Synthesis and Characterization of Doped Rare Earth Oxides for Environmentally Benign Nontoxic Reddish-yellow Pigments

Kalarical Janardhanan Sreeram,* Chervathoor Poulose Aby, and Balachandran Unni Nair
Chemical Laboratory, Central Leather Research Institute, Council for Scientific Industrial Research,
Adyar, Chennai 600 020, India

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$Ce_{10}Pr_xW_yO_z$, where x and y varied from 0.075 to 0.6 solid solutions of oxides of Ce, Pr, and W have been synthesized by solid-state route with a goal of employing them as environmentally friendly reddish-yellow colorants. Pigments were highly crystalline, chemically stable and could be employed for surface coating.

The characteristics required for commercial uses of pigments are: color-tone and saturation, hiding power, tinting strength, brightness, nonreactivity, insolubility, chalking resistance, dispersibility, etc.[1,2] Conventional inorganic pigments for the above applications contain potentially toxic elements such as cadmium, cobalt, chromium, lead, antimony, or selenium.[3] The rare earth elements offer a vast opportunity for developing environmentally secure alternatives. Rare earths, because of their unique electronic configuration of partially filled f orbitals, show unusual magnetic and optical properties.[4] The color developed depends on the number of unpaired electrons. The pigments derived from rare earths show their characteristic intense color due to charge-transfer interactions between a donor and an acceptor with the metal ion playing generally the role of an acceptor. Dopants based on rare earth elements in mixed oxide systems offer opportunity to tune in color response through manipulation of energy gaps and delocalization phenomena in conduction and valence bands.[5] Pigments based on CeO_2 are inorganic colorants with high-temperature stability and in the orange-pink hue when doped with praseodymium.[6] Lanthanum oxide (La_2O_3) and praseodymium dioxide (Pr_6O_{11}) dissolve in cerium oxide at 1300 °C forming a solid solution of the three oxides. CeO_2–PrO_2–La_2O_3 pigments give very interesting red hues in the ceramic glaze. These heat- and chemical-resistant pigments have a fluorite structure and represent potential environmentally friendly inorganic colorants.[6] In the present study, new inorganic pigments $Ce_{10}Pr_xW_yO_z$, where x and y varied from 0.075 to 0.6, have been synthesized by solid-state route with a goal of preparing environment friendly reddish-yellow colorants. The ionic radii of tungsten being lower than that of cerium and praseodymium, it is expected that tungsten would enter the crystal lattice of cerium and cause a change in the color owing to lattice defects.

All reagents used in this study were of Analar grade. The rare earth metal ions and transition-metal ions were taken in appropriate ratios, homogenized using a mortar and pestle and transferred to an alumina crucible. The mixture was calcined at a predefined temperature for predetermined duration at 15 °C/min. Ce:Pr:W in the ratio 10:0.15:0.3 (in moles), homogenized using a mortar and pestle, transferred to a alumina crucible and treated in a muffle furnace at 1300 °C for one hour with a heating rate equal to 5 °C/min. The obtained powder was cooled and homogenized, and the spectral characteristics were evaluated. The role of tungsten in the color of the resultant oxide was studied by varying the tungsten content from 0.075 to 0.6 mole keeping the ratio of Ce:Pr constant. The role of praseodymium in the color of the oxide was studied by varying the Pr content from 0 to 0.8 g keeping the ratio of Ce:W constant. Characterization techniques included powder X-ray diffraction, scanning electron microscopy, diffuse reflectance, and color coordinates.[7,8] The CIELab (1976) color space was used for color measurement.[9] The band-gap values were calculated using the Kubelka–Munk function which is given by $f(R) = (1 - R)^2/2R$, where R is the reflectance value. A plot of $f(R)$ against wavelength is drawn, and the absorption edge is determined from the plot. The value of the wavelength is substituted in the formula $E(\mathrm{eV}) = 1236/\mathrm{wavelength~(nm)}$. The pigments, ground well and separated to various sizes, were analyzed for their mass tone/hiding power. For this standard commercial paint composition consisting of a long oil alkyd, dispersing agents, and mixed drier was employed. Mineral turpentine was used as the medium. The hiding power was evaluated by coating on an opacity chart at a thickness of 150 µm.

The reflectance spectra for the resultant compounds are presented in Figure 1. A broad absorption maxima (reflectance minima) is observed over the 400–600-nm region, indicating that a range of colors is possible from these oxides. The band-gap energy values and the colors are presented in Table 1. It can be seen that the use of W gives a red-yellow hue with corresponding band-gap energy around 2.2 eV.

The color coordinates for the obtained oxides and the band gap energy values are presented in Table 1. It can be seen that on doping tungsten there is a rapid change in the L, a, and b values.

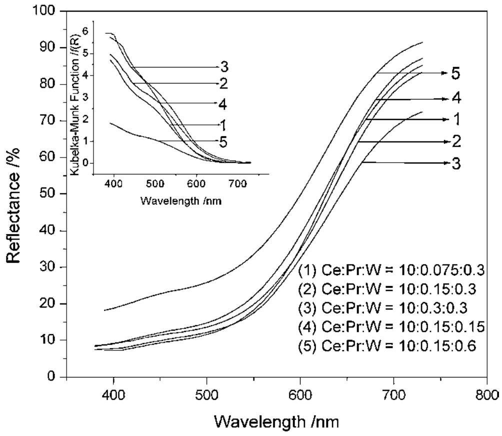

Figure 1. Reflectance spectra plot for $Ce_{10}Pr_xW_yO_z$, (inset shows the Kubelka–Munk function plotted against wavelength).

