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Evolution of Monoclinic $CaAl_2O_4$ Nanocrystallites via Chemical Route and Its Optical Investigations

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Abstract: Nanocrystalline calcium aluminate ($CaAl_2O_4$) powder is an adequate phosphor material. Calcium aluminate is a versatile member belongs to a category of alkaline earth aluminates phosphor. It has multifaceted applications in different areas such as photocatalysis, sensing, optoelectronic devices, displays, and imaging etc. In the present study, calcium aluminate has been prepared by well-known citrate sol-gel technique. X-ray diffraction (XRD) method has been used to analysis the amorphous and crystalline behavior of the prepared samples. The sample annealed at 800° indicates the monoclinic phase with enhanced intensity of the prominent diffraction peaks. By using Debye-Scherrer formula the grain size of crystalline powder is calculated ~10 nm. FTIR spectra confirmed the molecular orientation and bond structure in the prepared nanomaterial. Surface morphology and elemental composition present in prepared samples has been examined by Scanning electron microscope and energy dispersive spectroscopy. Uv-vis spectroscopy result showed red shift in the nanopowder with thermal treatment. In material science, due to their long-lasting photo-luminescence properties in visible region these aluminates are very attractive for evolution of new generation inorganic phosphor materials.

Keywords: $CaAl_2O_4$, Sol-gel method, XRD, FTIR, Band gap, SEM, etc.

Introduction

Oxide Phosphors substances are extensively tried in television, blaze lighting, in the process of light display of information. Lighting parameter of tools, such as blaziness, color of brightness, color presentation, transparency be dependent on the features of nanomaterial used for phosphors fabrications (Selyunina et al., 2019). In addition to Alkaline earth aluminates $CaAl_2O_4$ is a dominant composite for the devising of lifelong phosphor substancewhich has great luminescent characteristics, and potential candidates for optical information storage devices, giant beginning luminescent intensity, long lived time, worthy emission of color and chemically long lasting (Chen, GH 2006; Pati et al., 2002; Ryu and Bartwal 2009;

Zawrah and Khalil 2007). $CaAl_2O_4$ is belongs to tridymite group of monoclinic space group (space group: P21/n), where [AlO_4] tetrahedral formulate a three-dimensional skeleton. Every oxygen is accompanied with two aluminum ions. There are three Ca^{2+} sites in the $CaAl_2O_4$ lattice one is nine-coordinated and the others are six-coordinated by oxygen atoms traditionally calcium aluminate is synthesized by Solid state reaction but the main limitation of this solid-state reaction is that, it requires high temperature, a prolonged annealing time, stubby chemical consistency, considerable mean particle size and not desired phase with the end product. To improve these disqualities, there are many methods for the chemical synthesis of alkaline earth aluminates phosphors: hydrothermal, combustion, pechini, sol-gel, microwave and precipitation method were suggested which enable low synthesized temperature. Among them sol-gel method is precisely used, which may increase the reaction rate and produced fine particle size and occurs at low sintering temperature (Park and Kim 2008; Zhao and Chen 2007; Rodriguez et al., 2012; Choi and Hong 2010). The most important benefit in this method situated in the multi-story stages of homogenization of the beginning ingredient (Selyunina et al., 2019). This method decreases the energy expenditure (Botvinaa et al., 2018). The motive of study was to explore the procedure of evolution of $CaAl_2O_4$ and a luminescent material depends on it, their structural framework and properties.

