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The synthesis and characterization of environmentally benign praseodymium-doped $TiCeO_4$ pigments

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Abstract

Novel inorganic pigments of general formula $TiCe_{1-x}Pr_xO_{4-\delta}$ (x ranges from 0 to 0.7) were synthesized using a solid-state route with the aim of preparing environmentally friendly red pigments. Characterization using X-ray powder diffraction, UV−vis spectroscopy and color measurement revealed the formation of pigments with colors ranging from white to brick red. The color of the pigments arises from the introduction of an additional electronic energy level in the forbidden band of the unpaired 4f electron of the praseodymium ion. The red ceramic pigments were found to be interesting alternatives to existing inorganic red pigments for the coloration of plastics.

Keywords: Synthesis; Rare earth-TiO_2 based colorants; Environmentally benign pigments; Coloring of plastics

1. Introduction

The development of red ceramic pigments with high temperature stability is of great importance to the ceramic industry [1−3]. 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 [4−6]. However, some of these pigments are toxic and unstable above 900 °C. These materials can be easily replaced by rare earth metal oxides, which are generally having a low toxicity rating [7,8]. The intense coloration of rare earth based materials can arise from mostly charge transfer interactions between a donor and an acceptor with the metal ions playing generally the role of an acceptor. Dopants based on rare earth elements in mixed oxide systems offer an opportunity to tune the color response through the manipulation of energy gaps and delocalization phenomena in conduction and valence bands. This phenomenon offers wide scope for designing of colorants for specific applications.

Recently, many rare earth based red pigments have been proposed by several researchers including our group [9−13]. Rare earth−transition metal oxide materials, having the general formula: $(RE_xTM)O_y$, where RE is rare earth, TM is transition metal, x ranges from 0.08 to 12 and y ranges from $x+1$ to $2x+2$, have been reported as novel inorganic pigments for use in plastics, paints, coatings, glass enamels and other materials with various advantages over the traditional pigment formulations [9]. Earlier investigations reveal that the classical toxic inorganic pigments can be replaced by solid solutions of perovskites $CaTaO_2N$ and $LaTaON_2$, which give colors ranging from yellow to deep red [10]. Although these pigments are non-toxic 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. CeO_2 is a fluorite-structured oxide that can form extensive solid solutions with a variety of alien cations while retaining the fluorite crystal structure. Praseodymium-doped CeO_2 ceramic pigments are interesting because they produce colors ranging from brick red to dark brown, depending on the concentration of praseodymium, synthesis conditions and calcination temperatures [14−18]. However, some of the synthesis methods

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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. Accordingly, the major objective of the present investigation is to develop environmentally secure inorganic red pigments with high temperature stability to replace the toxic red ceramic pigments, currently used in the pigment industry. The new pigments of the formula $TiCe_{1-x}Pr_xO_{4-\delta}$ (x ranges from 0 to 0.7) have been synthesized by solid-state reaction of the respective oxides and characterized for their structure and optical properties.

2. Experimental section

2.1. Materials and methodology

Several compositions based on $TiCe_{1-x}Pr_xO_{4-\delta}$ (x ranges from 0 to 0.7) stoichiometries were prepared by ceramic method. The precursors employed for the traditional ceramic pigment synthesis route are the corresponding oxides: TiO_2 (99.9%), CeO_2 (99.9%) and Pr_6O_{11} (99.9%). In this method, the reactants were mixed and homogenized by wet milling with acetone in an agate mortar for 30 min. The homogeneous mixture was calcined in platinum crucibles in an electric furnace at a temperature of 1250 °C for 3 h. The heating of the furnace was programmed to increase the temperature initially at 10 °C/min up to 900 °C and afterwards the heating rate was decreased to 5 °C/min up to 1250 °C. In order to ensure the completion of the reaction, the calcination process was repeated thrice. To refine and homogenize the particle size after calcinations, the resulting products were ground in an agate mortar.

2.2. Coloration of plastics

Poly(methyl methacrylate) (PMMA; S.D. Fine chemicals, India) was utilized as a binder phase for fabricating the pigmented compact. The typical pigment sample, $TiCe_{0.9}Pr_{0.1}O_{4-\delta}$ (5 or 10 wt%) was ultrasonicated (Vibronics, 250 W, India) in an alcohol/water (1:4) mixture for 10 min to ensure the complete dispersion of the pigment particles. A viscous solution consists of PMMA (95 or 90 wt%) was made using a conventional electrical coil heater. The pigment dispersion was slowly added while stirring and converted into a thick paste. The paste after 2 h of curing, compressed uniaxially into a form of cylindrical discs using a hydraulic press (Lawrence & Maya, India) at a pressure of 25 MPa. Both sides of the pigmented polymer were lapped using a fine grade emery sheet for obtaining a polished surface.

