Synthesis and Characterization of $Ce_xZr_{1-x}O_2$ nanopigment

M. Nouri[1,*], A. Kompany[1], A. Khorsand[2]

1. Laboratory of Material and Electroceramics, Department of Physics, Faculty of Science, Ferdowsi University of Mashhad, Iran
2. Labratory of Nanotechnology, Esfarayen Institute of Higher Education, Esfarayen, Iran

Abstract

In this research, inorganic pigments having the general formula $Ce_xZr_{1-x}O_2$ (x = 0.6, 0.8, 1.0) have been synthesized by a sol-gel method in a green rout, using gelatin at 600°C calcination temperature, as viable alternatives to lead, cadmium and chromium based yellow toxic inorganic colorants. The starting materials were cerium nitrate, zirconium nitrate and gelatin, as the polymerization and stabilizer agent. The prepared samples were characterized by X-ray diffraction (XRD), Transmission electron microscopy, UV-Vis spectroscopy and the CIE L*a*b* colorimetric analysis. The produced pigments exhibited brilliant yellow colors, using the CIE L*a*b* system and the most vivid yellow hue was obtained for $Ce_{0.6}Zr_{0.4}O_2$.

Keywords: **inorganic pigments- sol-gel- cerium nitrate- zirconium nitrate.**

1-Introduction

Inorganic pigments synthesized in nano-size are abundance utilized in different applications such as paints, ceramics, inks, enamels and glasses [1,2]. The great of inorganic pigments for use high thermal, chemical stabilities and anticorrosion applications currently employed are derived from toxic metals such as cadmium, lead, chromium or cobalt. So, environmentally friendly inorganic alternative toxic pigments are essential. Among several non-toxic yellow pigments, CeO_2 and related materials such as ceria-zirconia composition have attracted much attention because of their opacity, low toxicity, hardness, good scratch resistance and high thermal stability [3,4]. In the present study, $Ce_xZr_{1-x}O_2$ nano pigments synthesized and characterized by XRD, TEM, UV-Vis and CIEL*a*b* system.

2-Experimental

Starting material used for $Ce_xZr_{1-x}O_2$ nanopigments (x = 0.6, 0.8, 1.0) were synthesized by sol-gel method in gelatin medium include $Ce(NO_3)_3.6H_2O$ (from Merck), $ZrO(NO_3)_2.6H_2O$ (from Merck) as precursor, gelatin as polymerization and stabilization agent and distilled water as solvent. Each nitrate was dissolved in distilled water in separate beakers then addition to gelatin at 80°C that except x=1.0 sample other samples transformed into the gel rapidly and in this temperature was stirred in oil bath for 10 h. The gel thus obtained was oven dried at 60°C for 25 h. The dried materials calcinated at 600°C for 4 h and further were crushed into powders using a mortar and pestle. Nanopigments were obtained yellow powder. The structural and morphology studies were performed by X-ray diffraction and transmission electron microscopy, respectively. The optical properties was carried out by UV-Vis spectroscopy and color scales estimated by the CIE L*a*b* spectrophotometric.

3-Results and Discussion

The XRD patterns of the $Ce_xZr_{1-x}O_2$ samples are shown in Fig. 1a All the patterns of the samples, the desired phase show no additional peaks and it was found that the powders are crystalline and cubic structure. The according of XRD patterns, with increasing amounts of Zr, the diffraction peaks are shifted toward larger angles that result from substitutions of Zr atoms with smaller ionic radius (0.086nm) in place of Ce atoms with larger ionic radius (0.11nm)[3]. The crystallite size calculated by Scherrer formula according to 1. Equations

$$D = k\lambda / \beta \cos\theta \qquad (1)$$

where D is the crystalline size (nm), λ is the wavelength (1.54056 Å for CuKα radiation), k is a constant equal to 0.94, β is the peak width at half-maximum intensity, and θ is the peak position.

Crystallite size and lattice constant are shown in table 1.

Fig. 1b shows the TEM micrograph and size distribution histograms of the TEM micrograph of the CeO_2 powders. The histograms indicate that the average particle sizes of the CeO_2 calcinated at 600°C were approximately about 12.3nm.

