



Precipitation Synthesis of Cerium Oxide Nano Pigment

Iis Nurhasanah^{1*}, Yayuk Astuti², Pandji Triadiyaksa¹

¹Department of Physics, Faculty of Science and Mathematics, Universitas Diponegoro, Semarang 50275, Indonesia

²Department of Chemistry, Faculty of Science and Mathematics, Universitas Diponegoro, Semarang 50275, Indonesia

*E-mail: nurhasanah@fisika.fsm.undip.ac.id

Article History

Received: 21 October 2022; Received in Revision: 4 March 2023; Accepted: 12 March 2023

Abstract

Pigments as colorants have a wide range of industrial applications. Commonly used pigments contain toxic elements. This study proposes cerium oxide as an alternative colorant to replace toxic pigments. Metal doping in cerium oxide can alter the color and properties of cerium oxide. Pure cerium oxide and iron-doped cerium oxide nanopowders were synthesized using the precipitation method. The x-ray diffraction and scanning electron microscope analysis revealed the formation of cubic fluorite structures of cerium oxide composed of spherical particles. The nanopowder of pure cerium oxide is pale yellow, while iron-doped cerium oxide is brick red. The N₂ adsorption-desorption measurement showed the mesoporous nature of both cerium oxide nanopowders. Incorporating iron into cerium oxide reduced crystallite size and increased surface area. Moreover, UV-Vis spectroscopy analysis indicated that iron doping significantly improves the UV absorption property and increases the bandgap energy of cerium oxide nanopowders. The results demonstrate the cerium oxide nanopowder synthesized using precipitation potential as a nano pigment.

Keywords: Cerium oxide, pigment, powder, precipitation, optical properties

1. Introduction

Utilizing nanomaterials in a wide range of industrial applications has provided many advantages. Nanomaterials application, such as nanopowder, improves many pigment properties and produces many purposes and functional pigments with high performance in their powder form. Only a few inorganic pigments in the red to yellow range with high performance, such as cadmium sulfoselenide, lead molybdate, and bismuth vanadate. However, pigments' toxicity and environmental risk are severe concerns in developing pigments (Wu et al., 2021).

Cerium oxide (CeO₂) nanopowder has a pale yellow color and is one of the important inorganic pigments with high-temperature stability, high chemical resistance, and nontoxic (Gonzaga et al., 2020). The colour hue of CeO₂ nanopowder-based pigment can be controlled by the incorporation of other lanthanide elements, such as praseodymium (Gonzaga et al. 2020), terbium (Sulcova et al., 2012), europium (Stojmenovi et al., 2015), or transition metal elements such as zirconium (Joseph, et al., 2020), Nickel (Miri et al., 2020), iron (Fe) (Olegario et al., 2014), and cobalt (Araujo et al., 2011). Iron is a transition

metal element in the first ferric oxide (Fe₂O₃) nontoxic conventional inorganic red pigments. The iron incorporation into the CeO₂ lattice changed the yellow of CeO₂ to a reddish-orange colour (Olegario et al., 2014). However, few studies have examined the potential of iron-doped CeO₂ nanopowder as a non-toxic pigment.

Various methods have been used to synthesize CeO₂. Precipitation is a more suitable method for preparing nanopowder than other methods, such as the Pechini method (Araujo et al., 2011), solid-state reaction (Bayyapagari et al., 2018; Kumar & Hymavathi, 2017; Olegario et al., 2014), self-propagating method (Micovic et al., 2019; Stojmenovic et al., 2015). These methods commonly require heat treatment at high temperatures (>500°C) for a long duration, which induces excessive particle growth. The present study aims to synthesize CeO₂ and CeO₂:Fe nanopowders and explore their potential as environmentally friendly pigments. CeO₂ and CeO₂:Fe nanopowders were synthesized using precipitation method, followed by heat treatment at a temperature of 500°C. Iron doping with a molar ratio of 0.05 concentration was chosen as a moderate

doping level, which is expected to get a red pigment.

2. Methodology

2.1. Materials

Cerium nitrate hexahydrate ($\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, $\geq 99,9\%$), Ferric nitrate nonahydrate ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, $\geq 99,9\%$) were purchased from Sigma-Aldrich Co., Ltd. Ammonium hydroxide 25%, isopropanol, and ethanol were purchased from Merck & Co., Inc.

2.2. Synthesis of CeO_2 and $\text{CeO}_2\text{:Fe}$ nanopowders

Pure CeO_2 and $\text{CeO}_2\text{:Fe}$ nanopowders were synthesized using the precipitation method. The solution of $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ was prepared in 42 mL of mixed isopropanol and demineralized water to obtain pure CeO_2 nanopowder. The ammonium hydroxide solution was dropped until constant pH of 10 was attained. The same procedure was used to synthesize $\text{CeO}_2\text{:Fe}$, except by adding $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ into $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ solution so that the molar ratio is 0.05. The precipitation process was carried out at room temperature. The obtained precipitates were washed and filtered, then dried at 100°C . The calcination at a temperature of 500°C was subjected to dried precipitate for 3 hours.