Experimental and characterizations

As prepared and annealed $CaAl_2O_4$ was prepared citrate sol-gel technique (Choi and Hong 2010; Botvinaa et al., 2018). The diagrammatic representation is given below:-

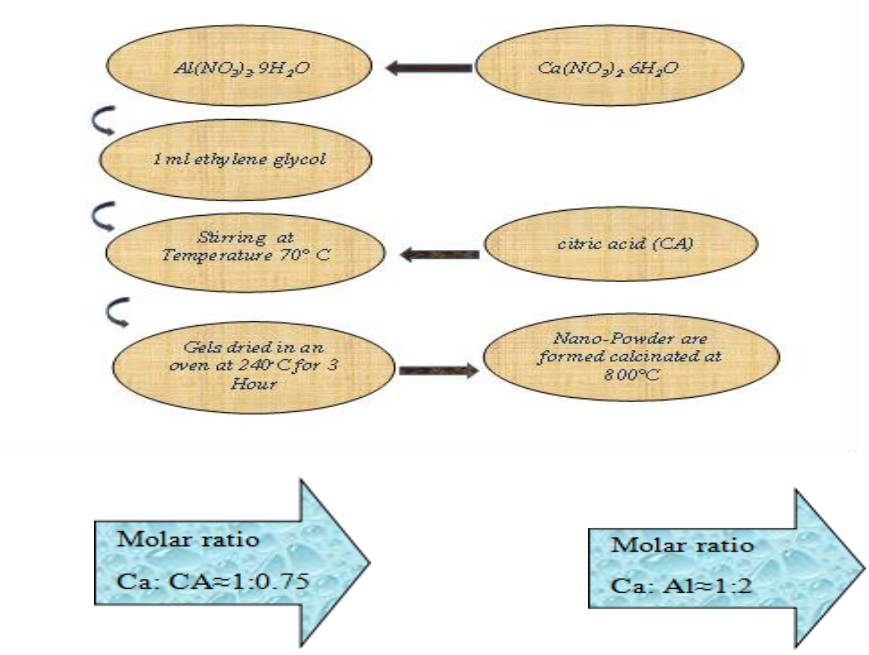

Fig. 1: Diagrammatic representation of the synthesis method.

To study of structural behavior and phase composition the samples were identify by XPERT-PRO x-ray diffractometer functioned at 45kV and 40 mA through Cu Kα monochromatic rays having wavelength 1.5406 Å in distinct arrays to produce x-ray pattern. The samples also go through FTIR spectra of Perkin Elmer 400 spectrophotometer in the range of IR region i.e., 400-4000 $cm^{-1}$with the help of KBr pellet technique. Surface morphology of the phosphor powders were obtained by NOVA NANOSEM 450. And the elementary composition prevailed with the help of energy dispersion spectroscopy (EDS). For recording the Absorption spectra Lambda 750 UV-vis spectrophotometer has to be used.

Results & Discussion

Phase Analysis by XRD:

XRD sketch of as synthesized and annealed powder samples of $CaAl_2O_4$turned out to be shown in Fig. 2(a). Fig. 2(a) conveyed that the x-ray powder diffraction pattern of as synthesized which is amorphous in nature (Botvinaa et al., 2018). And annealed $CaAl_2O_4$ synthesized by citrate sol-gel method, which accorded with (JCPDS PDF #70-0134) and confirmed monoclinic structure (Pati et al., 2002; Ryu and Bartwal 2009; Rodriguez et al., 2012; Choi and Hong 2010; Jayasekara and Monaghan 2018; Zhang et al., 2010; Zhang et al., 2015). The crystallinity is increased by increasing the temperature. Besides the predominant peak of $CaAl_2O_4$ at 2θ ~ 29.25°, few weak diffraction peaks of $CaAl_2O_4$ were also spotted at 2θ ~ 29.25°, 35.98°and 39.48°.

