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# Comparative study of nano-sized $Al_2O_3$ powder synthesized by sol-gel (citric and stearic acid) and aldo-keto gel method

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ABSTRACT

Inorganic $Al_2O_3$ nano-powders were synthesized by citric acid sol-gel, stearic acid sol-gel and aldo-keto gel method. The prepared samples were characterized by X-ray powder diffraction (XRD) for structural studies and the average particle size was calculated by Debye-Scherrer formula. The optical investigation was done through UV–vis and FL spectra analysis. The florescence properties were studied by fluorescence spectrophotometer (F-7000), indicating the emission of radiation of 397, 399, 401 nm by stearic acid sol-gel, aldo-keto gel and citric acid sol-gel method respectively, when nano powder absorbed UV radiation at 224 nm. However, it is found that blue shift in band gap was observed in stearic acid sol-gel, aldo-keto gel and citric acid sol-gel method respectively.



## 1. Introduction

Aluminum oxide (alumina, $Al_2O_3$) is one of the most useful oxide ceramics. It has several advantages over other ceramics such as its thermal, chemical, and physical properties when compared with several ceramic materials. These attractive properties of $Al_2O_3$ make it as a most studied oxide material. The $Al_2O_3$ is widely applicable in firebricks, abrasives and integrated circuit (IC) packaging [1,2]. It has been used in many fields of engineering such as coatings, heat-resistant materials, abrasive grains, cutting materials and advanced ceramics. This is because alumina is hard, highly resistance towards acids and bases, permit very high temperature applications and has very good wear resistance [3–5].

Nano-sized powders have been attracted much attentions due to their wide applications in the various field. There are several methods for synthesis of nano-alumina [3,6–9], and these are categorized into chemical and physical methods. Tok et al. [3] reported flame spray pyrolysis method to synthesized agglomerate-free nano-sized $Al_2O_3$ particles with a size range of 5–30 nm. Shizhong et al. [10] reported nano-sized $Al_2O_3$ powder synthesized by thermal Metal Organic Chemical Vapor Deposition (MOCVD) combined with plasma. Rodica et al. [11] discussed synthesis and characterization of alumina nano-powder obtained by sol-gel method.

Among the several methods, in our work we use gel methods for synthesize nano-sized $Al_2O_3$ powder. To our best knowledge these methods are novel namely stearic acid sol-gel method, citric acid sol-gel method and aldo-keto gel method for preparation of nano-sized $Al_2O_3$ and also their comparative study of structural and optical properties was done.