2.3. Characterization

The structural properties of CeO_2 and $\text{CeO}_2\text{:Fe}$ nanopowders were examined using an X-ray diffractometer (PANalytical Xpert Pro). The $\text{Cu K}\alpha$ radiation with a wavelength of $1,5406 \text{ \AA}$ was employed as an X-ray source that activated at 30 mA and 40 kV. The XRD data were recorded at 2θ in the 10 to 90° with step size 0.026° . The XRD data were used to estimate crystallite size and strain of nanopowder using the size-strain-plot (SSP) method described by Eq. 1 (Kumara et al., 2017).

$$(d_{hkl}\beta_{hkl} \cos \theta)^2 = \frac{K}{D_{XRD}} (d_{hkl}^2 \beta_{hkl} \cos \theta) + \left(\frac{\varepsilon}{2}\right)^2 \quad (1)$$

Remark:

β_{hkl} : full width at half of the maximum (FWHM) of diffraction peak

d_{hkl} : inter-planar spacing

$K = 3/4$ for a spherical particle

θ : diffraction angle

D_{XRD} : crystallite size

ε : the lattice strain

$h, k, \text{ and } l$: Miller's index

The lattice parameter was calculated by using Eq. 2.

$$a = \frac{\lambda \sqrt{h^2 + k^2 + l^2}}{2 \sin \theta} \quad (2)$$

Remark:

λ : the wavelength of X-ray.

The morphology and composition of CeO_2 and $\text{CeO}_2\text{:Fe}$ were investigated by a scanning electron microscope (SEM, JEOL JSM 6360) integrated with energy-dispersive X-ray spectroscopy (EDS). EDS was used to analyze atomic composition in CeO_2 and $\text{CeO}_2\text{:Fe}$.

The N_2 adsorption-desorption measurement (Quantachrome instrument) is a versatile method to characterize porous solids and fine powders. The N_2 adsorption-desorption isotherm was conducted at a temperature of 77 K to analyze the pore size of CeO_2 and $\text{CeO}_2\text{:Fe}$ nanopowders. Then, specific surface area (SSA) and pore size were calculated using multipoint the Brunauer-Emmett-Teller (BET) method and Barrett-Joyner-Halenda (BJH) method (Thommes et al., 2015). Furthermore, the SSA was used to calculate particle size using Eq. 3 (Nadjia et al., 2018).

$$D_{SSA} = \frac{6}{\rho \times SSA} \quad (3)$$

Remark:

ρ : the theoretical density of CeO_2 (g/cm^3).

The optical properties of CeO_2 and $\text{CeO}_2\text{:Fe}$ were analyzed by UV-Vis spectrophotometer (Shimadzu 1240). The absorbance spectra of CeO_2 and $\text{CeO}_2\text{:Fe}$ were measured in wavelength $200 - 800 \text{ nm}$. Tauc's plot method (Eq. 4) was utilized to determine bandgap energy.

$$(\alpha h \nu)^n = B(h \nu - E_g) \quad (4)$$

Remark:

h : Planck constant

ν : frequency

B : a constant

E_g : bandgap energy

$n = 2$ for direct transition

α : absorption coefficient

The absorption coefficient was evaluated from UV-Vis absorbance spectra using Eq. 5.

$$\alpha = \frac{2.303 \times 10^3 A \rho}{lc} \quad (5)$$

Remark:

A : absorbance

ρ : the density of CeO_2 (g/cm^3)

l : the optical path (1 cm)

c : the suspension concentration of CeO_2 nanopowder.

The refractive indices (n) of CeO_2 and $\text{CeO}_2\text{:Fe}$ was calculated using Eq. 6 (Soni et al., 2021).

$$\frac{n^2 - 1}{n^2 + 2} = 1 - \frac{\sqrt{E_g}}{20} \quad (6)$$

3. Results and Discussion

3.1. Structure of CeO_2 and $\text{CeO}_2\text{:Fe}$ nanopowders

The obtained CeO_2 and $\text{CeO}_2\text{:Fe}$ nanopowder prepared by the precipitation method is shown in Figure 1. As can be seen, the CeO_2 nanopowder was pale yellow. The doping 5 wt% iron causes the pale yellow color of CeO_2 to turn to brick red. The $\text{CeO}_2\text{:Fe}$ pigments prepared by solid-state reaction exhibited a brown to reddish-orange color (Olegario, et al., 2014). The other previous study reported that the 15 mol% mol Fe- CeO_2 designed by solvothermal was light brown (Jiang, et al., 2020). As a result, the color of $\text{CeO}_2\text{:Fe}$ depends on doping concentration and preparation method.