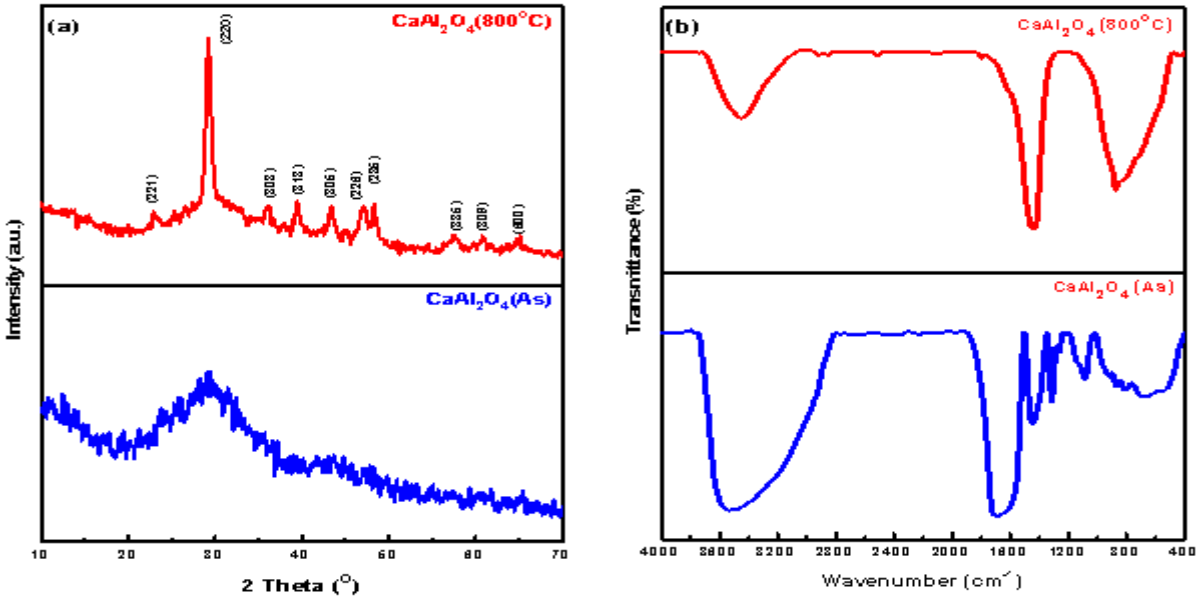

Fig. 2:(a) XRD pattern (b) FTIR spectra of as-prepared and annealed $CaAl_2O_4$ samples.

The standard nano crystalline size i.e., average size (D) has been calculated using Scherrer's equation (Goswami et al., 2018), corresponding the most intense x-ray diffraction peak (220) is given by following equation:

$$D = (0.89\ \lambda)/ (\beta\ \text{Cos}\ \theta) \quad (1)$$

Here; d (nm) stands for average or mean nanocrystallite size, λ(nm) denotes the x-rays wavelength, β representing the full width at half maxima (FWHM) of diffraction peak, θ(rad) isangle of diffraction peak (Goswami and Ahlawat 2019). The average nanocrystalline size comes out to be ~9±0.5. The crystallographic unit cell parameters were obtained as: 'a' =0.8699 nm, 'b' =0.8212 nm, 'c' =1.5207 nm, 'β' =90.1584°.

FTIR Spectral Analysis:

Fourier-transform infrared spectroscopy analyzed the bonding environment of as synthesized and calcinated $CaAl_2O_4$ at room temperature asdisplayed in Fig. 2(b). The deep study revealsthat assynthesized and calcinated sample shows numerous rigorous, sharp, small, intermediate & wide IR absorption bands. In both samples, the band comes out at 3425 cm^{-1} isallocated due to the antisymmetric or symmetric stretching environment of as synthesized and calcinated $CaAl_2O_4$ at room temperature asdisplayed in Fig. 2(b). The deep study reveals that assynthesized and calcinated samples show numerous rigorous, sharp, small, intermediate & wide IR absorption bands. In both samples, the band comes out at 3425 cm^{-1} is allocated due to the antisymmetric or symmetric stretching type modes of –OH molecule. The reason for arising this band may be spreading of humidity inthe samples from the airwhile the formation of KBr pellets (Zhang et al., 2010).Two little band occurs at 2927 and 2340 cm^{-1} is assigned C-H stretching vibration modes and deformation vibration of water molecules (Tangcharoen et al., 2019; Stringhini et al., 2014).A sharp peak at 1430 cm^{-1} revels the connection to amide bonds (Goswami et al., 2018). The absorption bands occur at 735-883 cm^{-1} and 553-629 cm^{-1} attributed due to Al-O bond stretching vibration in AlO_4 tetrahedral and AlO_6 octahedral (Zhang at al., 2015). Bands ranging below 800 cm^{-1} originate from metal-oxide (M-O) groups (Pan et al., 2018). Three-dimensional network was constituted of AlO_4 tetrahedron shared vertex, in gaps of which Ca^{2+} ions were filled. Therefore, it is observed that FTIR spectra of $CaAl_2O_4$ lattice structure was a not so much changed except only slight decrease in crystallinity which is also consistent with XRD result.

