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Synthesis and characterization of Eu^{3+} doped α-Al_2O_3 nanocrystalline powder for novel application in latent fingerprint development

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ABSTRACT

In the present study, we investigate upon the synthesis and characterization of inorganic Eu^{3+} doped Al_2O_3 nanophosphor for its structural and luminescent properties. The luminescent nanopowder was prepared using a combustion method in which the stoichiometric ratio of oxidizers and fuel was fixed to one, with varying concentration of Eu^{3+} ions acting as an activator. The prepared powder showed excellent thermal stability. For the identification of the phase and structure of the powder synthesized, X-ray diffractometer was used. From the XRD analysis, it is revealed that the rhombohedral crystallite phase of α-alumina was formed. The type of morphology and particle size was ascertained by Filed Emission-Scanning Electron Microscope (FE-SEM) and it was found that particles were having irregular spherical shape. A qualitative analysis of these nanophosphor particles was made using an Energy dispersive X-ray detector (EDS) and it was found that the samples were composed of Al, O and Eu ions. Photo-luminescence (PL) spectra were obtained using Spectrofluorometer absorption. The intense band position was observed at 618 nm and other less intense bands were also seen at 592 nm, 601 nm, 631 nm, while two weak bands were observed at 660 nm and 718 nm, when excited at 226 nm. The CIE color space chromaticity diagram was calculated from the CIE Calculator program using obtained PL spectra. The prepared nanophosphor powder was tested for latent fingerprint detection in forensic applications. The synthesized nanophosphor was successfully used as a latent fingerprint developing powder on various non-porous surfaces for forensic application. Copyright © 2016 VBRI Press.

Keywords: Luminescence; XRD; phosphor; CIE; nanocrystalline; latent fingerprint.

Introduction

The past decade has witnessed a rapid growth in the advances in materials science, specifically in luminescent materials for various photonic applications. Photoluminescence is an interesting phenomenon, caused by photo-excitation. In the world of luminescence, Rare Earth (RE) ion doped materials have grossed eminent attention due to their significant advantages such as good quantum efficiency, better photochemical stability, tailoring of emission wavelength through co-doping and manipulation of the host elements and narrower emission band with large anti-stoke shift. The properties like, large transparency window from an ultraviolet to near infrared wavelength, high melting point, chemical inertness, photochemical stability, dimensional stability and good mechanical strength makes Al2O3 as one of the best host matrix for RE ions as well as transition metal ions. With its diverse applications Al_2O_3 is the most commonly studied material for engineering and wide range of technical applications too. In short, Al_2O_3 is of immense technological importance **[1-4]**.

α-Al_2O_3 powders doped with Eu^{3+} and Eu^{2+} ions synthesized at low temperature, was studied by Rakov *et al.* in 2004 and by Liu *et al.* in 2014 **[4-7]**, but detailed study for the investigation of the morphology, crystal structure parameters and surface properties is required. Recently, Kumar *et al.* have worked on α-Al_2O_3 using the solution combustion method **[8]**. The purpose of the present research is to further investigate the structural and optical properties of inorganic Europium doped α-Al_2O_3 nanoparticles with varying percent of dopant (Europium-Eu^{3+} ion). The method adopted for synthesis is low temperature solution combustion method in which urea is employed as the organic fuel due to the fact the it is one of the best fuel for aluminum nitrates.

There are reports of utilization of Al_2O_3 in various applications, however, we tried to explore this material for the latent fingermark detection for forensic application. This is for the first time in this work α-Al_2O_3:Eu^{3+} nanophosphor material has successfully detected the fingermarks on various surfaces. We discussed in detail the possibility of present material for acting as fingerprint developing agent. Hence, herein the novel application of α-Al_2O_3:Eu^{3+} powder, with intense red luminescence in developing latent fingermarks using powder-dusting method, is reported.

