Low temperature synthesis of fluorite-type Ce-based oxides of composition $\text{Ln}_2\text{Ce}_2\text{O}_7$ ($\text{Ln} = \text{Pr}, \text{Nd}$ and Eu): photodegradation and Luminescence studies

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Abstract. In this work, we have studied the structural behavior of Fluortie-type (F-type) Ce-based oxides of compositions $\text{Ln}_2\text{Ce}_2\text{O}_7$ ($\text{Ln} = \text{Pr}, \text{Nd}$ and Eu). F-type oxides can be considered as multi-functional materials due to the deficiency of anions. $\text{Pr}_2\text{Ce}_2\text{O}_7$ (PCO), $\text{Nd}_2\text{Ce}_2\text{O}_7$ (NCO) and $\text{Eu}_2\text{Ce}_2\text{O}_7$ (ECO) were prepared by ethylene glycol-assisted sol–gel method. The structural investigation of these oxides was carried out by Powder XRD and Rietveld refinement. All the materials were found to crystallize in the cubic lattice with space group $Fm\bar{3}m$. Raman spectra of these materials are reliable with their XRD data. The morphology and bandgap energy of all the samples were obtained from SEM and KM plot, respectively. The visible light photocatalytic performance of these oxides was examined against the degradation of methylene blue under ambient conditions. The photoluminescence property of the rare earth ions was also studied, and the color coordinates were calculated using CIE 1931 chromaticity.

Keywords. Defect fluorite; powder X-ray diffraction; Raman spectra; photocatalytic activity; chromaticity.

1. Introduction

The structure of the Fluorite (AO_2) is deemed to be one of the most amenable structures for its ability to build superstructures or derivatives such as A_2O_4 , $\text{AA}'\text{O}_2$, A_4O_8 , and $\text{AA}'\text{BB}'\text{O}_8$.¹ Its geometry can be expounded as a face centered cubic arrangement of the cations with the anions filling all the tetrahedral spaces with $Fm\bar{3}m(225)$ space group. The cations positioned at 4a sites and oxygen ions occupying 8c sites are coordinated by four cations, as shown in Figure 1a. Fluorite (AO_2) with one-eighth of anion deficiency leads to giving $\text{AO}_{1.75}$, $\text{A}_{0.5}\text{B}_{0.5}\text{O}_{1.75}$ and $\text{A}_2\text{B}_2\text{O}_7$ type structures. Oxides with $\text{A}_2\text{B}_2\text{O}_7$ stoichiometry, depending on positions of A, B and O ions in their geometry, often crystallize in weberite, pyrochlore and layered perovskites type structures.

Pyrochlore is a naturally occurring mineral of composition $(\text{Na,Ca})\text{Nb}_2\text{O}_6\text{F/OH}$. Hence, the general formula of pyrochlore can be written as $\text{A}_2\text{B}_2\text{O}_7$ or $\text{A}_2\text{B}_2\text{O}_6\text{X}$ where $\text{X} = \text{OH}, \text{O}$ or F . Pyrochlore oxides (P-type oxides) crystallize in cubic lattice with space group

$Fd\bar{3}m$ (No.227). Since pyrochlores ($\text{A}_2\text{B}_2\text{O}_7$) can be reflecting as oxygen deficient fluorite oxide (F-type oxide, $\text{AO}_{1.75}$), as shown in Figure 1b, it is difficult to confirm whether the material belongs to P-type or F-type oxide. The size difference between cations on A and B sites is supposed to be the driving force to stabilize the pyrochlore structure.² It is perceived that stable $\text{A}_2\text{B}_2\text{O}_7$ compounds are formed when r_A/r_B is in the range 1.2–1.7. Materials whose radius ratio is nearby 1.2 are found to crystallize in defect fluorite while those with ratio close to 1.7 crystallize in ordered pyrochlore.³ It is also reported that the oxides with composition $\text{A}_2\text{B}_2\text{O}_7$, where $\text{A} = \text{Ln}$ ($\text{Ln} = \text{La}, \text{Nd}, \text{Sm}, \text{Eu}, \text{Gd}, \text{Y}$ and Yb) and $\text{B} = \text{Ce}$, are crystallized in C-type super structure with space group $Ia\bar{3}$ (Figure 1c). The C-type structure can be implicit as defect fluorite ($\text{AO}_{1.5}$) that 1/2 of the oxygen atoms of stoichiometric fluorite (AO_2) lattice are lost. The phase stability of F-type and C-type oxides can be explained on the basis of cation coordination number.⁴ The higher and lower size of cation will attribute to higher and lower coordination numbers and tends to stabilize the F-type and C-type phases, respectively. It is also explained that C-type phase for $\text{Ln}_2\text{Ce}_2\text{O}_7$ will exist if $r(\text{Ln}^{3+})/r(\text{Ce}^{4+})$ is smaller than 1.17.⁵ However,

