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Synthesis and Characterization of CeO_2–TiO_2–Pr_6O_{11} Solid Solutions for Environmentally Benign Nontoxic Red Pigments

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New inorganic pigments $Ce_{1-(x+y)}Ti_xPr_yO_2$ (x ranges from 0.05 to 0.195 and y ranges from 0.005 to 0.15) based on CeO_2–TiO_2–Pr_6O_{11} solid solutions have been synthesized by solid-state route with a goal of preparing environmentally secure red colorants. Characterizations using XRD, UV–vis spectroscopy and CIE 1976 color coordinates assessment reveals the formation of pigments displaying colors ranging from brick red to dark brown. The coloring mechanism is based on the introduction of additional electronic level of energy in the cerianite forbidden band from the unpaired 4f electron of lanthanide ion.

The development of red ceramic pigments with high-temperature stability is of great importance to the ceramic industry.[1] The classical red pigments used hitherto in the ceramic industry are of two types: iron oxide or cadmium sulfoselenide encapsulated in zircon matrixes and lead oxide in tin oxide matrix give pale red or pink colors. However, some of these pigments are toxic and unstable at above 900 °C. Recent investigations reveal that these toxic pigments can be replaced by solid solutions of perovskites $CaTaO_2N$ and $LaTaON_2$, which gives colors ranging from yellow to deep red.[2] Although these pigments are nontoxic and show excellent color hue, it is necessary to heat the starting materials in a flow of toxic and inflammable ammonia gas for a long time (20–60 h) to synthesize them. The CeO_2–PrO_2 system has been studied as ceramic pigment by various investigators using different methods: solid-state reactions,[3,4] coprecipitation,[5] and combustion.[6] However, the preparation methods employed for the above pigments uses toxic ammonia and mineral acids for dissolving the starting materials and mineralizers. Further, the obtained optical properties are not satisfactory for commercial use. Thus, serious need arises to search for environmentally friendly and economically viable materials for the replacement of toxic inorganic red pigments. In the present study, new red pigments having the formula $Ce_{1-(x+y)}Ti_xPr_yO_2$ (x ranges from 0.05 to 0.195 and y ranges from 0.005 to 0.15) have been synthesized by solid-state reaction of the respective oxides.

CeO_2 (99.9%), Pr_6O_{11} (99.9%), and TiO_2 (99.9%) were thoroughly mixed in the stoichiometric ratio in an agate mortar with a pestle. The mixture was calcined at 1200 °C for 3 h in air atmosphere furnace. In order to ensure the completion of the reaction, the calcinations process was repeated thrice. The obtained powders were characterized by means of X-ray powder diffraction (XRD) using Ni-filtered Cu Kα radiation with a Philips X'pert Pro diffractometer. Morphological analysis was performed by means of scanning electron microscopy with a JEOL JSM-5600LV SEM. Optical reflectance of the powder was measured with a UV–vis spectrophotometer (Shimadzu, UV–2450) using barium sulphate as a reference. The color properties are described in terms of CIE-$L^*a^*b^*$ 1976 color scales. The values a^* (the axis red-green) and b^* (the axis yellow-blue) indicate the color hue. The value L^* represents the lightness or darkness of the color as related to a neutral grey scale.

The XRD patterns of the pigments $Ce_{1-(x+y)}Ti_xPr_yO_2$ (x ranges from 0.05 to 0.195 and y ranges from 0.005 to 0.15) are given in Figure 1 which show the characteristic reflections of the cubic fluorite structure of CeO_2 and also in good agreement with the JCPDS No. 34-394. The intense and sharp peaks found in the diffraction patterns reveal the crystalline nature of the phase. The crystallite size is calculated from Debye Scherrer formula, $D = 0.9\,\lambda/\beta\cos\theta$, where D is the particle size, λ is the wave length of X-ray used, β and θ are the half width of X-ray diffraction lines and half diffraction angle of 2θ. The crystallite size of the pigments was found to be 7–19 nm. Doping of small amounts of praseodymium and titanium in cerium oxide retains the same fluorite structure except minor variations in the lattice parameter (Table 1). As the ionic radii of Ce^{4+} and Pr^{4+} in eightfold coordination are 0.097 and 0.096 nm,[7] respectively, only minor variations would be expected. The incorporation of 15% of praseodymium into CeO_2 lattice decreases the unit cell parameter to 5.4045 Å. On the other hand, doping of Ti^{4+} (19.5%) having a smaller ionic radii (0.074 nm) decreases relatively more to 5.3971 Å. The decrease in lattice parameter confirms $Ce_{1-(x+y)}Ti_xPr_yO_2$ solid-solution formation. The homogeneous and crystalline nature of the sample has also been noticed from the SEM photographs of $Ce_{1-(x+y)}Ti_xPr_yO_2$ pigments (Figure S1).[10]

Figure 2 depicts the diffuse reflectance spectra obtained for the CeO_2–TiO_2–Pr_6O_{11} in the solid solutions. The reflectance spectra show a greater absorption in the visible region with an increasing number of chromophore ions because the gap between the valence and conduction bands narrows. This causes color of the pigment to vary from brick red to dark brown (Figure

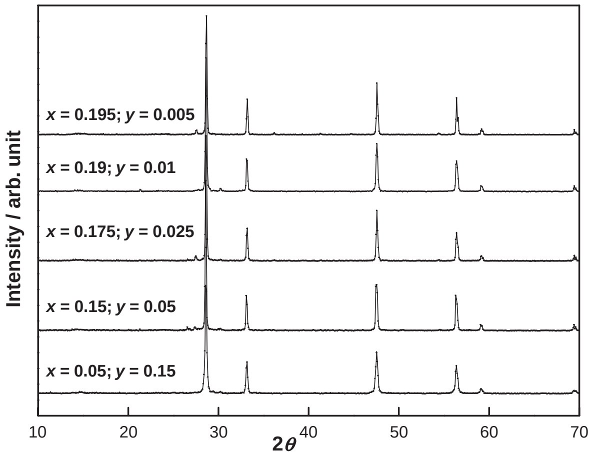

Figure 1. XRD patters of the pigments $Ce_{1-(x+y)}Ti_xPr_yO_2$.