Experimental

Materials synthesis

The α-Al_2O_3:Eu^{3+} phosphor-powder samples were synthesized using the conventional solution combustion

method. The precursors used were aluminium nitrate ($Al(NO_3)_3.9H_2O$), Europium nitrate ($Eu(NO_3)_3.H_2O$), and urea (NH_2CONH_2) as the organic fuel. All were of analytical purity grade (99.9 % pure) purchased from the Sigma Aldrich Company (India). The reagents were weighed in stoichiometric proportion representing one as the oxidizer: fuel ratio (O: F=1) as given in the reaction below. Different concentrations of Europium ions (0.50, 1.5, 2.0 mole %) were prepared.

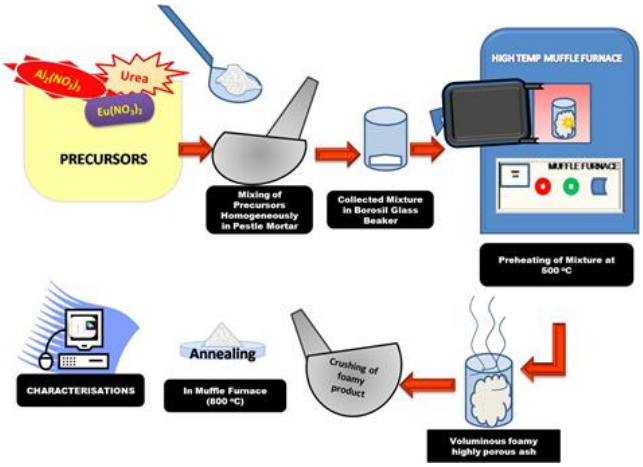

Fig. 1. Schematic illustrations of the synthesis process of Al_2O_3: Eu^{3+} nano-powder using combustion method.

Considering the Stoichiometric ratio the chemical equation is expressed as:

$$2(1\text{-}x)\ Al\ (NO_3)_3.9H_2O + x\ Eu(NO_3)_2 + 5\ CO(H_2N)_2$$

$$\downarrow$$

$$Al_{(2\text{-}x)}Eu_xO_3 + 5\ CO_2\ (g) + 8\ N_2\ (g) + 28\ H_2O\ (g)$$

Method

The precursors were weighed, homogeneously mixed and agitated with a very small amount of distilled water in a mortar pestle. The mixture was then collected in a Borosil beaker (250 ml) and placed in a pre-heated muffle furnace at 500 ºC as shown by schematic representation in **Fig. 1**. An exothermic redox reaction takes place, followed by the escape of gases during the chemical reaction **[9]**. Initially, the mixture undergoes vigorous boiling, and it takes less than 5 minutes for the completion of reaction by self-ignition with a bright flame, producing a white voluminous-foamy highly porous ash. This ash is then allowed to cool and then crumbled into fine powder using a mortar and pestle. The synthesized powder is calcined for 3 hours at 800 ^oC to enhance crystallinity and removal of non-stoichiometric phase.

Characterization

XRD patterns were obtained using X-ray diffractometer (Bruker D8) with Cu-K_α radiation, λ = 1.5406 Å, for the identification of the phase and structure of the powder synthesized. To record the morphology and surface composition of the synthesized nanophosphor Field Emission Scanning Electron Microscope (Hitachi SU-8010 FE-SEM) was used to study the morphology of the prepared phosphors and to estimate their particle size. Different images of the particles were taken with varying the accelerating voltage, magnification and working distance. Accelerating voltage used was varied from 10000-15000 volts, while the magnification and working distance was varied from 60000X-180000X and 8.8 mm to 12.8 mm, correspondingly. A qualitative analysis of these nanophosphor particles was made using Energy Dispersive X–ray detection analysis (EDXA). It was used to check the elemental composition of the powder samples and the presence of impurities, if any. Cary Eclipse Spectro-fluorometer was utilized to obtain the Photo-luminescence (PL) spectra, and the excitation wavelength for the PL study was 226 nm. The CIE 1931 color space chromaticity diagram was calculated from the Commission Internationale de l'Eclairage (CIE) Calculator program for the synthesized powders **[10]**.