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Figure 1. The structures of (a) Fluorite (F-type), (b) Pyrochlore (P-type) and (c) C-type oxides.

the phase formation can not only depend on the relative radii of the cations³ but also depends on the sample processing conditions.⁶ However, the deficiency of anions in F-type oxides facilitates substitution of a wide range of cations on A and B sites leading to several compositions with diverse properties such as conductive,^{7–9} dielectric,^{10–12} ferroelectric,^{2,13} magnetic^{14–16} and photocatalytic^{17–19} activities.

Rare earth-doped CeO_2 oxides have fascinated due to their remarkable electrical, catalytic, mechanical properties, low thermal conductivity, and high thermal expansion coefficients at high temperatures.^{20–24} It has been investigated that majority of the rare earth cerium oxides have potential to be used as new candidate materials for Thermal barrier coating systems (TBCs).^{25–30} Oxide ion conductivity of F-type rare earth doped CeO_2 or $\text{Ln}_2\text{O}_3\text{--CeO}_2$ due to the oxygen vacancies in its structure is well explored. Recently, Hongsong *et al.*, have reported F-type $\text{Ln}_2\text{O}_3\text{--CeO}_2$ ($\text{Ln}_2\text{Ce}_2\text{O}_7$, $\text{Ln} = \text{La}$ and Gd) photocatalyst for the degradation of methyl orange in the presence of UV light.⁶ But, nowadays researchers are looking for new visible light active photocatalysts with a view to utilize solar light. Hence, we have made an attempt to prepare $\text{Ln}_2\text{Ce}_2\text{O}_7$ ($\text{Ln} = \text{Eu}$, Nd and Pr) by sol-gel method at a lower temperature and study their photocatalytic properties against methylene blue degradation. Low-temperature sol-gel synthesis of $\text{Ln}_2\text{Ce}_2\text{O}_7$ ($\text{Ln} = \text{Eu}$, Nd and Pr) F-type oxides and their photocatalytic activity towards degradation of methylene blue have not been examined.

2. Experimental

Yamamura *et al.*, have prepared $\text{Ln}_2\text{Ce}_2\text{O}_7$ ($\text{Ln} = \text{La}$, Nd , Sm , Eu , Gd , Y and Yb) by solid state method using CeO_2 and Ln_2O_3 as starting materials at 1100°C for 5 h.⁵ In the present study, the sol-gel method was adopted for the first

time to prepare $\text{Ln}_2\text{Ce}_2\text{O}_7$ ($\text{Ln} = \text{Nd}$, Eu and Pr) oxides. Analytical grade rare earth oxides (Nd_2O_3 , Eu_2O_3 , Pr_6O_{11}), $(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$, aq NH_3 , citric acid and ethylene glycol were used as starting materials, as received. All rare earth oxides were sourced from Sigma Aldrich, USA and rest of the chemicals from S D Fine-Chem Limited, India. The procedure to prepare $\text{Pr}_2\text{Ce}_2\text{O}_7$ is shown in Figure 2 in the form of a flow chart.