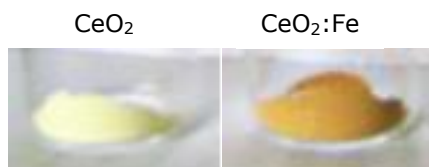


Figure 1. Photograph of CeO_2 and $\text{CeO}_2\text{:Fe}$ nanopowders

The XRD patterns of CeO_2 and $\text{CeO}_2\text{:Fe}$ nanopowders are shown in Figure 2 (a). CeO_2 and $\text{CeO}_2\text{:Fe}$ nanopowders had similar patterns with many diffraction peaks at 2θ : 28.43, 32.95, 47.52, 56.18, 58.99, 69.29, 76.64, 78.98, and 88.46°. The observed peaks corresponded to crystal planes of (111), (200), (220), (311), (222), (400), (331), (420), and (422) for the cubic fluorite structure of cerianite (JCPDS:34-0934). The sharp diffraction peaks with high intensity confirmed the high crystallinity of CeO_2 nanopowder. It also saw no additional diffraction peaks of other phases identified in CeO_2 and $\text{CeO}_2\text{:Fe}$ diffraction patterns. The result agreed with a previous report (Soni et al., 2021; Jiang et al., 2020). Therefore, the precipitation method propers for forming CeO_2 and $\text{CeO}_2\text{:Fe}$ nanopowders at a temperature of 500°C.

In addition, the diffraction peaks of $\text{CeO}_2\text{:Fe}$ possessed lower and broader intensity than the pure CeO_2 nanopowder and shifted to higher 2θ . This result indicates that Fe^{3+} ions with a smaller radius (0.645 Å) were successfully substituted into the lattice of Ce^{4+} ions with a larger radius of 0.97 Å. It is supported by the calculated lattice constant of $\text{CeO}_2\text{:Fe}$ (5.4090 Å), lower than the CeO_2 lattice constant (5.4208 Å). A similar result was described for $\text{CeO}_2\text{:Fe}$ preparation by hydrothermal (Jiang, et al., 2020) and Fe-Ce mixed oxide prepared by co-precipitation method (Bao, et al., 2017). Commonly, the substitution element with a radius smaller than CeO_2 would shift the diffraction peaks of CeO_2 to higher 2θ (Soni et al., 2021; Joseph et al., 2020). Since the calculated lattice constant of $\text{CeO}_2\text{:Fe}$ is lower than CeO_2 , then it is expected that the lattice experiences compressive stress.

The broadening x-ray diffraction peaks are attributed to crystallite size and microstrain in the crystalline material. The x-ray diffraction data of CeO_2 and $\text{CeO}_2\text{:Fe}$ were further analysed using the size strain plot (SSP) method. The SSP method considered a crystallite size and microstrain contribution to the diffraction peaks profile. The widened x-ray diffraction peaks reveal that CeO_2 and $\text{CeO}_2\text{:Fe}$ comprise nanometric-size crystallites. This phenomenon is supported by the determination of crystallite size using the SSP method. Figure 2(b) shows the SSP graph of CeO_2 and $\text{CeO}_2\text{:Fe}$ nanopowders. The experimental x-ray diffraction data (marked with a solid circle) are located along a straight line of the SSP graph. The correlation coefficients (R^2) are close to 1, implying that experimental x-ray diffraction data fit well with SSP analysis.

The average crystallite size and the lattice strain obtained from the slope and the intercept of the straight-line graph of SSP are represented in Table 1. The insertion of iron ions with a small radius into the cerium lattice reduced the crystallite size of the CeO_2 nanopowder from 6.3 to 5.3 nm. A similar phenomenon is found in other CeO_2 prepared by hydrothermal (Radovic, et al., 2013) and solvothermal (Jiang et al., 2020). Meanwhile, iron insertion increased the strain in our CeO_2 from 0.01 to 0.02. The increasing strain in CeO_2 can be correlated to a reduction in crystallite size and a reduction in crystal regularity in the CeO_2 lattice due to iron insertion. This explanation is likely attributed to the lower diffraction peaks intensity of $\text{CeO}_2\text{:Fe}$ than pure CeO_2 , as shown in figure 2(a).