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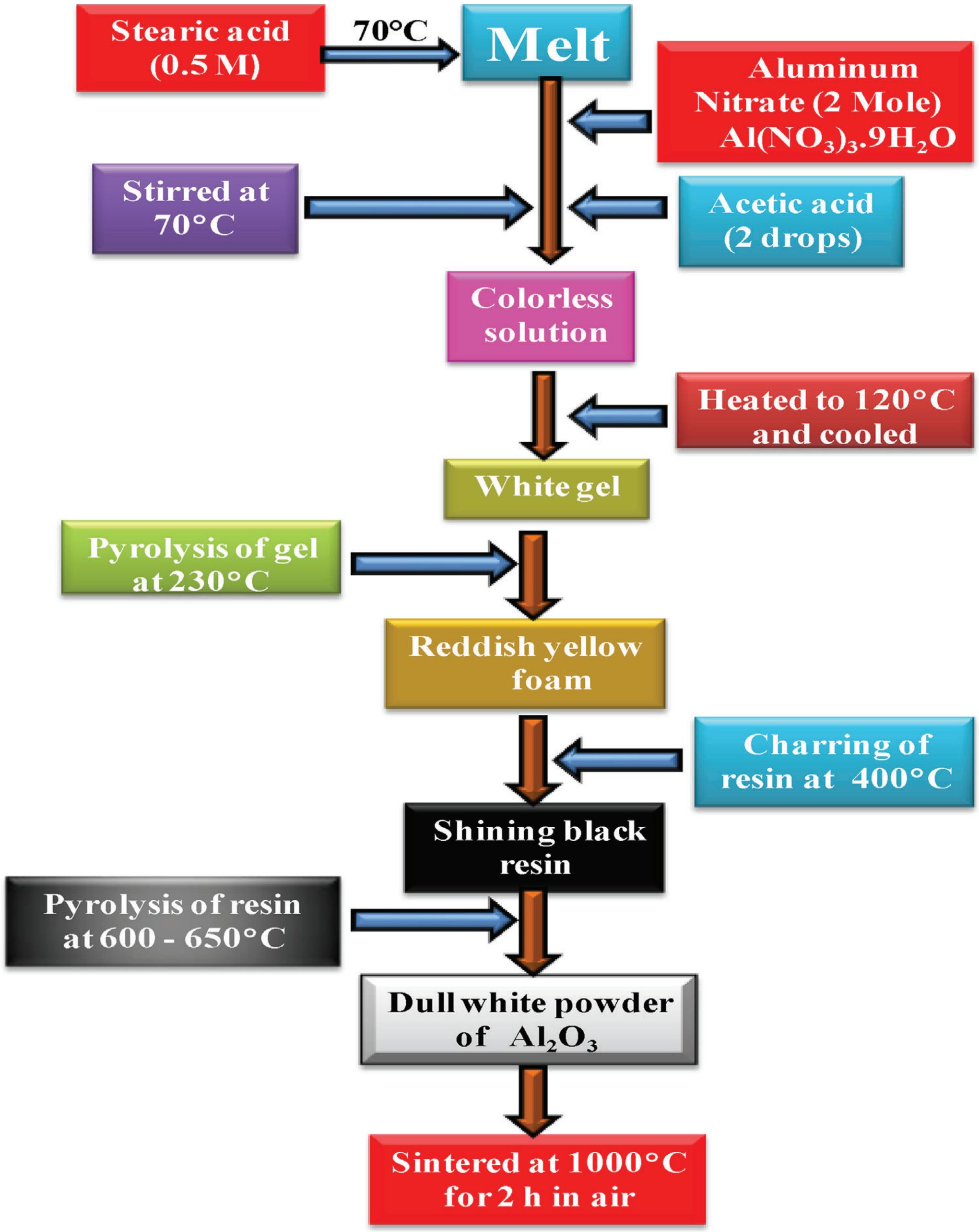


**Fig. 1.** Flow chart of $Al_2O_3$ synthesized by stearic acid sol-gel method.

## 2. Experimental

### *2.1. Stearic acid sol-gel method*

The dried precursor Al $(NO_3)_3{\cdot}9H_2O$ (2M) was taken in a china clay basin. The stearic acid 0.5M was heated slowly to 70 °C on hot plate in another china clay basin. It molted completely within 5 min. The dried precursor in the first basin was added to the molten stearic acid with the addition of 2 drops of acetic acid and was stirred continuously. This mixture was heated at 70 ºC with continuous stirring till the precursor dissolved completely leading to a colorless solution. On further heating to 120 ºC, the solution started boiling with the feeble evolution of fumes. The solution was then allowed to cool. White gel was formed after cooling.

After cool, the solution again heating slowly at 230 ºC yielding the reddish yellow resin which on pyrolysis at approximately 400 ºC converted into a shining black resin. It was milled into a fine black powder, which burnt approximately

700 ºC. The powder was sintered at 1000 ºC for 2 h yielding dull white powder of $Al_2O_3$. The complete process involved in the reaction was represented as a flow chart in Fig. 1. The projected chemical reaction is follows

$$6CH_3(CH_2)16COOH + 2Al(NO_3)_3 \rightarrow 2[CH_3(CH_2)16COO]_3Al + 3H_2O\uparrow + 6NO_2\uparrow + 3O\uparrow$$

$$2[CH_3(CH_2)16COO]_3Al + 156O_2 \rightarrow Al_2O_3 + 105H_2O\uparrow + 108CO_2\uparrow$$

### 2.2. Aldo-keto gel method

The precursor Al $(NO_3)_3 \cdot 9H_2O$ (2M) was taken in china clay basin and add some double distilled (DD) water in it. Acetone (1M) and Benzaldehyde (1M) were added to this mixture. The pale yellow mixture obtained was stirred continuously and slowly heated to 120 °C on hot plate. The color of the mixture changes to dark reddish brown. The process of gelation started at near about 130 ºC with the evolution of dark yellowish brown fumes. The mixture is then allowed to cool. Red gel is formed after cooling. The gel is further heated slowly to 300 ºC. Dark red foam was formed with evolution of yellowish brown fumes. On further slow heating, pyrolysis of foam was started at 250 ºC and completes up to 300 ºC and shining black material was formed at 300 ºC and burns into flame at 375 ºC started. It was finally sintered at 1000 ºC for 2 h. A snow-white powder of $Al_2O_3$ was obtained. The projected chemical reaction is-