The room temperature X-ray diffractograms of NCO, ECO and PCO were recorded using Rigaku MiniFlex 600 X-ray diffractometer ($\text{Cu K}\alpha$, $\lambda = 1.5406\text{\AA}$, $2\theta = 10 - 80^\circ$, with a step size of $(2\theta) = 0.02^\circ$ and scan step time of 0.15 s) for the phase confirmation. Raman spectra were recorded using a 632.81 nm line from a He–Ne laser and the scattered light was analyzed using HORIBA JOBIN YVON HR800. The laser was focused on a spot of $\sim 3\mu\text{m}$ and a 10X lens was used for the collection of back-scattered Raman signal. The SEM images were recorded on the HITACHI SU-1500 variable pressure scanning electron microscope (VP-SEM). JASCO V-650 UV-Vis spectrophotometer was used for UV-Vis diffuse reflectance spectra (DRS) measurements in the range 200–800 nm. BaSO_4 was used as the reflectance standard. The photoluminescence spectra were recorded with a JASCO FP-8500 spectrofluorometer. Interactive CIE software (CIE coordinate calculator) is used to find out the color coordinates of the samples.

The photocatalytic activities of ECO, NCO and PCO catalysts were carried out in HEBER Visible Annular Type Photo reactor, model HVAR1234 (Heber Scientific, Chennai, India). It consists of a cylindrical quartz double walled tube with provision for circulation of water. A 300 W tungsten lamp (380–840 nm) is placed inside the quartz tube. The temperature of the quartz tube was maintained at $27\text{--}30^\circ\text{C}$ by circulating cold water using a pump. The reaction mixture was prepared by adding 50 mg of the photocatalyst to 50 mL of MB aqueous solution of concentration $10^{-5}\text{ mol L}^{-1}$. A blank experiment (dye solution without catalyst) was also carried out. The reaction vessel is a glass tube of length $\sim 37\text{ cm}$ and diameter 2.5 cm. The distance between the lamp and the reaction vessel was $\sim 5\text{ cm}$. Provision was made to place 10 reaction vessels simultaneously. About 50 mL of the reaction mixture was placed in the reaction vessel and the suspension

Figure 2. Preparation procedure of $\text{Pr}_2\text{Ce}_2\text{O}_7$.

was stirred in dark for 1 h to attain adsorption equilibrium. Subsequently, all reaction vessels were irradiated with visible light. The air was bubbled into the reaction vessels. About 4 mL of the reaction mixture was collected at regular intervals and centrifuged to remove the catalyst particles. The supernatant solution was subjected to optical absorption measurements at 664 nm on a UV-Visible spectrometer. The degradation amount of dyes was calculated from the equation,

$$D = \left(\frac{C_0 - C}{C_0} \right) \times 100\% \quad (1)$$

Here, D is the percentage of degradation, C_0 is initial concentration of dye and C is the concentration at time t .

Controlled photocatalytic activity experiments using different radical scavengers (ammonium oxalate, benzoquinone and isopropanol as scavengers for photogenerated holes, superoxide radical and hydroxyl radical species, respectively)

were also carried out similar to the above photocatalytic oxidation of MB dye but with the addition of radical scavengers to the reaction system.

3. Results and Discussion

Yamamura *et al.*, have synthesized $\text{Nd}_2\text{Ce}_2\text{O}_7$ and $\text{Eu}_2\text{Ce}_2\text{O}_7$ by solid state method at 1100°C for 5 h.⁵ To our knowledge, the method of preparation of $\text{Pr}_2\text{Ce}_2\text{O}_7$ is not reported. We have prepared $\text{Pr}_2\text{Ce}_2\text{O}_7$, $\text{Nd}_2\text{Ce}_2\text{O}_7$ and $\text{Eu}_2\text{Ce}_2\text{O}_7$ by ethylene glycol-assisted sol-gel method. The precursors of all the samples were calcined at 200, 300, 400, 500, 600 and 700°C , separately for 2 h each and subjected to powder XRD measurements. The room temperature powder XRD patterns of PCO, NCO and ECO sintered at the above mentioned temperatures are shown in Figure 3. It is observed that PCO heated at

Figure 3. Powder X-ray diffraction patterns of PCO, NCO and ECO along with their observed and calculated powder patterns.

