this technique very small sample about 3 milligram was

loaded into chamber and exposed to high intense electron beam with 15 KV potential for about 5-6 minutes . After exposure software feature provide morphological details of alumina with structural changes in a higher resolution mode .

## 3. RESULTS & DISCUSSION

**3.1**. The XRD plot between intensity ( a.u) and angular position at different values ( $2\theta^0$ ) was shown in figure 1. The graph shows crystalline structure of the material , such that it shows inverse relationship of the broadness of XRD peak and size of crystallite . As shown XRD shows presence of peaks at $2\theta$ ( Miller indices ) = $25.594^0$ ( 012) , 35. $197^0$ ( 104 ) , $37.804^0$( 110 ) , 43. $381^0$ ( 113 ) , $52.588^0$ ( 024 ) , $57.538^0$ ( 116 ) , $59.782^0$ ( 211 ) , $61.333^0$ ( 018) , $66.547^0$ ( 214 ) and $68.230^0$ ( 119 ) , which coincide with the peak values reported for alpha phase alumina crystallite material [ 11 ] .

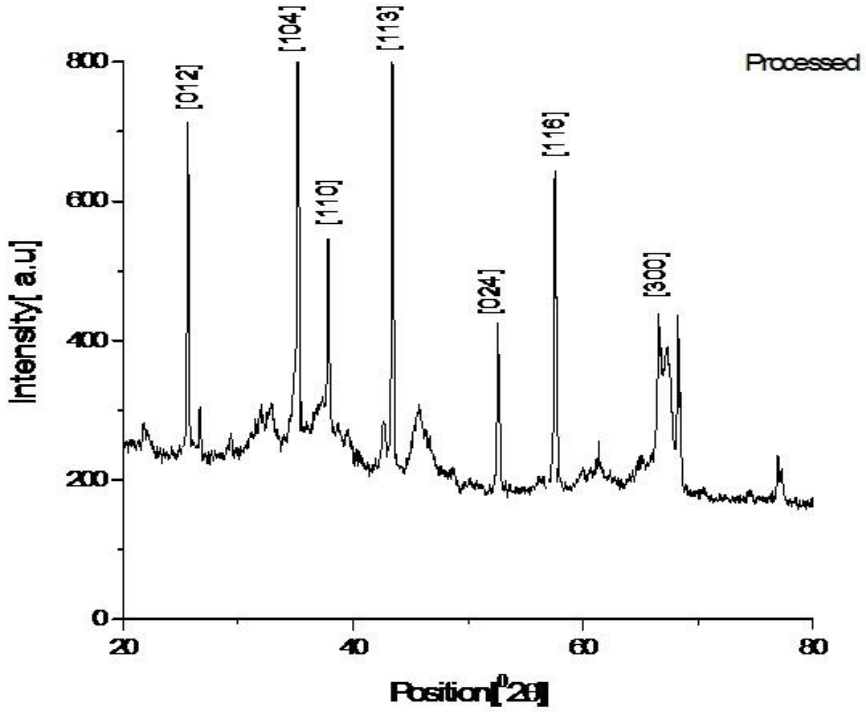


**Fig 1** Powder XRD graph of stable alpha (α ) phase alumina nanoparticle

The grain size is calculated by using Scherer's formula from full width at half maximum [FWHM] of diffracted peak as [12] where D is the grain size , $\lambda$ is the wavelength of the X-ray , β is the full width at half maximum of corresponding line and θ is the angle of diffraction of the peak . Similarly , dislocation density ( δ ) and microstrain ( ϵ ) were also calculated [13,14 ] respectively using :-

$$D_p = \frac{0.94\lambda}{\beta_{1/2}\cos\theta}$$

$$\varepsilon = \frac{\beta\cos\theta}{4}$$

$$\delta = \frac{1}{D^2}$$

The average grain size of crystallite domain calculated from Scherer data comes out to be 2.4 nm . Coherently , dislocation density and microstrain comes out to be ( D = 8 $A^0$ ) 0.014 * $10^{14}$ $lin^2$ / $m^2$ and 0.0299 respectively and found to be in agreement with reported literature [15,16] .