$$6C_6H_5CHO + 6(CH_3)_2CO + 2Al(NO_3)_3 \rightarrow 2[C_6H_5CH_9(OH)CHCOCH_3]_3Al + 3H_2O\uparrow + 6NO_2\uparrow + 3O\uparrow$$

$$2[C_6H_5CH_9(OH)CHCOCH_3]_3Al + 34O2 \rightarrow Al_2O_3 + 33CO_2\uparrow + 11H_2O\uparrow$$

The complete process involved in the reaction was represented as a flow chart in Fig. 2.

### 2.3. Citric acid sol-gel method

The precursor Al $(NO_3)_3 \cdot 9H_2O$ (2M) was taken in a glass beaker. Citric Acid ($HOOCCH_2C(OH)(COOH)CH_2COOH$, monohydrated (0.5M) was taken in another glass beaker and adds some DD water in it. Stir the solution up to citric acid get dissolve in DD water. The aqueous solution of citric acid then added in the precursor of first glass beaker with ethylene glycol ($C_2H_6O_2$), (1M). The mixture was continuously stirred and slowly heated. After achieving complete dissolution, the resultant colorless solution was transfer in to a china clay basin and heated on hot plate, with stirring, at near about 130 ºC to remove excess of solvents and promote polymerization. With continued heating at near about for 1 h, the solution becomes highly viscous with a change in color from colorless to pale yellow. The solution was allowed to condense. Finally it gelled to a transparent brown glassy resin. No visible formation of precipitation or turbidity was observed during the polymerization and gelation. Charring of the resin at 350 ºC gave a black mass, which was lightly ground to powder, to which we refer powder precursor. The powder precursor thus obtained was heat treated first at 600 ºC. The pyrolysis of black powder started. Finally it was heat treated at 1000 ºC for 2 h in a furnace in air. The fine structured white powder of $Al_2O_3$ was obtained. The projected chemical reaction is-

$$6HOC(CH_2CO_2H)_2CO_2H + 2Al(NO_3)_3 \rightarrow 2Al[HOC(CH_2CO_2H)COO]3 + 3H_2O\uparrow + 6NO_2\uparrow + 3O\uparrow$$

$$2Al[HOC(CH_2CO_2H)COO]3 + 27O_2\uparrow \rightarrow Al_2O_3 + 36CO_2\uparrow + 27H_2O\uparrow$$

The complete process involved in the reaction was represented as a flow chart in Fig. 3.

## 3. Results and discussion

### 3.1. XRD analysis

Fig. 4 shows the X-ray diffraction pattern of $Al_2O_3$ by citric acid sol-gel, stearic acid sol-gel and aldo-keto gel method. The formation of the crystalline phases was confirmed by X-ray diffraction. The XRD patterns for samples agree well with ICCD card No. *01-075-0783* for aldo-keto gel, steric acid sol-gel for citric acid sol-gel method.

The $Al_2O_3$ lattice possesses Trigonal structure with a space group *R-3C (167)* with lattice parameters a = 4.7517 Å, b = 4.7517 Å and c = 12.9650 Å and interfacial angles $\alpha = \beta = 900$ *and* $\gamma = 120^\circ$ for aldo-keto gel, steric acid sol-gel method. For citric acid sol-gel method the $Al_2O_3$ lattice possesses Trigonal structure with a space group R-3C (167) with lattice parameters *a = 4.7418* Å, *b = 4.7418* Å *and c = 12.9210* Å and interfacial angles $\alpha = \beta = 90^\circ$ *and* $\gamma = 120^\circ$. The average crystallite size of each sample were calculated from the Debye Scherrer equation [14–16]

$$D_{(hkl)} = \frac{k\lambda}{\beta\cos\theta}$$

Where k is the shape factor, λ the wavelength of X-ray of Cu Kα radiation, β the full width at half maximum (FWHM) of the (h k l) peak, and θ is the diffraction angle. The calculated crystallite sizes were shown in the table.