200°C gave a broad background without any diffraction features indicating the amorphous nature of the sample. The diffraction lines are observed for PCO sintered at or above 300°C. Thus, the crystallization temperature of PCO is around 300°C. The XRD patterns of PCO are comparable with PrCeO_{3+x} data [JCPDF: 52-1435] and free from impurities. The crystallization of NCO and ECO, starts at 400°C and completely crystallized at or above 500°C. The powder XRD patterns of NCO are akin to reported $\text{Nd}_2\text{Ce}_2\text{O}_7$ [JCPDF 75-0156]. The XRD profile of ECO is also similar with NCO. However, the studies on structural characterization of $\text{Nd}_2\text{Ce}_2\text{O}_7$ and $\text{Ce}_{1-x}\text{Nd}_x\text{O}_{2-\delta}$ ($0 < x < 1$)^{31–35} have revealed that $\text{Nd}_2\text{Ce}_2\text{O}_7$ phase is on the border between the F-type and C-type structure. Bevan *et al.*, reported that C-type phase was obtained at higher temperature whereas F-type phase was preferred at lower temperature in 50% rare earth doped CeO_2 .³⁵ According to Yamamura *et al.*, if the ionic radius ratio of $r(\text{Ln}^{3+})/r(\text{Ce}^{4+})$, is smaller

than 1.17, then the C-type phase will be formed.⁵ The ionic radius ratios of $r(\text{Pr}^{3+})/r(\text{Ce}^{4+})$, $r(\text{Nd}^{3+})/r(\text{Ce}^{4+})$ and $r(\text{Eu}^{3+})/r(\text{Ce}^{4+})$ are 1.161, 1.154 and 1.10, respectively. These values suggest that the C-type phase for PCO, NCO and ECO. The C-type phase is characterized by super structure lines corresponding to (2 1 1), (1 2 3), (4 1 1), (3 3 2), (1 3 4) and (2 2 5) planes [JCPDF 46-0508]. However, in the present investigation, the absence of the C-type superstructure diffraction peaks in their XRD patterns support the view that PCO, NCO and ECO are crystallized in F-type lattice. Hence, it should be noted that the numerical value of radius ratio r_A/r_B is used only as a broad guide line in view of some exceptions.³ Thus, based on the XRD profiles (Figure 3), it can be assumed that all the samples in the present investigation are formed in defect fluorite (F-type) phase with space group $Fm\bar{3}m$.

The structural investigation of PCO, NCO and ECO by Rietveld method using Fullprof.2k. was carried out

Table 1. The atomic positions (or Wyckoff position) and fractional coordinates of the atoms.

Atoms in NCO/ECO/PCO	Wyckoff position	<i>x</i>	<i>y</i>	<i>z</i>
Nd/Eu/Pr	4 <i>a</i>	0	0	0
Ce	4 <i>a</i>	0	0	0
O	8 <i>c</i>	0.25	0.25	0.25

Figure 4. The shift in the d-lines of PCO, NCO and ECO.

to confirm the type of lattice. The structural parameters of $\text{Nd}_2\text{Ce}_2\text{O}_7$ are given as initial parameters for the refinement of XRD data of PCO, NCO and ECO [Crystallography open database ID 1541466]. The XRD pattern of all these oxides can be satisfactorily fitted within the space group $Fm\bar{3}m$. The observed and calculated powder profiles of PCO, NCO and ECO are given in Figure 3. It is perceived from the Rietveld refinement that all the samples investigated in the present investigation are found to crystallize in the cubic lattice (F-type) with space group $Fm\bar{3}m$. The obtained lattice parameters for PCO, NCO and ECO are 5.49, 5.44 and 5.40 Å, respectively. The atomic positions, including fractional coordinates of the atoms are given in Table 1. The decrease in cell lengths for PCO to ECO depends on their respective ionic radius of rare earth ions. The change in the ionic radius of these ions will effect the 2θ (or d-lines) position in the XRD patterns. As the ionic radius of Eu^{3+} is lower compared to Pr^{3+} , the peak around 28° of ECO is shifted towards higher 2θ side than that of PCO, as shown in Figure 4. According to Bragg's law, the increase (or decrease) in *d* value should result in the decrease (or increase) in lattice parameters.