2.3. Characterization techniques

The calcined powders were characterized by X-ray powder diffraction (XRD) with a Philips X'Pert Pro diffractometer. The XRD patterns were recorded in the 10–70° 2θ range using Ni filtered Cu Kα radiation. Morphological analysis of the powders was performed by Scanning electron microscope, with a JEOL JSM-5600LV. The thermal stability of the colorant was checked by Pyris Diamond TG/DTA Perkin Elmer make.

The diffused reflectance spectra of the pigment samples were measured with a Shimadzu, UV-2450 spectrophotometer in the 380–780 nm range 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 particle diameter of the sample was measured by the laser scattering particle size distribution analyzer (CILAS 1180 Liquid).

3. Results and discussion

The XRD patterns of the pigments $TiCe_{1-x}Pr_xO_{4-\delta}$ ($x = 0$, 0.05, 0.1 and 0.3) are given in Fig. 1 which show the characteristic reflections of the cubic fluorite structure of CeO_2 [19] and also in good agreement with the JCPDS No. 34-394. The minor peaks can be assigned to Rutile TiO_2 (PDF No. 21-1276) [19]. On the other hand, with the increase of praseodymium content in $TiCeO_4$ ($x = 0.5$ and 0.7), structural transformation from cubic fluorite to pyrochlore can be noticed from the XRD patterns of the pigments $TiCe_{1-x}Pr_xO_{4-\delta}$ given in Fig. 2. When $x = 0.5$, both the fluorite and pyrochlore phases have been observed. Further, it is also clear from the XRD pattern of the pigment that when $x = 0.7$ only pyrochlore phase $Ti_2Pr_2O_7$ (PDF No. 35-267) has been formed. The intense and sharp peaks found in the diffraction patterns reveal the crystalline nature of the products. The homogeneous and crystalline natures of the samples have also been noticed from the SEM photographs (Fig. 3) of $TiCe_{1-x}Pr_xO_{4-\delta}$ pigments. The particle size distribution of the typical pigment, $TiCe_{0.5}Pr_{0.5}O_{4-\delta}$ investigated shows a distribution with 90% of the particles being smaller than 44.13 μm, 50% smaller than 16.03 μm and 10% smaller than 4.51 μm. The

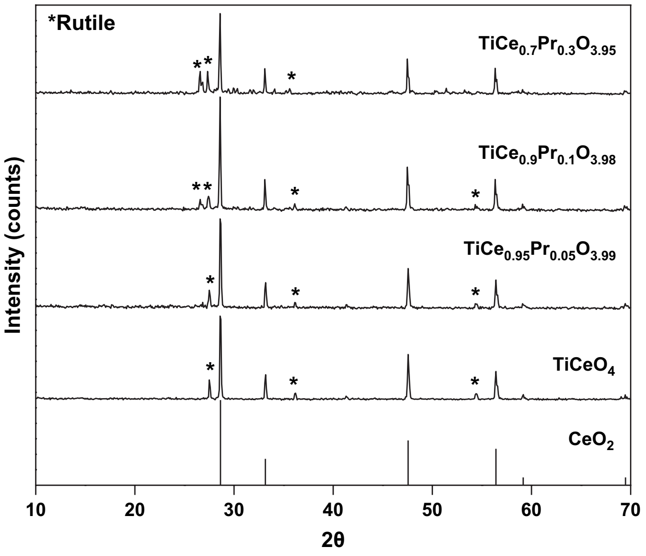

Fig. 1. XRD patterns of $TiCe_{1-x}Pr_xO_{4-\delta}$ pigments ($x = 0$, 0.05, 0.1 and 0.3).

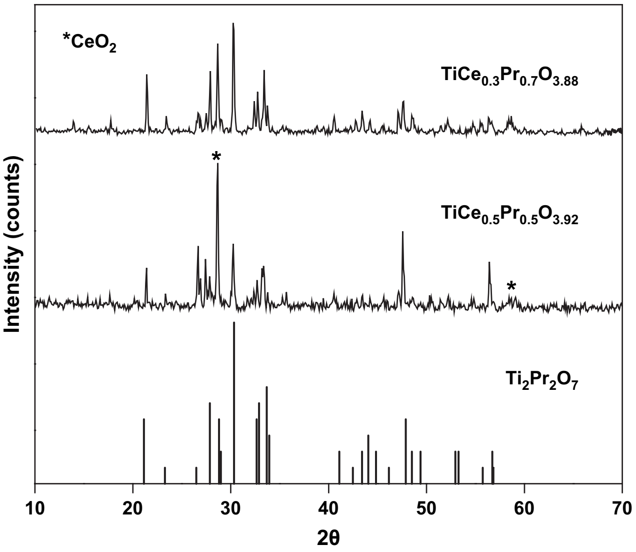

Fig. 2. XRD patterns of $TiCe_{1-x}Pr_xO_{4-\delta}$ pigments ($x = 0.5$ and 0.7).

mean particle diameter of the pigment sample was found to be 20.87 μm.