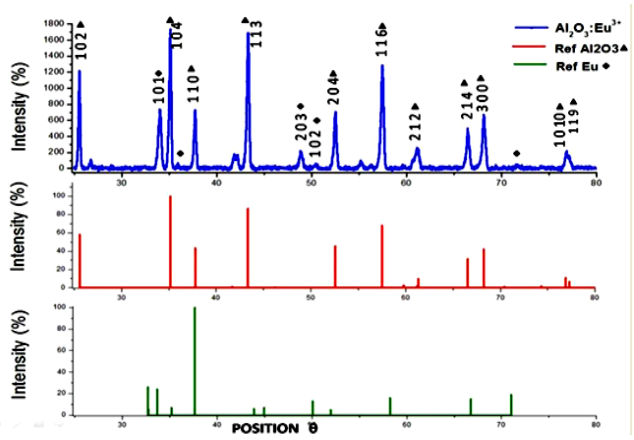

Fig. 2. XRD patterns of prepared α-Al_2O_3: Eu^{3+}(1.5mole %) is in good agreement with the standard pattern (reference code 01-074-1081), while few minor peaks are contributed by Europium.

Results and discussion

X-ray diffractometry (XRD)

The XRD pattern of α-Al_2O_3 with 1.5 mole % Eu^{3+} was used to identify the phase. The peaks were in agreement with reference code 01-074-1081 and have a rhombohedral crystallite phase of α-alumina (Corundum). Al_2O_3:Eu^{3+} phosphor has space group R-3c(167) and confirms the phase as shown in **Fig. 2**. The crystallite system of Al_2O_3: Eu^{3+} is found with cell parameters *a=b=4.754Å, c=12.96755 Å* and cell volume (a^3) = 254.09 $Å^3$. The miller indices h k l of every major peaks of the synthesized powder perfectly matches with that of α-phase of Al_2O_3 and was found similar to the work done by Rakov *et al.* (2007) **[4, 6]** and Liu D *et al.* (2014) **[5].**

The particle size was calculated following Debye-Scherrer formula **[11]** as:

$$\mathbf{D} = \frac{\mathbf{0.94}\boldsymbol{\lambda}}{\boldsymbol{\beta Cos\theta}}$$

where, λ is the x-ray wavelength, β is the Full width at half maxima (FWHM), 0.94 is a constant and θ is the angle of diffraction in degree. The particle size was ranged from 30.76 nm to 47.30 nm, and the average particle size was

found to be 36.38 nm. The h k l value of the strongest peaks with maximum intensity (~1600 a.u.), were found to be (1 0 4) and (1 1 3).

Table1. Various crystalline parameters of the α-Al_2O_3:Eu^{3+} (1.5 mol %) calculated for from XRD pattern.

2θ(°)	β (FWHM)	(hkl)	D (Particle size nm)	ε (Strain)	δ (Dislocation density, m^{-2})
25.55	0.204	(01 2)	39.93	0.052	6.27×10^{-4}
34.02	0.261	(10 1)	31.73	- 0.069	9.89×10^{-4}
35.11	0.209	(1 0 4)	39.86	0.058	6.29×10^{-4}
37.73	0.219	(1 1 0)	38.26	0.055	6.83×10^{-4}
43.30	0.229	(1 1 3)	37.19	- 0.054	7.23×10^{-4}
48.89	0.272	(2 0 3)	32.08	0.053	9.72×10^{-4}
50.43	0.286	(1 0 2)	30.76	0.071	10.57×10^{-4}
52.49	0.259	(2 0 4)	34.26	0.028	8.5×10^{-4}
57.45	0.264	(1 1 6)	35.04	- 0.059	8.14×10^{-4}
61.09	0.195	(2 1 2)	47.30	0.030	4.50×10^{-4}
66.45	0.245	(2 1 4)	38.70	- 0.015	6.67×10^{-4}
68.19	0.272	(3 0 0)	35.27	- 0.061	8.03×10^{-4}
76.79	0.278	(1 0 10)	36.44	0.054	7.53×10^{-4}
77.17	0.312	(1 1 9)	32.50	0.050	9.46×10^{-4}