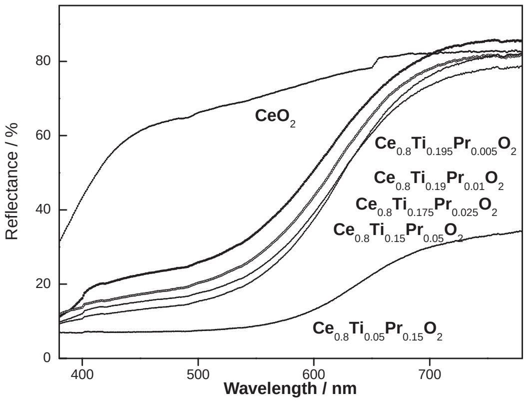

Figure 2. Reflectance spectra of the pigments.

S2).[10] The coloring mechanism is based on the shift of the charge-transfer band of the CeO_2 to higher wavelengths. A band can be observed at $\lambda < 600$ nm attributed to the characteristic charge-transfer process of this system. The position of the absorption edge critically depends on the praseodymium content and is red-shifted (Figure 2) with the increase of praseodymium. This evaluation is consistent with the observed charge-transfer spectra of tetravalent lanthanide ions in oxides.[3,8] By doping CeO_2 with Pr^{4+} ions, the $4f^1$ electron of the praseodymium valence shell introduces an additional electron level of energy between the O^{2-} valence and Ce^{4+} conduction band and reduces the band gap to ≈1.88 eV (Table 1). The CeO_2 band gap falls in the indigo region in the visible wavelength, and a complementary light yellow color is observed. In contrast, $Ce_{1-(x+y)}Ti_xPr_yO_2$ absorbs in the wavelength region below 600 nm producing a red color.

It is clear from the $L^*a^*b^*$ values of the $Ce_{1-(x+y)}Ti_xPr_yO_2$ pigments summarized in Table 1 that the present values are significantly higher than recently reported praseodymium-doped ceria powders (5% praseodymium-doped CeO_2:$L^* = 66$; $a^* = 12$; $b^* = 9.5$), synthesized by microwave-assisted hydrothermal route.[9] Nahum et al.[3] have reported similar color properties as found in the present study with Pr^{4+}-doped ceria pigments calcined at 1400–1500 °C. The present L^*, a^*, b^* values are also comparable with that of commercially available red pigment (Zinc–Iron–Chromite: $L^* = 39.92$; $a^* = 20.5$; $b^* = 19.63$) marketed by Kawamura Chemicals, Japan. The progressive addition of titanium to the CeO_2–Pr_6O_{11} solid solution significantly increases the lightness (L^*) of the pigment retaining the color coordinates corresponding to the red hue. Further, it is also clear from this study that the solid solutions of these pigments can be prepared at lower calcination temperatures by the addition of titanium as compared to the previously reported CeO_2–Pr_6O_{11} solid solution.[3] On the other hand, the increase of praseodymium content decreases the L^*, a^*, b^* values considerably and responsible for the change of color from brick red to dark brown.

It is clear from the TG/DTA analysis (Figure S3)[10] of $Ce_{0.8}Ti_{0.175}Pr_{0.025}O_2$, 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.

Table 1. Color coordinates and unit cell parameter (a) and band gap (E_g) of $Ce_{1-(x+y)}Ti_xPr_yO_2$ pigments

Pigment composition	Color coordinates			a /Å	E_g /eV
	L^*	a^*	b^*		
$Ce_{0.8}Ti_{0.195}Pr_{0.005}O_2$	61.83	15.34	17.67	5.3971	1.87
$Ce_{0.8}Ti_{0.19}Pr_{0.01}O_2$	56.81	17.21	18.01	5.4016	1.89
$Ce_{0.8}Ti_{0.175}Pr_{0.025}O_2$	53.09	17.86	17.02	5.4010	1.89
$Ce_{0.8}Ti_{0.15}Pr_{0.05}O_2$	51.33	18.79	17.39	5.4054	1.88
$Ce_{0.8}Ti_{0.05}Pr_{0.15}O_2$	34.50	10.74	7.42	5.4045	1.86
CeO_2	77.65	1.31	9.86	5.4113	3.01

In summary, new inorganic pigments based on CeO_2–TiO_2–Pr_6O_{11} solid solutions have been successfully synthesized having colors ranging from brick red to dark brown. It is suggested that the coloring mechanism is based on the shift of the charge-transfer band of the CeO_2 to higher wavelengths, introducing an additional electronic level by doping praseodymium. Better lightness of the pigments can be achieved by addition of titanium to the CeO_2–Pr_6O_{11} solid solution. Further, the addition of titanium is also expected to improve the color properties such as hiding power and tint strength. Thus, they are expected to be new environment-friendly pigments and form an alternate to the existing toxic red pigments.

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10 Supporting Information is available on the CSJ-Journal web site, http://www.csj.jp/journals/chem-lett/index.html.

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