Fig. 4 depicts the diffused reflectance spectra obtained for the $TiCe_{1-x}Pr_xO_{4-\delta}$ pigments. The reflectance spectra show a greater absorption in the visible region with increasing number of chromophore ions because the gap between the valence and conduction bands narrows. This causes the color of the pigment vary from white to brick red (Fig. 5). 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 (Fig. 6) with the increase of praseodymium. This evaluation is consistent with the observed charge transfer spectra

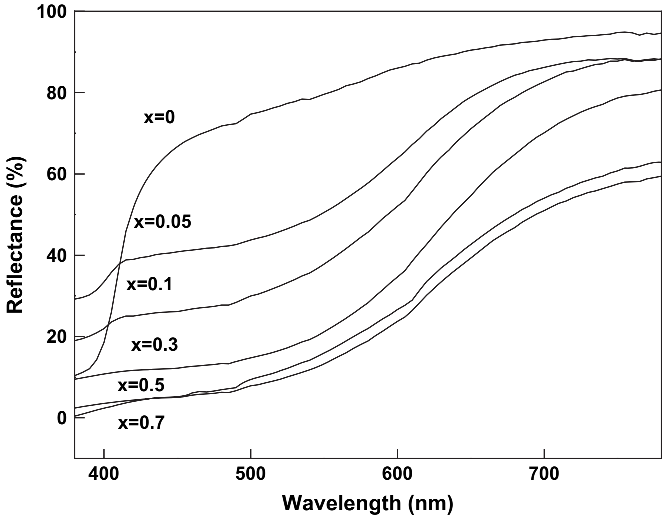

Fig. 4. Reflectance spectra of $TiCe_{1-x}Pr_xO_{4-\delta}$ pigments.