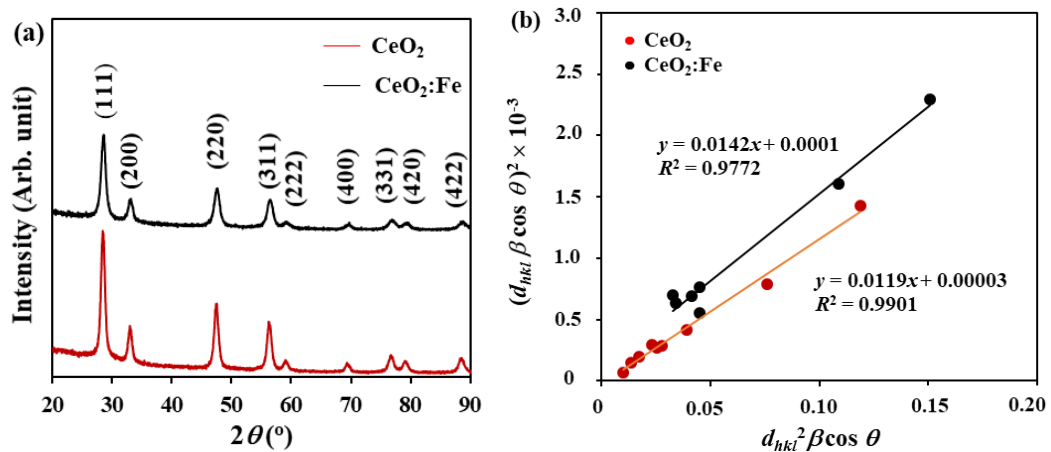


Figure 2. (a) XRD pattern and (b) SSP method of CeO_2 and $\text{CeO}_2\text{:Fe}$ nanopowders

Tabel 1. The crystallite size, strain, specific surface area and particle size of CeO_2 and $\text{CeO}_2\text{:Fe}$ nanopowder

Sample	Crystallite size (nm)	Strain	Lattice constant (Å)	BET Particle size (nm)
CeO_2	6.3	0.01	5.4208 Å	12.7
$\text{CeO}_2\text{:Fe}$	5.3	0.02	5.4090 Å	10.6

3.2. Morphology of CeO_2 and $\text{CeO}_2\text{:Fe}$ nanopowders

The SEM images of CeO_2 and $\text{CeO}_2\text{:Fe}$ nanopowders are shown in Figure 3. The SEM images indicate that the spherical primary and agglomerate secondary particles arrange CeO_2 and $\text{CeO}_2\text{:Fe}$ nanopowders. There was no particle shape difference between CeO_2 and $\text{CeO}_2\text{:Fe}$ nanopowders, but weak agglomeration appears for $\text{CeO}_2\text{:Fe}$. The result shows that iron doping reduces agglomeration particles and the crystallinity of CeO_2 nanopowder. The particle size of both CeO_2 in SEM images appeared higher than the estimated crystallite size from XRD analysis. It can be explained due to the several crystallites that compose the particles due to the polycrystalline structure of CeO_2 . Generally, the small-sized particle exhibits a large surface area and high surface energy. These characteristics lead agglomeration tendency of particles to reduce their surface energy. Consequently, primary particles adhere to each other to form agglomerated secondary particles. This phenomenon also appears in $\text{CeO}_2\text{:Fe}$ synthesised by hydrothermal method. The bundle structure morphology of CeO_2 and $\text{CeO}_2\text{:Fe}$ comprises nanorod-shaped primary particles and no effect of iron variation on CeO_2 morphology (Jiang, et al., 2020). In another study, weak agglomeration was found in CeO_2 doping Zn synthesised by sol-gel method and calcination

at a range temperature of 400 – 600°C for 2 hours (Soni et al., 2021).

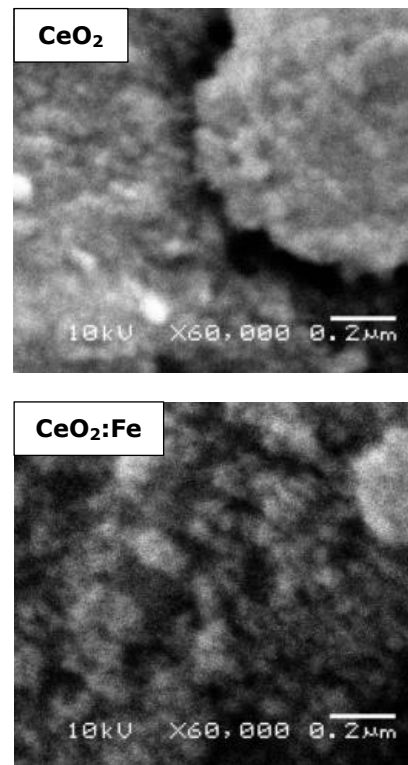


Figure 3. SEM images of CeO_2 and $\text{CeO}_2\text{:Fe}$ nanopowders

The incorporation of iron doping into the CeO_2 lattice was investigated by EDS analysis. According to the theoretical calculation of stoichiometric CeO_2 consists of 81 wt% cerium and 19 wt% oxygen, whereas the atomic composition of 0.05 molar ratio iron to CeO_2 equals 1.67 wt%. The atomic composition of CeO_2 and $\text{CeO}_2\text{:Fe}$ nanopowder from EDS analysis is summarized in Table 2. As can be seen, the cerium and oxygen atomic composition in CeO_2 and $\text{CeO}_2\text{:Fe}$ are almost the same as the theoretical calculation. The composition of oxygen atom in CeO_2 and $\text{CeO}_2\text{:Fe}$, i.e., 18.59 and 18.65 wt%, are smaller than the theoretical value of 19 wt%. The result indicates that oxygen defect is present in both CeO_2 . Moreover, the existence of the iron atom in CeO_2 was found to be 1.21 wt%. As a consequence, the atomic composition of cerium decreased from 81.41 wt% in pure CeO_2 to 80.14 wt% in $\text{CeO}_2\text{:Fe}$. The atomic composition analysis suggested that iron ions replaced cerium ions in the CeO_2 lattice.