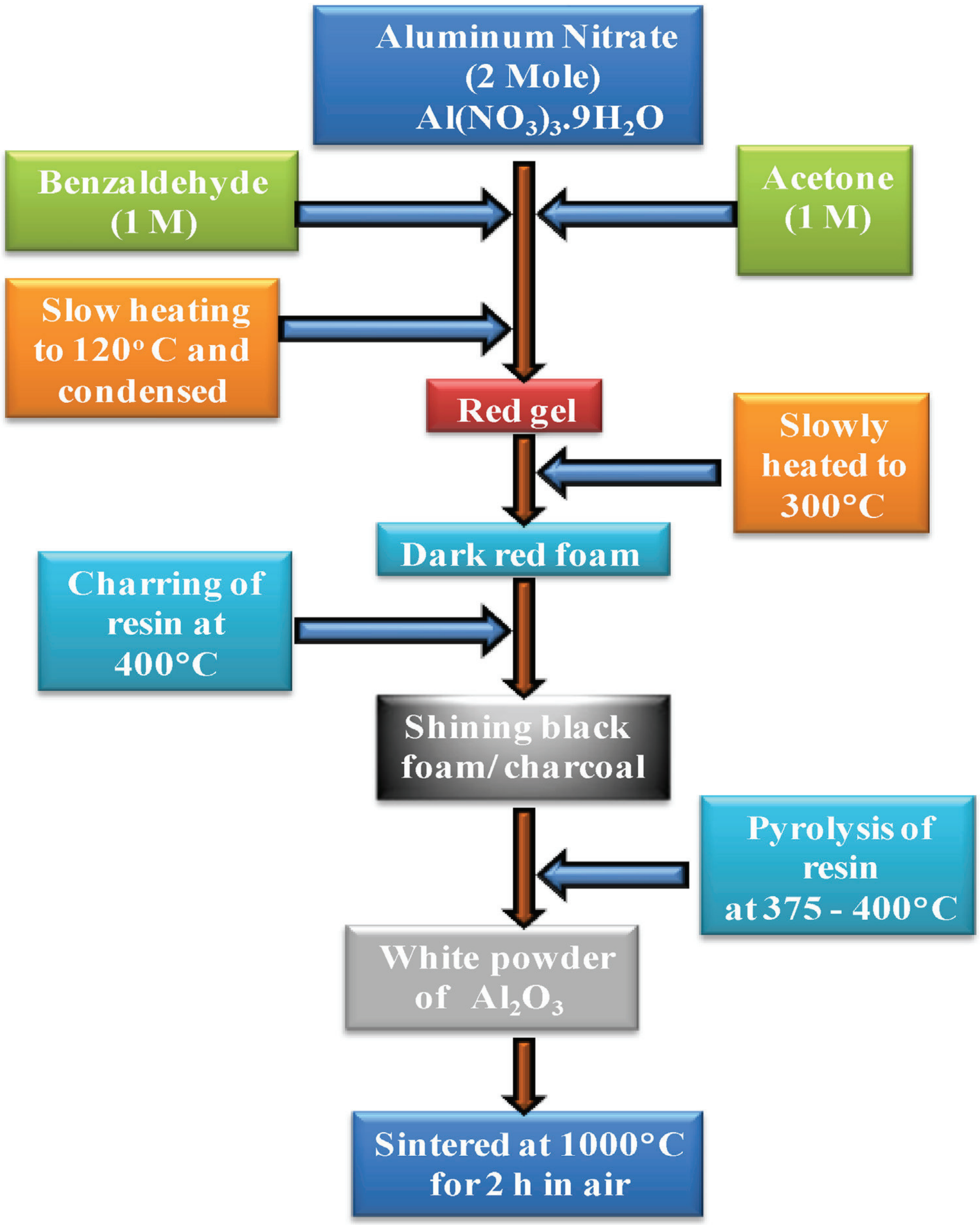


**Fig. 2.** Flow chart of $Al_2O_3$ synthesized by aldo-keto gel method.

| Sr. No. | Method of Synthesis | Crystallite Size by XRD |
|---|---|---|
| 1. | stearic acid sol-gel | 33.1149 nm |
| 2. | aldo-keto gel | 31.8497 nm |
| 3. | citric acid sol-gel | 29.3247 nm |