The F-type phase for present systems is further endorsed by their Raman spectra. Generally, Raman

Figure 5. Raman spectra of PCO, NCO and ECO.

spectrum is employed to ascertain the solid solution phase and evoking the local structure of the oxides. Figure 5 shows the Raman spectra of PCO, NCO and ECO. Fluorite-type oxide CeO_2 shows characteristic Raman peak at 465 cm^{-1} which belongs to F_{2g} mode. When the rare earths are doped into CeO_2 , the changes in its band positions and line width, along with defect-induced additional bands in their spectra, are expected due to the formation of oxygen vacancies. The Raman spectra of PCO and NCO samples are characterized by bands in the region of $250\text{--}260\text{ cm}^{-1}$, $360\text{--}370\text{ cm}^{-1}$, $455\text{--}475\text{ cm}^{-1}$ and $580\text{--}595\text{ cm}^{-1}$. The Raman spectrum of ECO is characterized by two less intense broad bands at 437 and 576 cm^{-1} . From the observed bands of these samples, it is evident that local structures of these oxides are similar as that of oxygen-deficient fluorite-type oxides.⁵ The observed regular right shift of Raman bands from ECO to PCO toward higher wave number, as shown in Figure 5, can be ascribed to lower ionic radius of Eu^{3+} (1.07 Å) as compared to Pr^{3+} (1.14 Å). The lower ionic radius can lead to the increase in-force constant, which can cause an increase in its vibrational frequency.⁶

The photocatalytic performances of the as-prepared ECO, NCO and PCO oxides were evaluated by following the degradation MB pollutant in water under visible

Figure 6. KM plot of PCO, NCO and ECO.

light irradiation ($380 \text{ nm} < \lambda < 840 \text{ nm}$) in aerated conditions. Typically, a photocatalytic dye degradation process is initiated by illumination of light energy equal to or greater than the bandgap energy of catalyst, to create the charge carriers (electron-hole pairs), which assist in catalysis by producing hydroxyl/superoxide radicals to degrade the dye molecules. Therefore, the bandgap energy (E_g) of the catalysts plays a significant role in the dye degradation process. The bandgap energy of the as-prepared oxides was obtained from the plot of KM ($(Kh\nu)^{1/2}$) versus $h\nu$, where K is reflectance transformed according to Kubelka-Munk [$K = (1 - R)^2 / 2R$, where R is reflectance] and $h\nu$ is photon energy. Extrapolation of linear portion of the plot to $(Kh\nu)^{1/2} = 0$ (i.e., onto the x-axis) gives an estimation of bandgap energy (Figure 6).³⁶ The E_g for PCO, NCO and ECO is found to be 1.55, 2.66 and 3.01 eV, respectively. The lower bandgap energy may lead to the higher photocatalytic activity. This phenomenon is always not true because the photocatalytic activity of catalyst not only depends on bandgap energy but also on crystallinity of the sample, crystallite size, surface area, rate of electron-hole pair generation and recombination, etc.

Prior to the irradiation, the MB in the presence of as-prepared oxides is kept in the dark chamber to attain the adsorption-desorption equilibrium. The degradation of MB is measured by following the changes in maximum absorption in their UV-visible spectra at 664 nm. Figure 7 shows the temporal change in concentration of MB dye in the presence of LnCO (Ln = Pr, Nd and Eu) catalyst for 180 min of the light irradiation along with the blank experiment. The maximum adsorption on the surface of all the catalysts during the blank reaction is in the range of 6–8%. As shown in Figure 7, in the absence of catalyst, the decomposition of dye

Figure 7. The temporal changes in concentration of MB in the presence of PCO, NCO and ECO.

is about 24%. On the other hand, the degradation of MB in the presence of PCO, NCO and ECO is 85, 77 and 56%, respectively. This result shows that direct photolysis of MB is negligible under the present experimental conditions, while the photodegradation in the presence of LnCO is considerable. Along with bandgap energy, the photocatalytic activity of the material also depends on surface structure and crystallite size of the material which influence the dye adsorption capability followed by photoactivity. The structural morphology of all as-prepared materials seem to be large needle type crystals with considerable agglomeration (Figure 8) and the average crystallite size of the PCO, NCO and ECO calculated from Debye Scherrer equation is 18, 11 and 34 nm, respectively. The material with lower crystallite size has more adsorption property because of more surface area. As per the obtained crystallite size, the dye adsorption on NCO would be expected to be more. But, the adsorption of dye on all the catalysts is nearly same. Hence, the higher photocatalytic activity of PCO catalyst compared to the rest of the oxides in the degradation of MB can be attributed to its lower bandgap energy.