Various other parameters of the crystal were calculated from the XRD pattern of α-Al_2O_3: Eu^{3+} (1.5 mole %) and are given in the **Table 1**, where, δ is dislocation density, ε is strain of crystal. Dislocation density is the measure of number of dislocations per unit volume of a crystalline material and is a line defect. Whereas, strain is the measure of deformation, representing the relative displacement between particles in a crystalline material.

Dislocation density (δ) was calculated using the formula $\delta = 1/D^2$, where D is the particle size and the average crystallite dislocation density was found to be 7.83×10^{-4} m^{-2}. Crystallite Strain (ε) was calculated using the following formula:

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

and the average strain was calculated to be 0.0137.

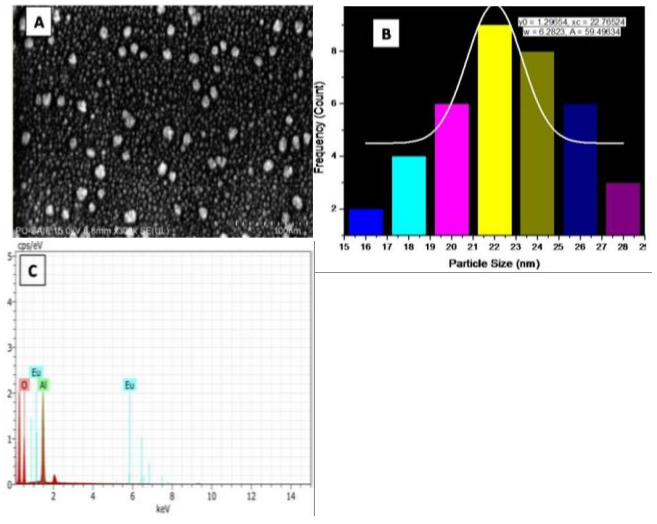

Fig. 3. (a) FE-SEM Micrograph, (b) their particle size distribution and (c) SEM-EDXA of Al_2O_3: Eu^{3+} nanocrystals showing the elemental composition.

SEM and EDXA

To analyze the particle size SEM study was performed confirming the size to be in nano-scale. **Fig. 3(a)** shows the FE-SEM micrograph and particle size distribution corresponding to this electron micrograph. **Fig. 3(b),** the average particle size calculated and was found to be 22.76 nm as is shown in the figure. A qualitative analysis of these nanophosphor particles was made using an Energy dispersive X-ray detector (EDS) and it was found that the samples were composed of Al, O and Eu ions only. **Fig. 3(c)** is the result of SEM-EDXA, showing the presence of Aluminum, Oxygen, and Europium in the nanopowder, which confirms the absence of any other impurities in the prepared powder.

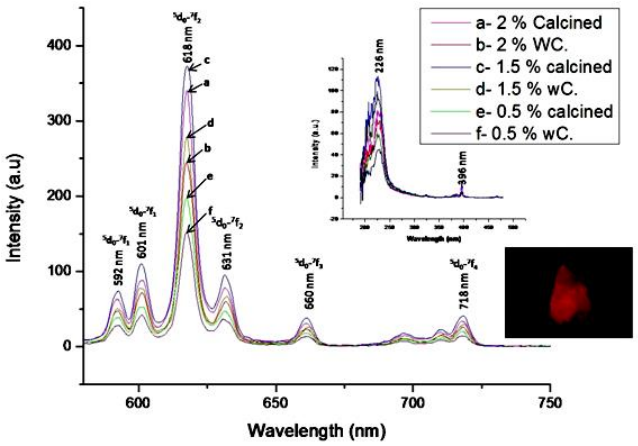

Fig. 4. Photoluminescence spectra of Al_2O_3: Eu^{3+} nanopowder showing emissions at wavelength 618 nm, 592 nm, 601 nm and 631 nm when excited with 226 nm wavelength. Inset graph is the PLE excitation spectrum showing intense band at 226 nm and a weak band at 396 nm.