### *3.2. UV–vis analysis*

Fig. 5 shows the UV–vis absorption spectrum of $Al_2O_3$ by citric acid sol-gel, stearic acid sol-gel and aldo-keto gel method. The spectra show clearly an intense band-to-band absorption in the ultraviolet region. The UV–vis spectrum shows a complete agreement with that of nano-sized $Al_2O_3$ materials in the literature [12]. It showed an absorption peak at 224 nm with weak bands in the region of 300–350 nm corresponding to the charge transfer bands from Al–O. The band gap value were determined by extrapolation of the linear portion of ($\alpha h\nu$) plotted versus the photon energy ($h\nu$) in electron volt (eV). The band gap from the graph were found to be $E_g$ = 4.2, 4.7 and 5.08 eV by stearic acid sol-gel, aldo-keto gel and citric acid sol-gel method. The value obtained very much supports the semiconducting behavior of the material. It show that the band gap of

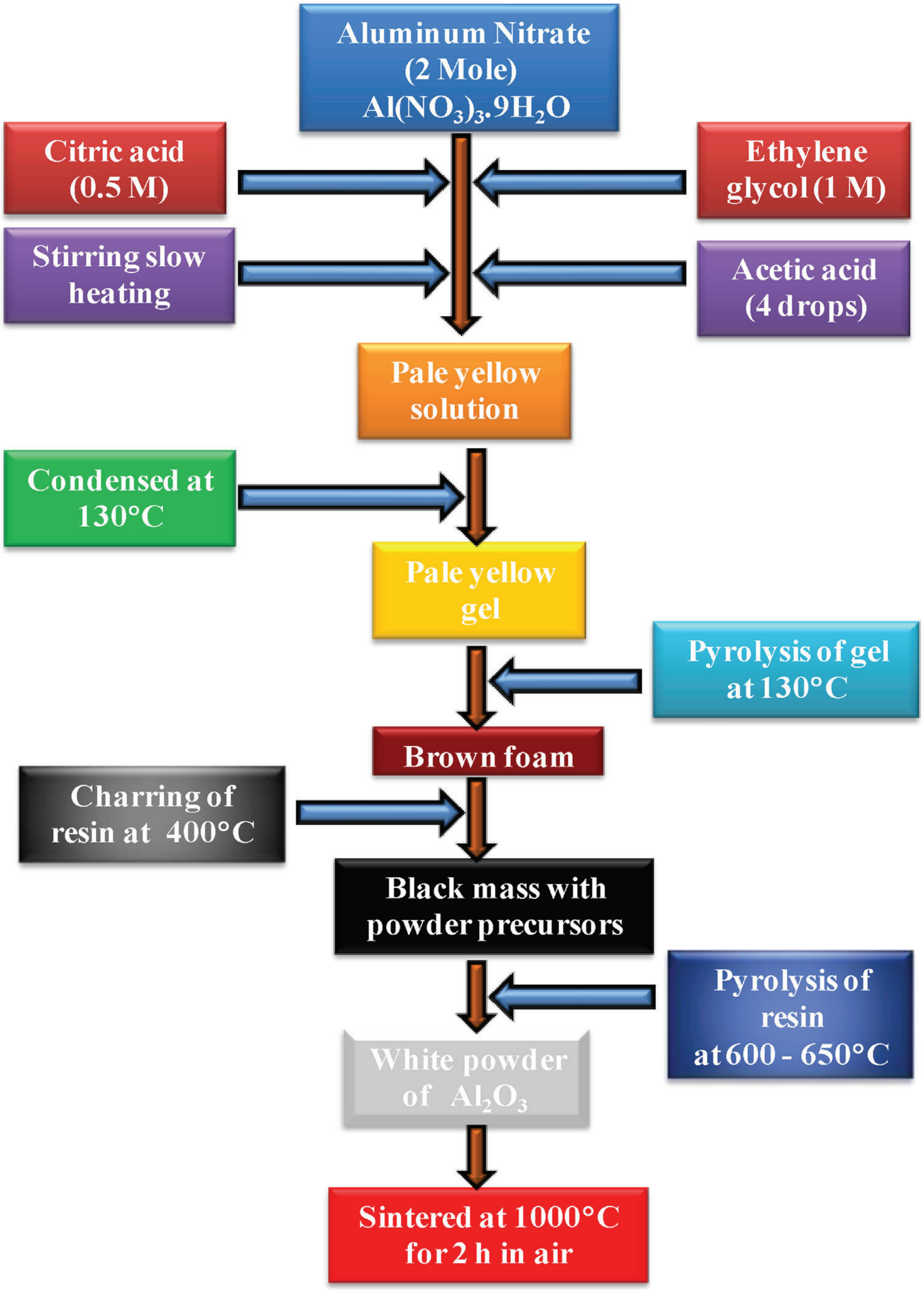