UV-Vis Spectroscopy Analysis:

To find out the relation between morphological arrangement and energy band gap, the UV-Vis absorption spectra are studied and both are dispersed in ethanol were recorded as shown in Fig. 3(a). In Uv-vis spectra of prepared samples, the bands are found with maximaat 215 and 300 nm, respectively and accredited to the band-to-band transition of group like AlO_6 anion in $CaAl_2O_4$. The correlation of falling photoenergy (hν) and the coefficient of absorbance (α) are deduced by the equation:

$$(\alpha h\nu)^{1/n} = A\,(h\nu - E_g) \qquad (2)$$

Here A represents a constant, and E_g stands for band gap energy of the substance and the integer n =1/2. By schematic i.e., plotting a graph between $(\alpha h\nu)^2$ verses hν direct band gap of the samples is estimated. After that, extrapolating the linear region of the curve on hν axis at α = 0 as depicted in inset of Fig. 3(b). As synthesized and calcinated samples has been obtained band gap energy ~ 3.6 eV and 1.8 eV, respectively.

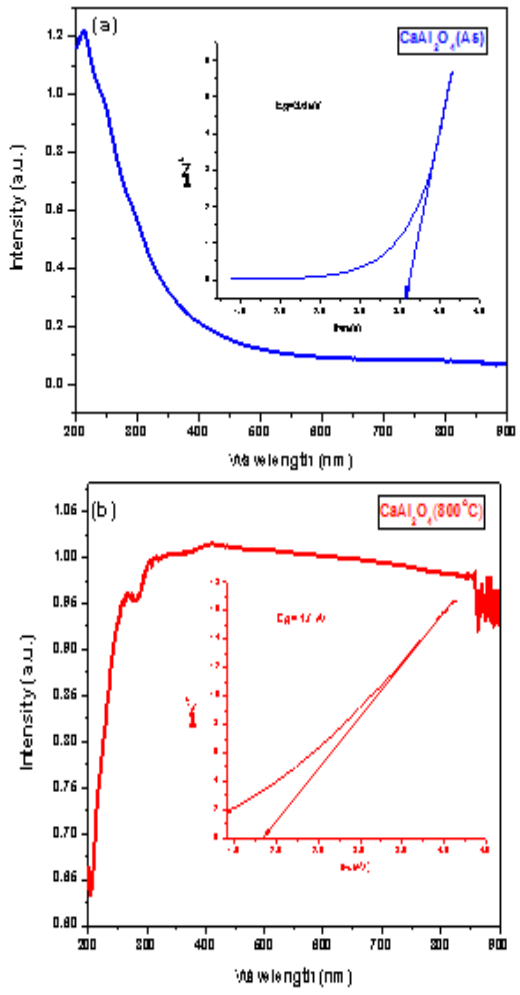

Fig. 3: Absorption spectra and band gap energy of (a) as prepared and (b) calcinated $CaAl_2O_4$ samples

Scanning Electron Microscopy (SEM) Analysis:

The microstructure evolution of as synthesized and annealed sample of $CaAl_2O_4$ was studied by scanning electron microscope. The surface morphology is in the shape of small grainy structure and is inter linked with each other, dominant to the origination of bigger particles. As shown in Fig. 4, slightly agglomerated phenomenon was observed in both the samples which are attributed to the annealing temperature (800°C). The elemental layout was sure by the EDS technique. In as prepared sample wt % are obtained as 49.10, 11.71, 25.33, 11.89 and 1.97for the existence of Ca, O, Al, C and N elements of $CaAl_2O_4$ nanopowder.