Photoluminescence study

Photoluminescence emission spectra of Al_2O_3:Eu^{3+} with varying concentrations of dopants from 0.5 to 2.0 mole % with and without calcinations (WC) was recorded at different excitation wavelengths (226 nm, 364 nm and 396 nm) as shown in **Fig. 4**(inset). The main emission band with maximum intensity is at 618 nm, which corresponds to the red color. The other peaks were at 592 nm, 601 nm and 631 nm, corresponding to the range of orange to red region of visible spectra as shown in **Fig. 4**. There were two more bands observed with feeble most intensity, corresponds to 660 nm and 718 nm wavelength. The emission peaks as observed are due to the characteristic electronic transition of Eu^{3+} ions [**12**] as shown in **Fig. 4**.

The dopant concentration is varied from 0.5 % to 2 % and it is clearly demonstrated by the PL emission spectra that with the increase in dopant concentration there is increase in peak intensity up to 1.5 % of dopant concentration. The strongest emission intensity occurs in the sample with Eu^{3+} concentration of 1.5 mole %. And the after concentration quenching occurs when the concentration is larger than 1.5 %.

So it was also observed that with the heating effect (Calcination) there is improvement in luminescence efficiency to a greater extent irrespective of the dopant concentrations. It may be attributed due to the reason that

with heating there will be the creation of shallow color centers in the crystalline material. Moreover, heating also enhances the crystallinity.

The corresponding CIE 1931Chromaticity color space Co-ordinates were shown in the **Fig. 5**. The (x, y) co-ordinates for CIE chromaticity space diagram for 1.5 mole % Eu^{3+} sample without heat treatment were (0.661, 0.337) and that of calcined nanopowder was (0.659, 0.340). All the measurements were carried out at room temperature. There was a slight shift of color coordinates with post annealing as seen in **Fig. 5(a, b)**.