The kinetic plot of $\ln(C/C_{eq})$ versus time of ECO, NCO and PCO gave a straight line suggesting a pseudo first order kinetics (Langmuir-Hinshelwood model) for MB degradation (Figure 9).³⁷ The equation is,

$$\ln(C/C_{eq}) = -kt \quad (2)$$

where, C is the concentration of MB at regular interval of irradiation time and C_{eq} is the concentration of MB after attaining adsorption-desorption equilibrium during the dark reaction. The rate constants (k) for the reaction are obtained by the slope of the linear line. The half-life

Figure 8. SEM images of PCO, NCO and ECO.

Figure 9. Kinetic study in the presence of PCO, NCO and ECO catalyst.

time ($t_{1/2}$) calculated from the equation:

$$t_{1/2} = \frac{\ln 2}{k} \quad (3)$$

The obtained kinetic parameters are given in Table 2.

Table 2. The kinetic parameters (k , $t_{1/2}$) for MB photocatalytic reactions in the presence of PCO, NCO and ECO.

Catalyst/Dye	$k(\text{min}^{-1})$	$t_{1/2}(\text{min.})$	R^2
PCO/MB	1.12×10^{-3}	26.8	0.988
NCO/MB	0.82×10^{-3}	36.7	0.976
ECO/MB	0.51×10^{-3}	58.9	0.978

As discussed above, the photogenerated electron-hole pairs play a vital role in the photocatalytic dye degradation. The generated electron-hole pairs would migrate to the catalyst surface to react with adsorbed H_2O and O_2 and produce hydroxyl and super oxide radicals, respectively. These radicals subsequently degrade the dye molecules into harmless inorganic molecules such as CO_2 and H_2O .³⁶ To unravel the participation of reactive species in the photocatalytic process, competitive reactions using radical scavengers were applied. The hole, hydroxyl and superoxide radicals formation during MB degradation has been experimentally corroborated using radical quenchers. Ammonium oxalate (AO), iso-propyl alcohol (*i*-PrOH), and benzoquinone (BQ) were used to

Figure 10. Variation of concentration of MB in the presence of quenchers IPA, BQ and AO and PCO, NCO and ECO catalysts.

quench the holes (h^+), hydroxyl ($\bullet OH$), and superoxide ($O_2^{\bullet -}$) radicals, respectively.^{36,38} The photodegradation of MB was carried out by adding individually 2 mM of AO, 2 mM of *i*-PrOH, and 2 mM of BQ to the PCO catalyst under identical conditions. As shown in Figure 10, the MB degradation is reduced noticeably by the addition of quenchers. The degradation percentages of MB after the addition of AO, *i*-PrOH and BQ quenchers are 40, 54 and 67%, respectively. Based on these results, it is believed that holes (h^+), hydroxyl ($\bullet OH$) radicals, and super oxide ($O_2^{\bullet -}$) radicals play a pivotal role in the photocatalytic degradation of MB. Therefore, the possible mechanistic pathway of photocatalytic degradation of MB dye can be inferred as follows:

The chemical stability and reusability of the photocatalyst are essential issues for practical and marketable applications. The catalyst, PCO, is recovered after first cycle of photodegradation of dye and the same is mixed with fresh dye solution for second cycle of photoactivity experiment. The process is repeated three times. The results of cyclic runs of photodegradation of MB are shown in Figure 11. It is remarkable to notice that even in the third cycle of degradation, the photoactivity of

Figure 11. Cyclic runs in photocatalytic degradation of MB in the presence of PCO.

PCO is almost the same compared to first cycle. These results illustrated that PCO is a novel, high-response visible light photocatalyst and can be reused efficiently for at least three times. Thus, it may be considered as potential visible light active catalyst.

The rare earth ion-containing materials exhibit photoemission and absorption properties because of electric and magnetic optical transitions within their 4f states. Though, f-f transitions are Laporte forbidden, due to crystal field surrounding the rare earth ion, the selection rules are relaxed, and absorption/emission are observed. An attempt is made to study photoluminescence properties of PCO, NCO and ECO. Among these, only ECO showed the luminescence property. The other two materials have not shown any emission peaks at the reported excitation wavelengths of Nd^{3+} and Pr^{3+} .