Table 2. Atomic composition of CeO_2 and $\text{CeO}_2\text{:Fe}$ nanopowders

Sample	Atomic composition (wt%)		
	Ce	O	Fe
CeO_2	81,41	18,59	-
$\text{CeO}_2\text{:Fe}$	80,14	18,65	1,21

3.3. Surface area and porosity of CeO_2 and $\text{CeO}_2\text{:Fe}$ nanopowders

The N_2 adsorption-desorption isotherm curves, as shown in Figure 4, were analysed to determine the porous properties of CeO_2 and $\text{CeO}_2\text{:Fe}$ nanopowders. According to the hysteresis loop type of the IUPAC (International Union of Pure and Applied Chemistry) classification, both CeO_2 nanopowders belong to H3 hysteresis loop of type IV physisorption isotherm. The such hysteresis loop is typically observed in N_2 adsorption by agglomerated particles. A lower closure point shows it near $0.42 P/P_0$. This explanation is supported by the SEM image analysis that showed agglomerated particles. Meanwhile, type IV isotherm takes place by mesoporous material (Thommes et al., 2015). As a result, CeO_2 and $\text{CeO}_2\text{:Fe}$ are composed of mesoporous agglomerated particles.

Furthermore, the relevant type IV isotherm was analysed using the BET method to find the surface area. The BET-specific surface area of CeO_2 and $\text{CeO}_2\text{:Fe}$ nanopowders were 65.26 and 78.14 m^2/g , respectively, as depicted in Table 3. Both CeO_2 and $\text{CeO}_2\text{:Fe}$ nanopowders show sizeable specific surface area. Insertion

of iron into CeO_2 enlarged the specific surface area of pure CeO_2 nanopowder. Additionally, the particle sizes derived from BET surface-specific area are 12.7 and 10.6 nm for CeO_2 and $\text{CeO}_2\text{:Fe}$, respectively.

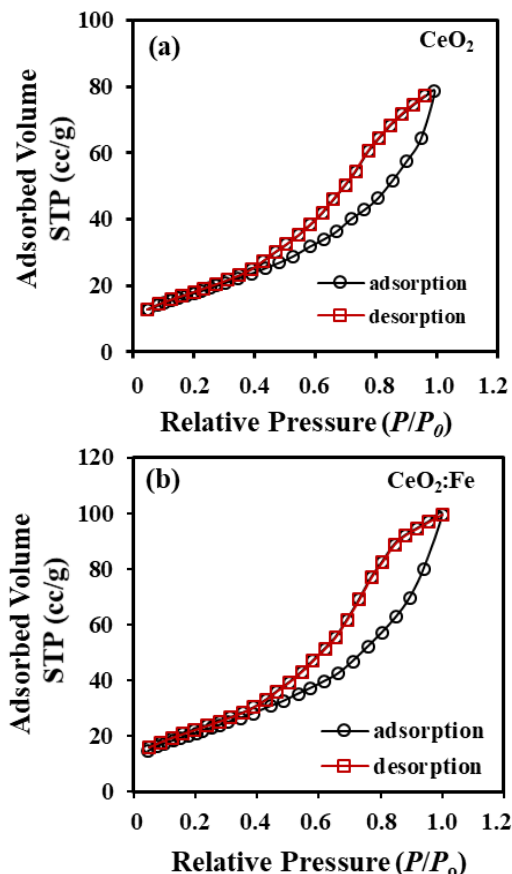


Figure 4. The N_2 adsorption-desorption Isotherm curves of (a) CeO_2 and (b) $\text{CeO}_2\text{:Fe}$ nanopowders

Table 3. The BET surface area, porevolume, and pore radius of CeO_2 and $\text{CeO}_2\text{:Fe}$ nanopowders

Sample	Surface area (m^2/g)	Pore volume (cm^3/g)	Pore radius (nm)
CeO_2	65.26	0.20	2.93
$\text{CeO}_2\text{:Fe}$	78.14	0.29	3.69

The $\text{CeO}_2\text{:Fe}$ with a larger specific surface area showed a smaller particle size than pure CeO_2 . The decreasing particle size of CeO_2 due to iron doping is in harmony with the estimated crystallite size obtained from the XRD analysis. The decreased crystallite size of CeO_2 due to iron doping is associated with the replacement of cerium ion by smaller ionic radii of iron without structure to be changed leading to a smaller lattice constant as seen in Table 1. The enlargement specific surface area of CeO_2 by doping iron described in precipitation synthesis of CeO_2 , which calcined

at a temperature of 550°C for 5 h for hydrogen production application (Mansingh, et al., 2016), as well as CeO₂ synthesized solvothermal for catalytic oxidation (Jiang et al., 2020). Interestingly, the specific surface area of CeO₂ and CeO₂:Fe in this study is more prominent than in another previous study (Mansingh, et al., 2016). Nanopowder with a large specific surface area provides advantages for paint pigment application.