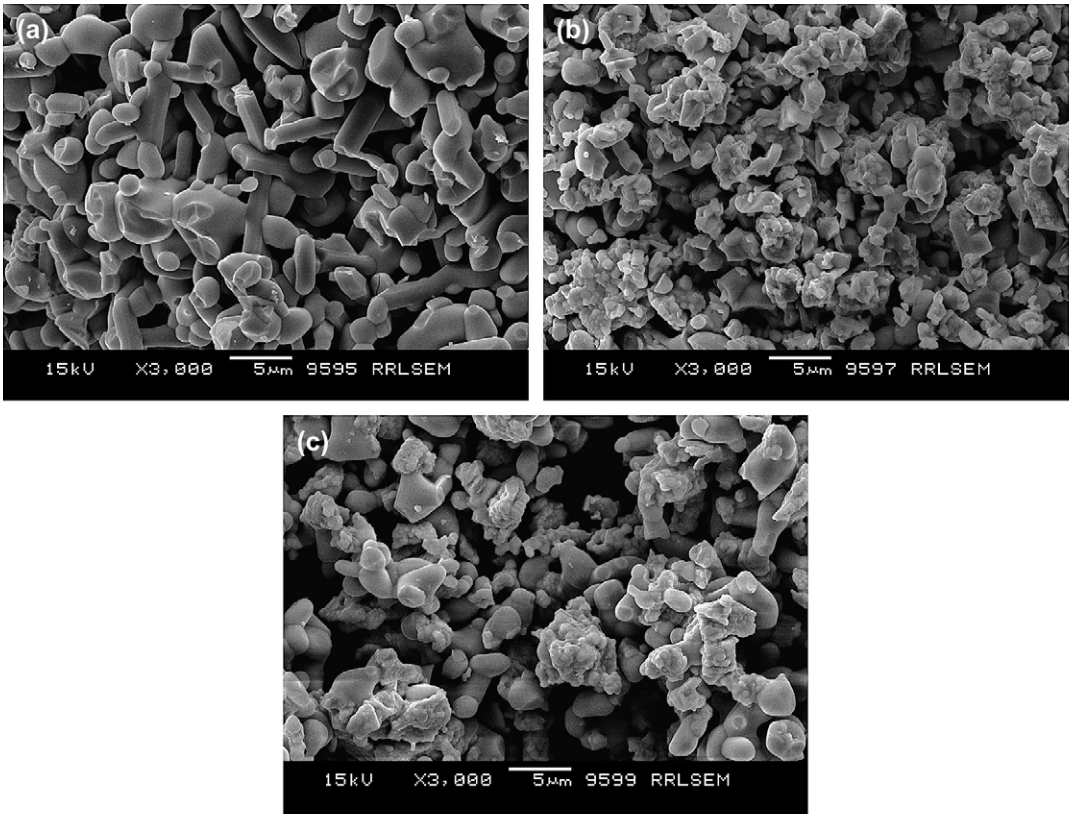

Fig. 3. SEM micrographs of (a) $TiCeO_4$, (b) $TiCe_{0.3}Pr_{0.7}O_{4-\delta}$, and (c) $TiCe_{0.5}Pr_{0.5}O_{4-\delta}$.

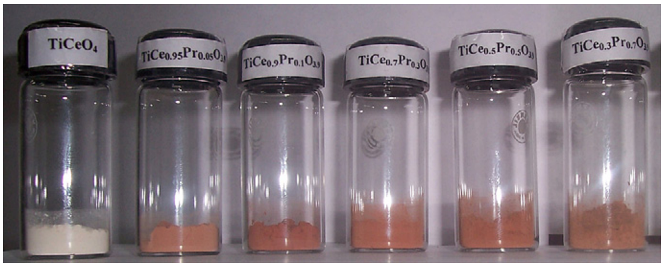

Fig. 5. Photographs of $TiCe_{1-x}Pr_xO_{4-\delta}$ pigments.

Table 1
Color coordinates and band gap of pigments

Pigment composition	Color coordinates			Band gap (eV)
	L^*	a^*	b^*	
$TiCeO_4$	90.51	0.023	9.46	2.96
$TiCe_{0.95}Pr_{0.05}O_{4-\delta}$	64.50	14.11	20.60	1.91
$TiCe_{0.9}Pr_{0.1}O_\delta$	54.53	17.92	21.47	1.89
$TiCe_{0.7}Pr_{0.3}O_\delta$	61.73	16.18	25.14	1.87
$TiCe_{0.\ 5}Pr_{0.5}O_\delta$	53.36	16.57	25.83	1.84
$TiCe_{0.3}Pr_{0.7}O_\delta$	57.82	13.48	25.52	1.83
$TiCe_{0.9}Pr_{0.1}O_\delta$ (5%) + PMMA	46.17	20.01	22.60	
$TiCe_{0.9}Pr_{0.1}O_\delta$ (10%) + PMMA	52.05	18.48	20.12	

of tetravalent lanthanide ions in oxides [4,20]. By doping $TiCeO_4$ 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 the Ce^{4+} conduction band, and reduces the band gap from 2.96 to 1.84 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, $TiCe_{1-x}Pr_xO_{4-\delta}$ absorbs in the wavelength region below 600 nm producing a brick red color.

It is clear from the $L^*a^*b^*$ values of the $TiCe_{1-x}Pr_xO_{4-\delta}$ 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 [17]. Nahum et al. [4] 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 pigments (Zinc–Iron–Chromite: $L^* = 39.92$; $a^* = 20.5$; $b^* = 19.63$) marketed by Kawamura Chemicals, Japan. It is also clear from the present study that the solid solutions of red pigments can be prepared at lower calcination temperature by the addition of titanium as compared to the previously reported CeO_2–Pr_6O_{11} solid solutions [4,21]. The increase of praseodymium content in $TiCeO_4$ decreases the lightness of the pigment from 90.51 to 57.82. On the other hand, a^* b^* values considerably increase which is responsible for the change of color from white to brick red of the pigment.

It is clear from the TG/DTA analysis (Fig. 7) of $TiCe_{0.5}Pr_{0.5}O_{4-\delta}$ that there is no loss of weight and phase transformation in the temperature range 50–1000 °C. Among the series of colorants prepared, typically $TiCe_{0.3}Pr_{0.7}O_{4-\delta}$ was tested for its acid resistance and alkali resistance. A small quantity of weighed pigment sample is mixed with 10% HNO_3, HCl, H_2SO_4 and NaOH, and soaked for half an hour with constant stirring using a magnetic stirrer. Then, the pigment was filtered, washed with water, dried and weighed. Negligible weight loss was noticed for all the acids and alkali tested. The typical $L^*a^*b^*$ values after acid and alkali resistance tests were found to be ($L^* = 59.18$; $a^* = 13.98$; $b^* = 26.13$ and $L^* = 58.20$; $a^* = 14.21$; $b^* = 25.05$ for HNO_3 and NaOH, respectively) same as that of the pigment powder samples. This indicates that the pigment samples are chemically and thermally stable.