The ground state of Eu^{3+} is 7F_0 . It gives emission lines accompanying with radiative relaxations from 5D_0 level to its low-lying multiplets, 7F_j ($j = 0$ to 6). Figure 12 depicts the excitation and emission spectra of all the samples. The excitation spectra of ECO monitored for the emission at 612 nm are shown in Figure 12a. This spectrum shows two peaks at 394 and 465 nm corresponding to $^7F_0 \rightarrow ^5L_6$ and $^7F_0 \rightarrow ^5D_2$ transitions, respectively, of Eu^{3+} .³⁹ Figure 12b shows the emission spectrum of ECO, monitored for the excitation at 465 nm. The emission bands are observed at 580, 593, 612 and 630 nm, and are assigned to electronic transitions $^5D_0 \rightarrow ^7F_0$, $^5D_0 \rightarrow ^7F_1$, $^5D_0 \rightarrow ^7F_2$ and $^5D_0 \rightarrow ^7F_3$ of Eu^{3+} , respectively. Figure 13 shows the Commission International de l'Eclairage (CIE) x-y color coordinate diagram for ECO. The color coordinates (x, y) indicate the color of any phosphor material or light source in color space. The emission spectrum of the

Figure 12. (a) The excitation (at $\lambda_{\text{em}} = 612 \text{ nm}$) and; (b) emission spectra (at $\lambda_{\text{ex}} = 465 \text{ nm}$) of ECO.

Figure 13. CIE Chromaticity Diagram of ECO.

ECO phosphor is converted to the CIE 1931 chromaticity diagram using its photoluminescence data and CIE coordinate calculator. The obtained color coordinates give the information that ECO phosphor is appropriate for green component in LED. The color purity of a phosphor can be calculated using the equation,

$$\text{Colorpurity} = \frac{\sqrt{(x - x_i)^2 + (y - y_i)^2}}{\sqrt{(x_d - x_i)^2 + (y_d - y_i)^2}} \times 100\%$$

where, (x, y) and (x_i, y_i) are the color coordinates of the emission light and CIE white illuminate (0.33, 0.33), respectively, and (x_d, y_d) are chromaticity coordinates of the dominant wavelength points. The (x, y) and (x_d, y_d) values for ECO is (0.304, 0.496) and (0.277, 0.711),

respectively. The selective color of light depends on the color purity of the phosphor material. The color purity for the ECO phosphor is found to be 19%. In general, the phosphor materials with low and high color purity are preferred as white and monochromatic light sources, respectively. Hence, the ECO can be considered as a phosphor which may be used in the white light source.

4. Conclusions

The results of the present work show that $\text{Ln}_2\text{Ce}_2\text{O}_7$ ($\text{Ln} = \text{Pr}, \text{Nd}$ and Eu) are formed in defect fluorite (F-type) phase with cubic lattice and space group $Fm\bar{3}m$. The obtained lattice parameter for PCO, NCO and ECO are 5.49, 5.44 and 5.40 Å, respectively. The higher cell length of PCO is attributed to the ionic radius of Pr^{3+} ion. Raman bands of the these materials, support that structure of these oxides is similar to that of oxygen-deficient fluorite-type oxides. The regular right shift of Raman bands from ECO to PCO toward higher wave number was explained based on the ionic radius of rare earth ions. The bandgap energy of the materials for PCO, NCO and ECO are obtained as 1.55, 2.66 and 3.01 eV, respectively. The photocatalytic behavior of these oxides is explained on the basis of bandgap energy and crystallite size of the material. The higher photocatalytic activity for PCO can be endorsed to its lower bandgap energy. Mechanistic photodegradation study in the presence of these catalysts is investigated using radical quencher and possible mechanism is given. The catalyst PCO is chemically stable and can be reused more than three times for MB dye degradation and the photocatalytic activity results of PCO illustrates that it may be a potential visible light active catalysts. The color coordinates and color purity of ECO is determined

by using CIE coordinate calculator. The color purity for the ECO phosphor is found to be 19% and it may be used as a phosphor for white light source.

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