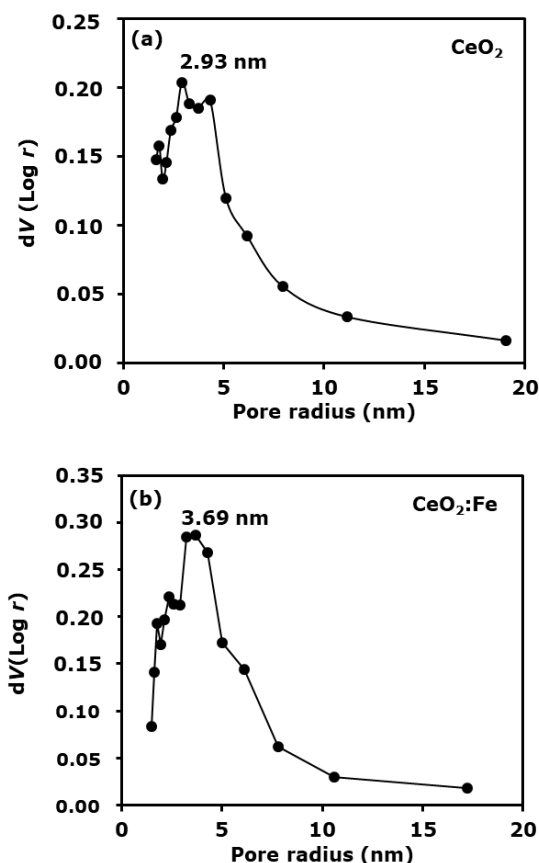


Figure 5. Pore size distribution of (a) CeO₂ and (b) CeO₂:Fe nanopowders

In addition, pore size distribution is another crucial aspect for the practical application of porous material. The BJH (Barrett-Joyner-Halenda) method is appropriate for calculating the pore size of mesoporous materials. Figure 5 displays the BJH pore size distribution of CeO₂ and CeO₂:Fe. CeO₂ and CeO₂:Fe show narrow pore size distribution in the 2 to 20 nm range, indicating uniform pore size. The peak of pore radius centred at 2.93 nm for CeO₂ and 3.69 nm for CeO₂:Fe nanopowders. Those pore radii correspond with a pore volume of 0.20 cm³/g and 0.29 cm³/g, as tabulated in Table 3. The doping of iron into CeO₂ increased pore size and pore volume. Thus surface area of CeO₂:Fe is higher than pure CeO₂.

3.4 Optical properties of CeO₂ and CeO₂:Fe nanopowders

The absorption is an essential property to evaluate the characteristic of pigment. Figure 6(a) presented UV-Vis absorbance spectra of CeO₂ and CeO₂:Fe nanopowders. The absorption spectra showed the absorption peak at around 307 nm, which revealed the absorption characteristic of CeO₂. The insertion of iron significantly increased the absorption property of CeO₂. In contrast, the shifted absorption band edge to the lower wavelength indicates widening bandgap energy.

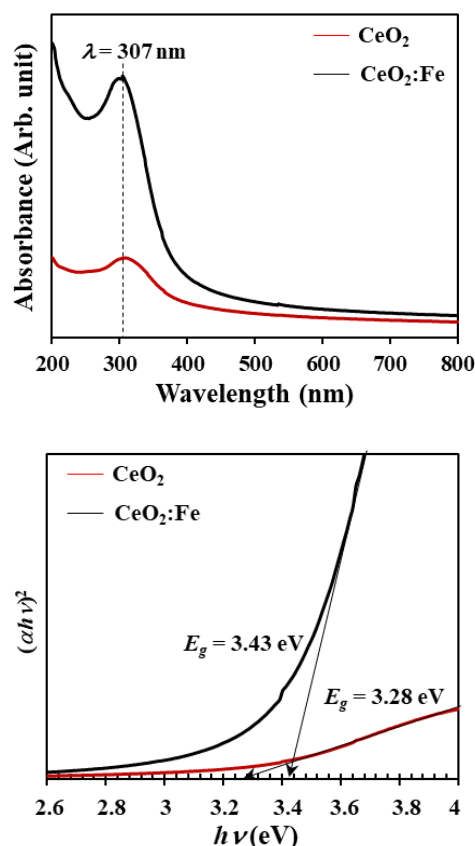


Figure 6. (a) UV Vis absorbance spectra (b) Tauc's plot of CeO₂ and CeO₂:Fe nanopowders