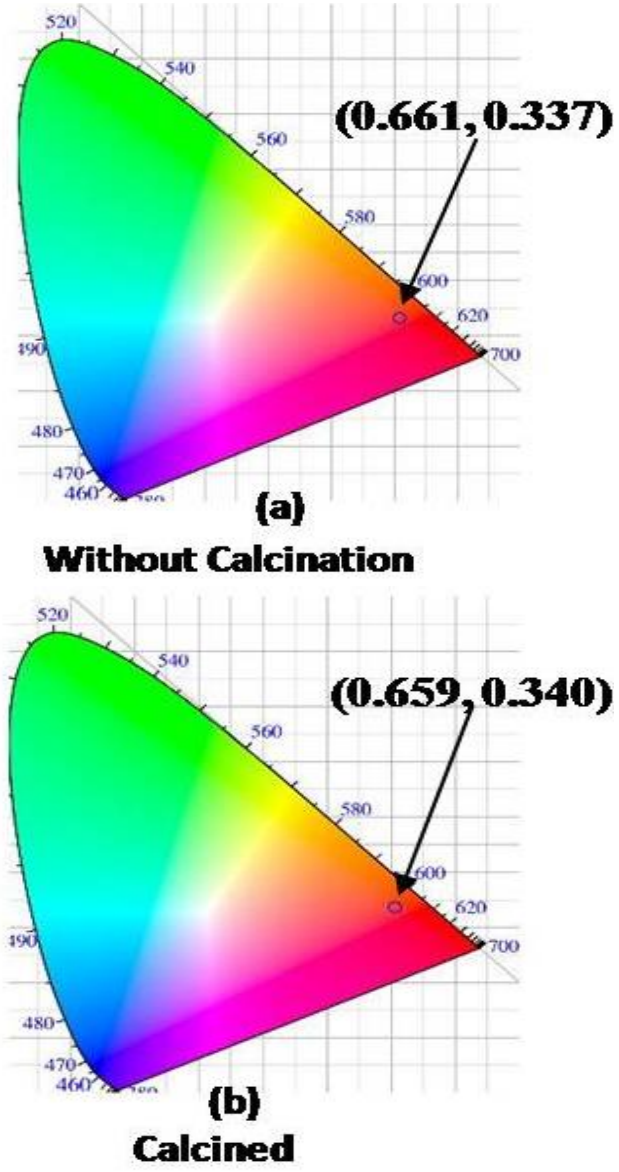

Fig 5. CIE 1931 chromaticity diagram of α-Al_2O_3: Eu^{3+} (1.50 mole %) showing CIE color co-ordinates without calcinations and calcined, respectively.

Application in fingerprint development

Fingerprints were collected with consent from healthy individuals (aged 25-28), free from any skin disorder and any skin disease. The donors were first asked to wash their hands to eliminate any possible contamination and were asked to dry their hands naturally in the normal atmospheric conditions. They were then asked to clench their hands for a minute or two ensuring fair amount of sweat secretion, following which the fingerprints were deposited on various surfaces by gentle pressure on the surface. The donors were then made to deposit their fingerprints on various surfaces such as aluminum foil, stainless steel plate, glass slide, stainless steel bowl (curved surface) and highlighter pen's flat surface. All the experiments were conducted in July to August 2015 in Chandigarh, India, when the temperature and humidity was 30-35 ºC & 40-50 % respectively.