**Fig. 3.** Flow chart of $Al_2O_3$ synthesized by citric acid sol-gel method.

nano-sized $Al_2O_3$ powder via stearic acid sol-gel, aldo-keto gel and citric acid sol-gel method increases with decreasing the particle size. The blue shift in band gap confirms the formation of nano-sized $Al_2O_3$ powder [12]. This can be explained on the basis of defect chemistry, as there may be the presence of different sub-energy levels in the band gap, related to surface defects. The band gap of any materials is controlled by the changing concentration of defects. In $\alpha$-$Al_2O_3$, both donor (oxygen vacancies) and acceptor defects (Al interstitials) create energy levels below and above the conduction band and the valence band, respectively [1,12]. The optical band gap is depends upon the size of a particles, it is increase with a decrease in the particle size [13].

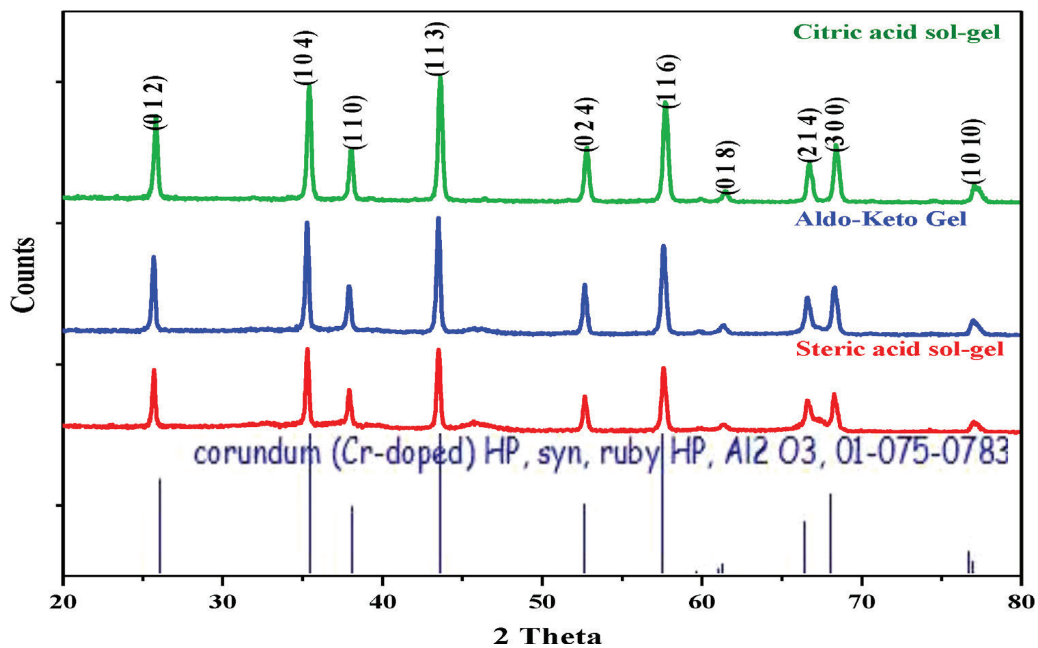


**Fig. 4.** XRD patterns of the nano-sized $Al_2O_3$ powder synthesized by citric acid sol-gel, stearic acid sol- gel and aldo-keto gel method.