The direct bandgap energy of CeO₂ and CeO₂:Fe was estimated using Tauc's plots, as shown in Figure 6(b). The extrapolating linear part of absorption spectra to $\alpha h\nu = 0$ gives a bandgap energy value of 3.28 eV and 3.43 eV for CeO₂ and CeO₂:Fe, respectively. The bandgap energies of both CeO₂ are more significant than the bandgap energy of CeO₂ bulk, i.e., 3.19 eV. Others have observed an increase in the bandgap energy of CeO₂ due to iron doping (El-Hagary et al., 2019; Bayyappagaria et

al., 2018). The considerable bandgap energy of both CeO_2 in this study attributing to the quantum confinement effect or blue-shift phenomenon due to the nanometric particle size of CeO_2 as confirmed by XRD and SSA analysis. In contrast to the hydrothermally synthesised CeO_2 , the bandgap energy of $\text{CeO}_2\text{:Fe}$ is smaller than pure CeO_2 due to the presence of the second phase of FeO and oxygen defect in the bandgap (Radovic et al., 2013).

The refractive index value is another important optical property of pigment. The refractive index of oxide semiconductors strongly correlates to bandgap energy. The obtained bandgap energy then uses to estimate the refractive index of CeO_2 and $\text{CeO}_2\text{:Fe}$ nanopowders using Eq. 6. The values of refractive indices are 2.37 and 2.29 for CeO_2 and $\text{CeO}_2\text{:Fe}$, respectively. The obtained refractive indices values are close to the refractive indices of bulk CeO_2 , i.e., 2.2. The $\text{CeO}_2\text{:Fe}$ nanopowders with higher bandgap energy possess lower refractive indices than pure CeO_2 nanopowder.

4. Conclusion

The CeO_2 and $\text{CeO}_2\text{:Fe}$ nanopowder pigments with cubic fluorite structure were obtained by precipitation at a calcination temperature of 500°C . The $\text{CeO}_2\text{:Fe}$ nanopowder possessed a smaller crystallite size, higher specific surface area, and more substantial absorption properties than pure CeO_2 nanopowder. The incorporation of iron into CeO_2 shifted the absorption edge to a lower wavelength and changed the pigment colour from yellow to brick red. The results suggest that precipitation is useful to produce cerium oxide nano pigment.

Acknowledgement

The authors acknowledge the financial support provided by The Ministry of Research and Technology/National Research and Innovation Agency of Republic Indonesia (No. 187-29/UN7.6.1/PP/2022).

References

- Araujo, V.D., Bernardi, M.I.B., 2011). Synthesis and optical and structural characterization of $\text{Ce}_{(1-x)}\text{O}_2\text{:M}_x\text{O}$ ($\text{M} = \text{Cu}, \text{Co}$) pigments. *J. Therm. Anal. Calorim.* 103, 501–506. DOI 10.1007/s10973-010-0892-8
- Bao, H., Qian, K., Fang, J., Huang, W., 2017. Fe-doped CeO_2 solid solutions: Substituting-site doping versus interstitial-site doping, bulk doping versus surface doping. *Appl. Surf. Sci.* 414, 131–139. <https://doi.org/10.1016/j.apsusc.2017.04.018>
- Bayyappagaria, B., Shaik, K., Nasinac, M.R., Inturud, O., Dugasanie, S.R., 2018. Effect of Fe substitution on optical and magnetic properties of CeO_2 nanoparticles. *Optik.* 154, 821–827. <https://doi.org/10.1016/j.ijleo.2017.10.025>
- El-Hagary, M., Shaabanb, E.R., Moustafa, S.H., Gad, G.M.A. (2019) The particle size-dependent optical band gap and magnetic properties of Fe-doped CeO_2 nanoparticles, *Solid State Sci.* 91, 15–22. <https://doi.org/10.1016/j.solidstatesciences.2019.03.005>
- Gonzaga, L.A., Santana, V.T., Bernardi, M.I.B., Hruby, J., Neugebauer, P., Mesquita, A., 2020. CeO_2 and $\text{CeO}_2\text{:Pr}$ nanocrystalline powders prepared by the polymeric precursor method: Yellow and red pigments with tunable color. *J. American Ceram. Soc.* 103(11), 6280–6288. <https://doi.org/10.1111/jace.17339>
- Jiang, C., Wanga, H., Wanga, Y., Xue, C., Yang, Z., Yu C., Ji, H., 2020. Modifying defect States in CeO_2 by Fe doping: A strategy for low temperature catalytic oxidation of toluene with sunlight. *J. Hazard. Mater.* 390, 122182. <https://doi.org/10.1016/j.jhazmat.2020.122182>
- Joseph, A., Mathew, K.P.J., Vandana, S., 2021. Zirconium-Doped Ceria Nanoparticles as Anticorrosion Pigments in Waterborne Epoxy–Polymer Coatings, *ACS Appl. Nano Mater.* 4(1), 834–849. <https://doi.org/10.1021/acsanm.0c03162>
- Kumar, B.R., Hymavathi, B., 2017. X-ray peak profile analysis of solid-state sintered alumina doped zinc oxide ceramics by Williamson–Hall and size-strain plot method. *J. Asian Ceram. Soc.* 5, 94–103. <https://doi.org/10.1016/j.jascer.2017.02.001>