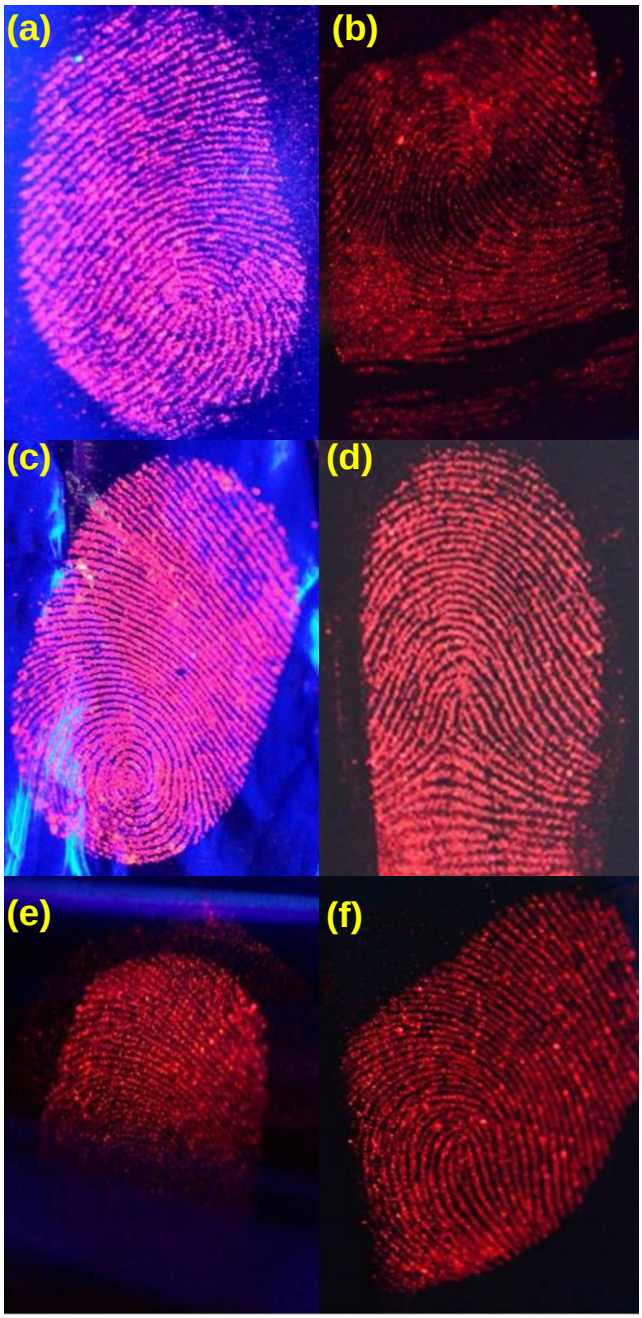

Fig 6. Shows latent fingerprins developed using Al_2O_3: Eu^{3+} nano-powder on Stainless steel plate (a,b), on aluminium foil (c), of glass slide (d), curved surface of stainless steel bowl (e), and highlighter pen (f).

Latent fingerprints were then developed on various surfaces using the prepared Al_2O_3:Eu^{3+} nano-phosphor and illuminated under ultraviolet light (UV) excitation at

254 nm with the most intense 1.5 mole % nanophosphor powder. The fingermarks developed using prepared nano powder was photographed using Nikon DSLR D-7000 Camera with attached Micro lens, and UV filter. The developed fingermarks visualized under UV light were showing the similar results. **Fig. 6** shows fingerprint developed on various surfaces (as mentioned above), photographed under UV light using the synthesized $Al_2O_3:Eu^{3+}$ nanocrystalline powder. Good contrast prints were developed which can be used for the study of comparison of minutiae ridge detail for fingerprint matching in forensic applications. On all the surfaces we got good results. Therefore, it is concluded that $Al_2O_3:Eu^{3+}$ can be a good substitute for ordinary luminescent powders as it has intense luminescence which is highly required for quality fingerprint development. The prepared luminescent powder has very less interference with the background, which is highly required while studying the developed fingerprints.

Conclusion

α-$Al_2O_3:Eu^{3+}$ was successfully prepared using self-propagating solution combustion method. The emission spectra recorded at 226 nm, 364 nm and 396 nm shows the broad absorption band at 618 nm and other band were observed at 592 nm, 601 nm and 631 nm. Two other feebly intense bands were also detected at 660 nm and 718 nm. In the XRD study the major peaks were found at $2\theta = 35.12°$ and 43.30° with intensity ~1600 a.u. having (hkl) corresponds to (1 0 4) and (1 1 3) respectively.

However, their corresponding d-values were 39.86 nm and 37.19 nm respectively. The calculated average particle size of Al_2O_3 doped with Eu^{3+} was ~36.38 nm. From the XRD pattern, it can be suggested that all the diffraction peaks form a single phase and also the phosphor is in nano crystallite form. All their XRD peaks correspond to the α-phase of Alumina, which is in good agreement with the value with reference code 01-074-1081 of α-Al_2O_3. The prepared α-$Al_2O_3:Eu^{3+}$ powder is having a rhombohedral structure with cell parameters *a=b=4.754 Å, c=12.96755 Å* and cell volume (a^3) =254.09$Å^3$. The dislocation density was calculated and found to be 7.83 $x10^{-4}$ m^{-2}, while the average crystallite strain (ε) was 0.01378.The EDXA and XRD analysis was performed and it was observed from both the analysis that there was no impurity in the α-Al_2O_3: Eu^{3+} powder. From the Photo-luminescence (PL) studies it was observed that the intense band position was observed at 618 nm and other less intense bands were also seen at 592 nm, 601 nm, 631 nm, along with two weak bands at 660 nm and 718 nm, when excited at 226 nm. The corresponding CIE 1931 Chromaticity color space Co-ordinates were shown and found to be on orange-red color. The prepared nano-powder was successfully utilized as a fingerprint developing powder via the dusting method, the results showed intense red luminescent developed fingerprints when illuminated under UV excitation, providing clear contrast, making the fingermarks perceptibly clear. In the present study it has been revealed that the synthesized nanocrystalline powder of Al_2O_3: Eu^{3+} is having good potential and can be applied as fingermark developing agent for unhiding the latent fingermarks on various non-porous surfaces than ordinary fingerprinting powder.

Acknowledgements

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