The UV–Vis spectra of the nanopigments calcinated at 600°C are shown in Fig. 2. Moreover, the direct band gap energies estimated from a plot of $(\alpha h \nu)^2$ versus the photon energy ($h \nu$) according to the Tauc method (in the inset of Fig. 2), α (absorption coefficient) can be calculated from Beer-Lambert relation according to 2. Equation

$$\alpha = 2.303 A/D \qquad (2)$$

Where A is the absorbance and D is crystallite size [12]. The confluence of the line tangent to the curve at the inflection point, with the energy axis gives the size of the band gap. The band gap of 3.3, 3.15 and 3.11 were obtained for the samples x= 0.1, 0.8, 0.6, respectively (table 1).

The CIE $L^*a^*b^*$ color parameters of synthesized samples are summarized in Table 2. Under this method, L^* is the brightness axis or intensity of the pigments [black (0) to white (100)]; a^* axis represents the green-red and b^* the blue-yellow, respectively. CIE $L^*a^*b^*$ values indicate bright yellow for samples. The increase of b^* value with the increase of dopant Zr in CeO_2 indicates in more yellowish the color of the pigments. The a^* value is responsible for the green tinge of the pigment samples. The decrease in the L^* value corresponds to reduce lightness of the samples.

4-Conclusion

The $Ce_xZr_{1-x}O_2$ nanopigments were synthesized by sol-gel method in gelatin media and were characterized by XRD, TEM techniques and UV-Vis spectroscopy. By analyzing the XRD spectra can be seen that the desired structure is formed cubic structure. The crystallite size calculated from the Scherrer formula about 4-12nm. The TEM micrographs of the CeO_2 showed that the average particle size is about 12.30nm. The band gap of the samples was estimated from UV–vis spectra according to the Tauc relation. These pigments have brilliant yellow colors that derived by CIE L*a*b* parameters.

Reference

1. P.Prabhakar Rao, M.L.P. Reddy. Dyes and

2. kalarical Janardhanan Sreeram, Radhika Srinivasan, Jeyapragasam Meena Devi, Balachandran Unni Nair, Thirumalachari Ramasami. Dyes and Pigments, 75, 687–692, 2006.

3. V.S. Vishnu, Giable George, V. Divya, M.L.P. Reddy. Dyes and Pigments, 82, 53–57, 2009.

4. Lidan Yang, Mingquan Ye, Aijun Han. Advanced Materials Research, Vols. 399-401, pp 514-518, 2012.

Table 1. structural parameters and band gap values.

Sample	$D_{sherrer}$ (nm)	E_g	a (nm)
CeO_2	11.48	3.3	5.41
$Ce_{0.8}Zr_{0.2}O_2$	6.15	3.15	5.35
$Ce_{0.6}Zr_{0.4}O_2$	4.85	3.1	5.31

Table 2. The color coordinates of the powder nanopigments.

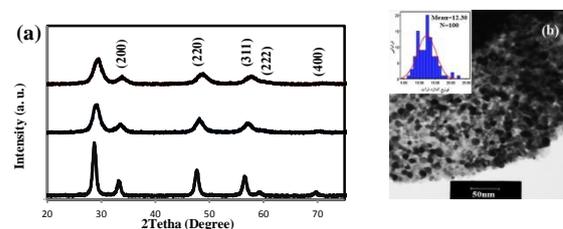| Sample	L^*	a^*	b^*	C^*
CeO_2	98.86	-5.11	30.71	31.14
$Ce_{0.8}Zr_{0.2}O_2$	94.9	-4.42	39.78	40.03
$Ce_{0.6}Zr_{0.4}O_2$	94.4	-4.08	40.56	40.76

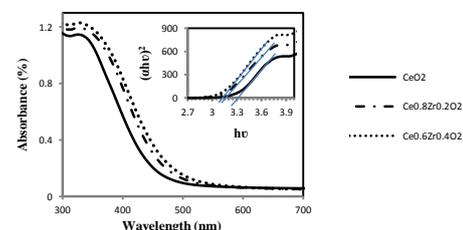**Fig. 1. (a) XRD pattern samples and (b) TEM micrograph of CeO_2.**

Fig. 2. The UV-Vis spectroscopy of samples.