- Mansingh, S., Padhi, D.K., Parida, K.M., 2016. Enhanced photocatalytic activity of nanostructured Fe doped CeO₂ for hydrogen production under visible light irradiation, *Int. J. Hydrog.* 41, 14133-14146.
<https://doi.org/10.1016/j.ijhydene.2016.05.191>
- Micovic, D., Pagnacco, M.C., Bankovic, P., Maletskic, J., Matovic, B., Djokic, V.R., Stojmenovic, M., 2019. The influence of short thermal treatment on structure, morphology and optical properties of Er and Pr doped ceria pigments: Comparative study. *Process. Appl. Ceram.* 13(3), 310-321.
<https://doi.org/10.2298/PAC1903310M>
- Miri, A., Sarani, M., Khatami, M., 2020. Nickel-doped cerium oxide nanoparticles: biosynthesis, cytotoxicity and UV protection studies. *RSC Adv.* 10, 3967-3977.
<https://doi.org/10.1039/C9RA09076B>
- Nadjia, L., Abdelkader, E., Naceur, B., Ahmed, B., 2018. CeO₂ nanoscale particles: Synthesis, characterization and photocatalytic activity under UVA light irradiation. *J. Rare Earths.* 36, 575e587.
<https://doi.org/10.1016/j.jre.2018.01.004>
- Olegário, R.C., Ferreira de Souza, E.C., Borges, J.F.M., Marimon da Cunha, J.B., Chaves de Andrade, A.V., Antunes, S.R.M., Antunes, A.C., 2014. Synthesis and characterization of CeO₂.α-Fe₂O₃ and CeO₂.Pr₆O₁₁ ceramic pigments through the solid state reaction and modified sol-gel method. *Dyes Pigm.*, 106, 14e19.
DOI:10.1016/j.dyepig.2014.02.017
- Radovic, M., Dohcevic-Mitrovic, Z., Golubovic, A., Fruthb, V., Predab, S., Scepanovic, M., Popovic, Z.V., 2013. Influence of Fe³⁺-doping on optical properties of CeO_{2-γ} nanopowders. *Ceram. Int.* 39, 4929-4936.
<https://doi.org/10.1016/j.ceramint.2012.11.087>
- Soni, B., Makkar, S., Biswas, S., 2021. Defect induced tailored optical and magnetic properties of Zn-doped CeO₂ synthesized by facil sol-gel type process. *J. Alloys and Comp.* 879, 160149. □
DOI:10.1016/J.JALLCOM.2021.160149
- Stojmenovi, M., Milenkovi, M.C., Bankovi, P.T, Zuni, M., Gulicovski, J.J., J.R. Panti, J.R., Bo-skovi, S.B., 2015. Influence of temperature and dopant concentration on structural, morphological and optical properties of nanometric Ce_{1-x}Er_xO_{2-δ} (x = 0.05-0.20) as a pigment. *Dyes Pigm.* 123, 116e124.
<https://doi.org/10.1016/j.dyepig.2015.07.030>
- Sulcova, P., Vecera, J., Strnadlova, L., 2012. Study of doped CeO₂ prepared by different synthesis. *J. Therm. Anal. Calorim.* 108, 519-523. DOI 10.1007/s10973-011-2148-7
- Thommes, M., Kaneko, K., Neimark, A.V. , Olivier, J.P., Rodriguez-Reinoso, F., Rouquerol, J., Sing, K.S.W., 2015. Physisorption of gases, with special reference to the evaluation of surface area and pore size distribution (IUPAC Technical Report. *Pure Appl. Chem.* 87(9 - 10), 1 - 19.
<https://doi.org/10.1515/pac-2014-1117>
- Wu, F., Li, X., Li, Y., Wang, Z., Hong, Y., Shen, Z., Song, F., 2021. Design and preparation of a type of γ-Ce₂S₃@c-SiO₂-coated red pigment with a plum pudding mosaic structure: The effect of pre-sintering temperature on pigment properties. *Microporous Mesoporous Mater.* 311, 110699.
<https://doi.org/10.1016/j.micromeso.2020.110699>