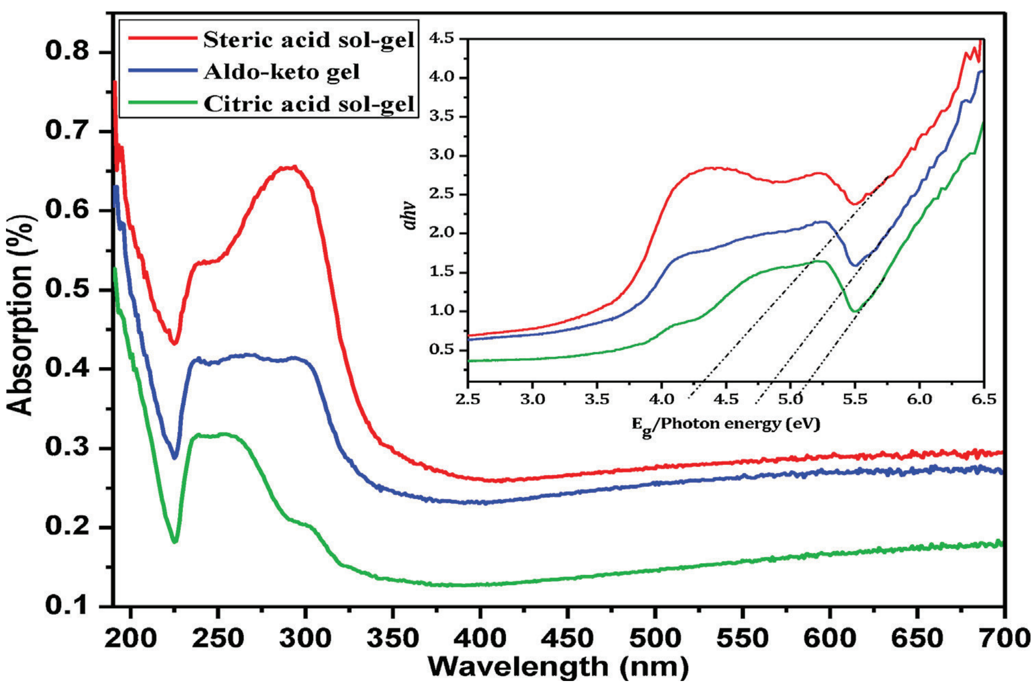


**Fig. 5.** UV–vis spectra of nano-sized $Al_2O_3$ powder synthesized by citric acid sol-gel, stearic acid sol-gel and aldo-keto gel method.

### 3.3. Fluorescence analysis

Materials in quantum state are said to be self-fluorescent nano-crystals [1]. However, in order to calculate the particle size, a fluorescence measurement was made from 300 to 700 nm and is as shown in Fig. 6. In the present work, our materials show an intense blue luminescence under a 224 nm irradiation at room temperature. The peak value of the emission is observed at 397, 399, 401 nm by citric acid sol-gel, aldo-keto gel and stearic acid sol-gel method, and this assigned to the presence of defects. It is well known in quantum dots that as the particle size varies, the fluorescence wavelength also varies [12]. Litty et al. [13] discussed that the shifting in fluorescent spectra due to the variation of particle size. If the particle size is increases then peak of fluorescent spectra shifting towards the longer wavelength.

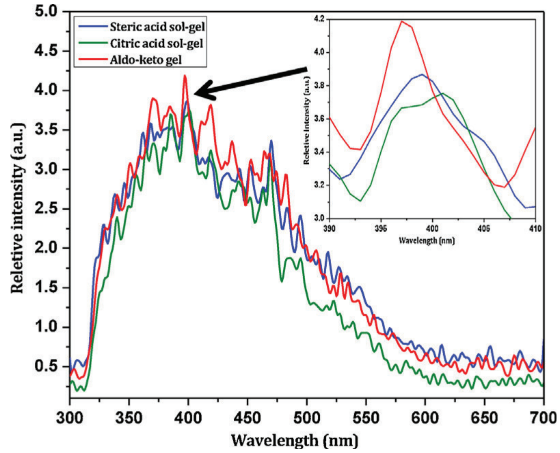


**Fig. 6.** Photoluminescence spectrum of nano-sized $Al_2O_3$ powder synthesized by citric acid sol-gel, stearic acid sol- gel and aldo-keto0 gel method.

## 4. Conclusions

Inorganic $Al_2O_3$ nano-powders have been successfully prepared by using a novel stearic acid sol-gel, aldo-keto gel and citric acid sol-gel method. The XRD pattern completely agrees with ICDD file and supports a complete crystalline nature of the prepared materials. The UV–vis and FL analysis confirms the blue shift in band gap, the formation of nano-sized $Al_2O_3$ powder.

The material exhibits a good UV absorption at 224 nm and a blue emission peaks at 397, 399, 401 nm by stearic acid sol-gel, aldo-keto gel and citric acid sol-gel method respectively. The prepared material may possibly find applications as ceramic, sensing, and biocompatible materials.

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