Conclusions

Successfully as prepared and annealed $CaAl_2O_4$samples have been prepared via the technique of 'citrate sol-gel'. The structural and vibrational results revealed that the annealed sample contain highly monoclinic $CaAl_2O_4$ phase with average size in nanometer range. It is concluded that after calcinated the sample at 800°, both crystallinity and particle morphology affected in a significant way. Energy Dispersive x-ray Spectroscopy revels confirmation of the anticipated elements (Ca, Al and O).The morphology of prepared samples has been confirmed by Scanning Electron Microscopy. It is concluded that bandgap energy is decreased due to annealing as many defect states are generated in between conduction and valence band.

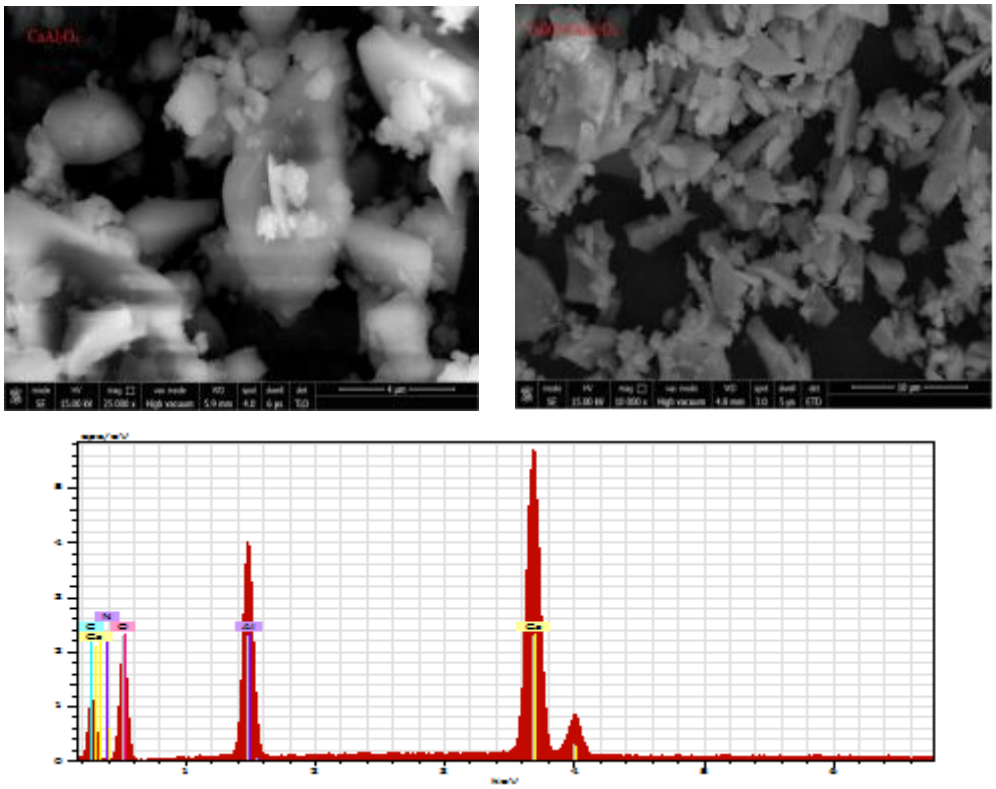

Fig. 4: SEM micrographs and EDX of as prepared and annealed $CaAl_2O_4$ powder samples.