Table 1. Color coordinates for $Ce_{10}Pr_xW_yO_z$

Pr offer (moles)	W offer (moles)	L	a	b	E/eV
0	0.3	88	5	10	
0.075	0.3	64	21	35	2.24
0.15	0.3	61	22	33	2.21
0.3	0.3	59	21	33	2.23
0.15	0	88	4	18	
0.15	0.15	61	25	39	2.22
0.15	0.6	72	16	27	2.24

While the L value decreased a and b values showed an increase in the tungsten-doped system. But when the tungsten content was increased from 0.15 to 0.6 mole the L value increased and a and b values showed a decrease. This indicates that when tungsten was equal to 0.15 moles the resulting oxide has a red-yellow hue while an increased concentration of tungsten shifts the color towards a green-blue hue. A decrease in L values with tungsten indicates an increase in intensity of color. The values are in agreement with the band-gap energy values which also showed a similar trend. The change in color due to doping could be attributed to the substitution of tungsten into the lattice of cerium, owing to its lower ionic radii.

The obtained color coordinates of the resultant oxides where Pr was varied are also presented in Table 1. It can be found that a and b values remained almost constant in the entire range of praseodymium concentration investigated, indicating an increase in concentration of praseodymium does not influence the color of Ce–Pr–W oxides. However, praseodymium influences the color of Ce–W lattice, possibly by entering into cerium lattice. No major change in the spectra is observed indicating that the colors remain more or less the same. Praseodymium contributes to a decrease in L value, thereby increasing the observed intensity of color.

In order to understand the role of particle size on the color of the oxides of the type $Ce_{10}Pr_{0.3}W_{0.3}O_z$, the oxides generated were ball milled for varying durations of time and the resultant particle size evaluated. It was found that the color of the oxide was lighter as the particle size was reduced from 620 to 340 nm. No significant change was observed in the hue of the pigment as the particle size reduced to ≈300 nm.

The XRD pattern of the oxide indicates a crystalline character at 1000 °C. The pattern matches that of the cubic fluorite structure of cerium oxide. No evident difference of the lattice parameter between CeO_2- and Pr/W-doped CeO_2 has been observed. This is possibly because the low amount of doping does not affect the crystal lattice. The homogeneous and crystalline nature of the sample has also been noticed from the SEM micrographs of the colorant (Figure 2). From Figure 2, it is quite clear that there is an even grain distribution; the average grain size is about 300 nm. The inset of Figure 2 shows distribution patterns of the elements. It can be seen that doping was uniform throughout the pigment surface. The particle size calculated from the Debye–Scherrer formula was 32–35 nm.

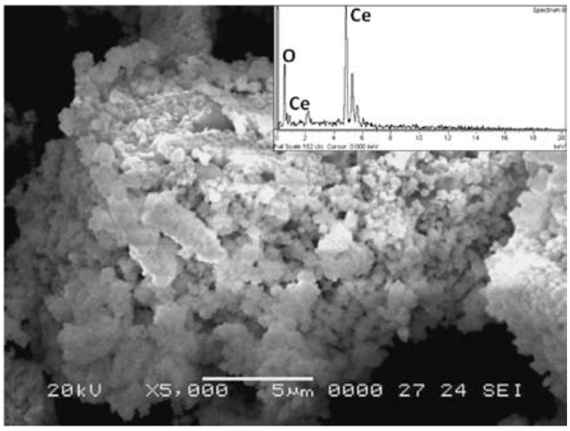

Figure 2. SEM micrograph of $Ce_{10}Pr_{0.15}W_{0.3}O_z$ at 1000 °C, dwell time 60 min and rate of heating 15 °C/min. The inset shows the EDAX pattern of the same.

It is clear from the TG/DTA analysis of $Ce_{10}Pr_{0.3}W_{0.3}O_z$ that there is no loss of weight and phase transformation in the temperature range 50–500 °C. Further, the pigment sample was tested for its acid and base resistance capacity. Negligible weight loss was observed in both mineral acids and alkali solution (10% concentration), which indicates that the pigment samples are chemically resistant.

The pigment was able to transfer its color to the paint medium fairly well, indicating that it had a good mass tone. The ΔE (the total color difference between black and white areas) was only eight units, indicating ability of the paint formulation to cover black areas.

In summary $Ce_{10}Pr_{0.3}W_{0.3}O_z$ class of oxides developed in this study serve as ideal environmentally benign reddish-yellow pigments.

References and Notes

1 G. Buxbaum, *Industrial Inorganic Pigments*, New York, Wiley-VCH, **1997**.

2 P. Escribano, J. B. Carda, E. Cordoncillo, *Esmaltes y Pigmentos Cera'micos* in *Enciclopedia Cera'mica*, ed. by Faenza Editrice Ibe'rica, **2001**, Vol. 3.

3 M. Jansen, H. P. Letschert, *Nature* **2000**, *404*, 980.

4 S. Petoud, S. M. Cohen, J.-C. G. Bunzil, K. N. Raymond, *J. Am. Chem. Soc.* **2003**, *125*, 13324.

5 A. J. Silversmith, D. M. Boye, K. S. Brewer, C. E. Gillespie, Y. Lu, D. L. Campbell, *J. Lumin.* **2006**, *121*, 14.

6 P. Sulcova, M. Trojan, *Dyes Pigm.* **1999**, *40*, 87.

7 R. S. Hunter, R. W. Harold, *Instruments for the Chromatic Attributes of Object Appearance* in *The Measurement of Appearance*, 2nd ed., New York, Wiley, **1987**, p. 290.

8 D. B. Judd, G. Wyszecki, *Tools and Technics* in *Color in Business, Science and Industry*, 3rd ed., New York, JohnWiley & Sons Inc., **1975**, p. 105.

9 F. W. Billmeyer, M. Saltzmann, *Color and Color Difference Measurement* in *Principles of Color Technology*, 2nd ed., New York, Wiley, **1982**, p. 67.