**3.2**. Brunauer – Emett – Teller ( BET ) graph as shown in figure 2, measure the specific area of the powder by utilizing adsorption / desorption of nitrogen on the surface of material . it give us clear idea about the porous structure of alumina with mean pore diameter 26.126 nm and surface $a_{s,BET}$ of 23.687 [ $m^2 g^{-1}$] . The existence of porosity provide an idea of existence of alumina in the nanomaterial state as compared to its bulk counterpart .

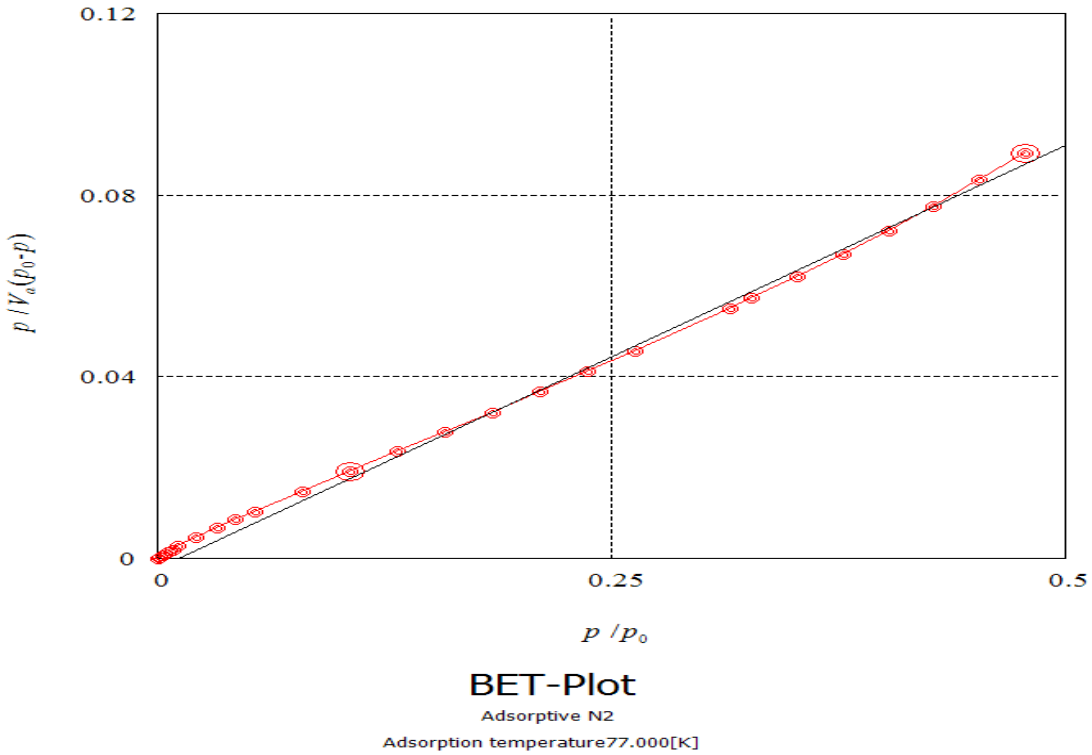


**Fig 2:** BET plot of nanoporous alpha (α ) phase alumina material

**3.3**. The morphological characterization after cryogenic treatment was shown in figure 3. FE SEM of nanoporous alumina sample show different images which highlighted several broken secondary particles and nanorod structure formation . This demonstrate that at a very lower temperature where entropy of the system reduces to a lower value cause these secondary particles ( agglomerated particles ) to broken away from agglomerated state arose due to higher thermal treatment [17] into free primary particles state . The interesting 1-D Nanorod and other structure formation as shown in figure 3. has demonstrated the impact of cryogenic treatment ( with liquid nitrogen at -196$^0$Celsius . on alumina nanoporous material .