References

Botvinaa, TM, Botvina, VV, Selyuninaa, LA and Mishenina, LN (2018) Synthesis of CalciumAluminate-Based Luminophores by the Citrate Nitrate Sol–Gel Process. J. Ing. Chem, 63: 1262–1267

Chen, GH (2006) Mechanical activation of calcium aluminate formation from $CaCO_3$–Al_2O_3 mixtures, J. Alloy and Comp., 416: 279-283.

Choi, SW and Hong, SH (2010) Size and morphology control by planetary ball milling in$CaAl_2O_4$:Eu^{2+} phosphors prepared by Pechini method and their luminescence properties, J. material science and Eng., 171: 69-70.

Goswami, B, Rani, N and Ahlawat, R (2018) Structural and optical investigations of Nd^{3+} doped Y_2O_3-SiO_2 nanopowder, J. of Alloys and Comp, 73: 450-457.

Goswami, B and Ahlawat, R (2019) Characterizations of Pb^{2+}: $ZnAl_2O_4$ spinels synthesized via citrate sol-gel technique, AIP Conference Proceedings 2142, 070021

Jayasekara, AS and Monaghan, BJ (2018) the effect of calcium aluminates on the coke analogue gasification, J. Long. Fuel, 225: 18-25.

Pati, RK, Panda AB and Pramanik P (2002) Preparation of Nanocrystalline Calcium Aluminate Powders, J. of Materials Synth. and Processing, 10: 157-161.

Park, YJ and Kim YJ (2008) Blue emission properties of Eu-doped $CaAl_2O_4$ phosphors synthesized by a flux method,

J Material Science and Engineering, 146: 84-88.

Pan, X, Zhang, D Wu, Y and Yu, H (2018) Synthesis and characterization of calcium aluminate compounds from gehlenite by high-temperature solid-state reaction, Ceramic Inter., 44:13544-13550.

Ryu, H and Bartwal KS (2009) Exploration and optimization of Dy co doping in polycrystalline $CaAl_2O_4$: Eu, J. Alloy and Comp., 476: 379-382.

Rodriguez, MA Aguilar, CL and Aghayan MA (2012) Solution combustion synthesis and sintering behavior of $CaAl_2O_4$, J. Ceramic Inter., 38: 395-39.

Stringhini, FM, Foletto, EL, Sallet, D, Bertuol, DA, Filho, OC, and Nascimento, CAO (2014) Synthesis of porous zinc aluminate spinel ($ZnAl_2O_4$) by metal-chitosan Complexation method, J.of Alloy and Comp., 588: 305-309.

Selyunina, L, Mishenina, L, Belyaninova T and Botvina T (2019) Sol-Gel Synthesis of Fluorescent Materials Based on Tricalcium Aluminate, J. Phys. Conf. Ser., 1145: pp 1-9.

Tangcharoen, T, Thienpraser, T and Kongmark, C (2019) Effect of calcination temperature on structural and optical properties of MAl_2O_4 (M = Ni, Cu, and Zn) aluminate spinel nanoparticles, Adv. Cerams., 8(3): 0-0.

Zawrah, MF and Khalil NM (2007) Synthesis and characterization of calcium aluminate nanoceramics for new applications, J. Ceramic Inter, 33: 1419-25.

Zhao, C and Chen, D (2007) Synthesis of $CaAl_2O_4$: Eu, Nd long persistent phosphor by combustion processes and its optical properties, J. Material Letters, 61: 3673-3675.

Zhang, X, Dong, H and Mei, Z (2010) Structure and luminescence properties of Sm^{3+} doped in $CaAl_2O_4$ phosphor, J. Optoelectronics and Advanced Materials, 4: 28-32.

Zhang, D, Pan, X, Yu, H and Zhai, Y (2015) Mineral Transition of Calcium Aluminate Clinker during High-Temperature Sintering with Low-lime Dosage, J of Mat. Science and Tech., 31:1244-1250.