The coloring performance of the typically synthesized pigment, $TiCe_{0.9}Pr_{0.1}O_{4-\delta}$ was tested for its coloring application in a substrate material like PMMA. Typically 5 or 10 wt% pigment sample was dispersed in PMMA and compressed to a cylindrical disc (Fig. 8). The color coordinates of the test pieces were measured and depicted in Table 1. These test pieces exhibit very fine and uniform brick red hue. Thus the developed

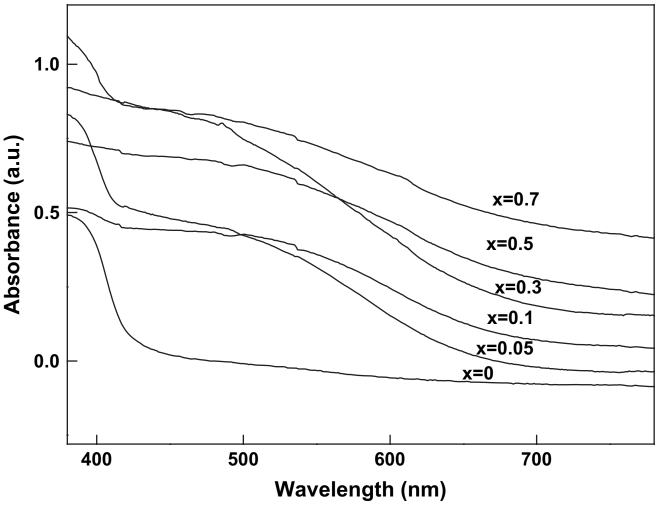

Fig. 6. Absorbance spectra of $TiCe_{1-x}Pr_xO_{4-\delta}$ pigments.

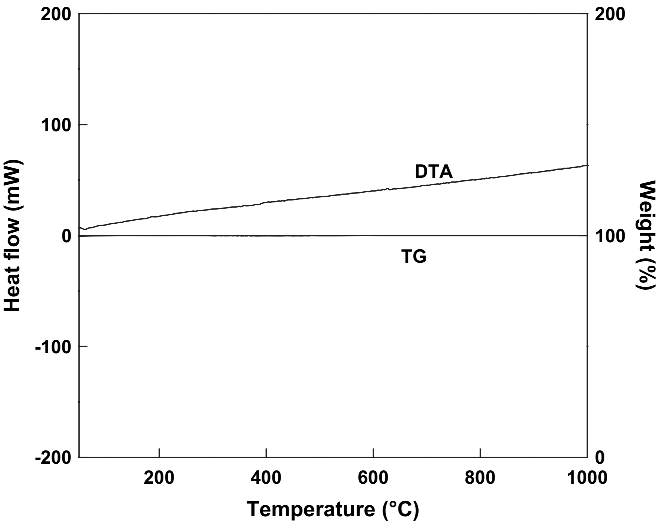

Fig. 7. The TG/DTA of $TiCe_{0.5}Pr_{0.5}O_{4-\delta}$ pigments.

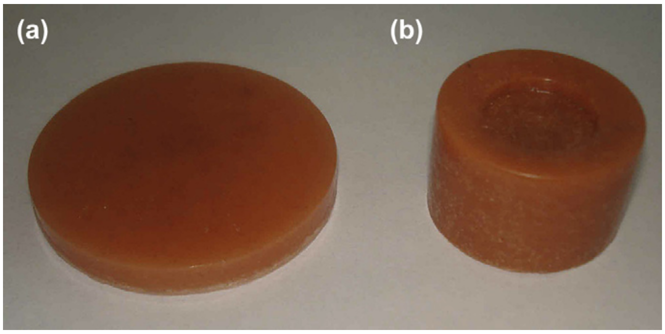

Fig. 8. Photographs of (a) $TiCe_{0.9}Pr_{0.1}O_{4-\delta}$ (5%) + PMMA and (b) $TiCe_{0.9}Pr_{0.1}O_{4-\delta}$ (10%) + PMMA.

pigments may find potential applications in coloring of various plastic materials.

4. Conclusion

Novel environmentally secure inorganic pigments by doping praseodymium into the CeO_2 matrix of $TiCeO_4$ have been successfully synthesized having colors ranging from white to brick red. It is suggested that the coloring mechanism is based on the shift of charge transfer band of CeO_2 to higher wavelengths, introducing an additional electronic level by doping praseodymium. The developed pigments are found to be thermally and chemically stable and also do not contain toxic metals. Thus, the present pigments may find potential alternative to the classical toxic inorganic red pigments for coloring plastics and paints.

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