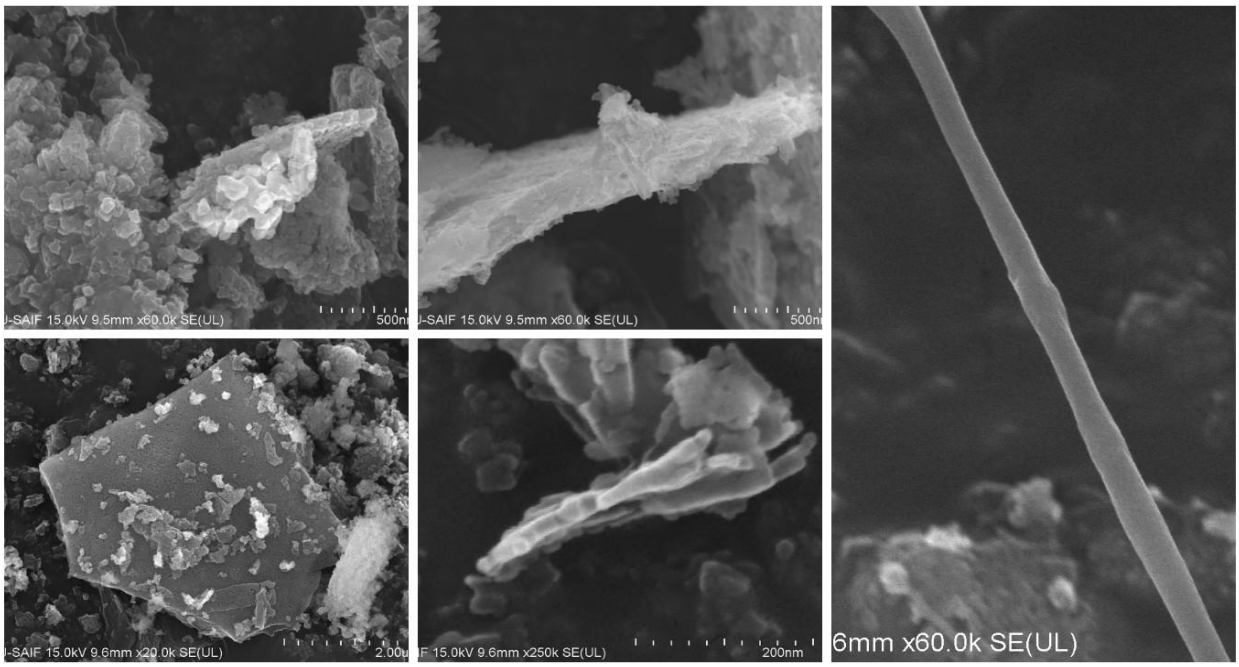


**Fig 3:** FE - SEM ( HITACHI SU8000 ) images of 1-D Nanorods and other structures formed after treating alumina nanoparticles with Liquid Nitrogen at Cryogenic Temperature.

This might shows that at deep cryogenic treatment during exposure time , Ostwald ripening [10] and higher crystallinity of particles led to the formation of sheet of micrometer size . After , cryogenic treatment sample environment was at very lower temperature of $-196^0$Celsius and during its transformation to a room temperature there was expected formation of Nanorods .This might happen due to reassembly of atoms which causes alumina particles to reassemble by the process of self assembly of similar size structures to form stable symmetrical Nanorods .

## 4. CONCLUSION

The synthesis of alpha phase alumina Nanoporous material involves heating at a very higher temperature . This process is associated with the random and uncontrolled process of agglomeration . So, by cryogenic treatment an effort is made to reduce this agglomeration by lowering entropy associated with the system to certain extent . Also exposure to such a lower temperature initiate self driven symmetrical forces and led to the formation of 1-D nanostructures . Therefore , cryogenic treatment reduces agglomeration and form 1-D nanostructure in alpha phase alumina nanoporous material.

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