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Short Communication

The synthesis of $Ce_{0.95-y}Pr_{0.05}Nd_yO_{2-y/2}$ pigments

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Abstract

The synthesis of some new inorganic pigments has been investigated. Emphasis was placed on the preparation of heat-resistant pigments by high-temperature calcination of CeO_2 and Pr_6O_{11} and on a determination of the optimum conditions for pigment formation. The pigments were examined for their structures, colour and ability to dye ceramic glazes.

Keywords: Ceramic pigments; Solid solutions; CeO_2–PrO_2 pigments; Optical properties

1. Introduction

The pigments employed for colouring ceramics are usually inorganic products composed of metal oxides or compounds capable of forming metal oxides. They must possess thermal and chemical stability at high temperatures and must be inert to the chemical action of the molten glaze [1]. These requirements limit ceramic pigments to a very small number of refractory compounds that are relatively inert to the medium in which they are dispersed, and has dominated research and development in recent years.

Our approach to achieving the above-mentioned challenges focuses on the preparation of pigments based on cerium dioxide (CeO_2) that are stable at very high temperatures. Pigments based on CeO_2 give various pink-orange hues in ceramic glazes [2] and are prepared by high-temperature calcination of CeO_2 and Pr_6O_{11}. The latter dissolves in CeO_2 during the heating step, forming a $Ce_{1-x}Pr_xO_2$ solid solution. The compounds based on cerium dioxide are less known ceramic pigments CeO_2.

The new pigments in the present investigation are of the formula $Ce_{1-(x+y)}Pr_xNd_yO_{2-y/2}$. Neodymium oxide ($Nd_2O_3$) and praseodymium dioxide (PrO_2) dissolve in CeO_2 at 1300°C, forming a solid solution of the three oxides. CeO_2–PrO_2–Nd_2O_3 pigments give very interesting reddish hues in the ceramic glazes and are heat and chemical resistant pigments with fluorite structures. As such they representing new inorganic pigments from the environmental point of view [2]. These pigments are characterised by heat stability and chemical resistance. Unlike the starting oxides, the pigments are insoluble in concentrated H_2SO_4 and HCl. This property reflects the strength of the crystal lattice of the pigments prepared.

2. Experimental

CeO_2 of 95% purity, Pr_6O_{11} of 90% purity, Nd_2O_3 of 99% purity were obtained from Indian

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Rare Earths Ltd. (India), for the preparation of $Ce_{1-(x+y)}Pr_xNd_yO_{2-y/2}$ pigments.

The starting mixtures containing CeO_2, Pr_6O_{11} and the required amount of Nd_2O_3 ($y = 0.05$, 0.15, 0.25, 0.35, 0.45, 0.55, 0.65, 0.75, 0.85) were homogenised in an agate mortar. The mixtures were then calcinated in corundum crucibles in an electric resistance furnace, increasing the temperature at 10°C/min. Calcination was conducted at 1300°C for 1 h. The resultant pigments were added to a middle-temperature borate–silicate glaze in amounts of 10% (w/w) at 1000°C, and the temperature was held for 15 min. The final glazes were evaluated for colour change, by measuring spectral reflectance in the visible region using a MiniScan instrument (Hunter Lab, USA).

X-ray diffractograms of pigment powders were obtained using a vertical X-ray diffractometer HZG-4B (Freiberger Präzisionsmechanik, Germany) equipped with a 25-cm diameter goniometer. Cu K_α ($\lambda = 0.154178$ nm) radiation was used for the angular range of $2\theta < 35°$ and $K_{\alpha 1}$ ($\lambda = 0.154051$ nm) for the range of $2\theta > 35°$, employing a nickel filter for attenuation of the K_β radiation. A proportional detector was used.

3. Results and discussion

A key goal of this investigation was to develop optimum conditions for the synthesis of pigments based on the fluorite structure of CeO_2 containing Nd_2O_3. The influence of this lanthanum oxide on the colours of $Ce_{0.95-y}Pr_{0.05}Nd_yO_{2-y/2}$ pigments was also studied.

The effect of increasing Nd content on the colour of pigment powders and pigments mixed with borate–silicate glaze was determined. From Table 1, it is seen that L^* values increase with increasing Nd content, with the pigment containing 85 mol% Nd having the highest L^*. The powdered pigments containing 5–55 mol% Nd gave red-brown hues, with the powder pigment containing 5 mol% Nd giving the darkest hue. At higher Nd content, the L^* value increases and the pigment powders gives the highest % reflectance (Fig. 1). Increasing Nd content above 55 mol% decreases the red character of these pigments (Fig. 2).

Based on experimental data for these pigments in borate–silicate glaze, it can be seen that increasing Nd content produces $Ce_{0.95-y}Pr_{0.05}Nd_yO_{2-y/2}$ pigments having dark pink-orange to light yellow-orange hues (Fig. 3). Increasing Nd content increases the L^* value while the colour coordinate a^* decreases. Nd content of 5–45 mol% in the present pigments gives intense pink-orange hues. At higher Nd content (55–75 mol%), the colour intensity and red character of these pigments decrease (Fig. 4). Neodymium content of 85 mol% increases L^* and b^* values and pigment colour is shifted to yellow and becomes lighter.

When $Ce_{0.95-y}Pr_{0.05}Nd_yO_{2-y/2}$ pigments having Nd content of 5, 15, 25, 35, 45, 55 and 65 mol% were subjected to X-ray diffraction analyses, diffraction lines characteristic of the fluorite structure of CeO_2 were observed. All of the pigments

Table 1
The effects of Nd content on the colour properties of $Ce_{0.95-y}Pr_{0.05}Nd_yO_{2-y/2}$ pigments

Formula	Powder pigments			Pigments applied in glaze		
	L^*	a^*	b^*	L^*	a^*	b^*
$Ce_{0.90}Pr_{0.05}Nd_{0.05}O_{1.975}$	46.63	10.68	7.63	58.71	24.16	28.39
$Ce_{0.80}Pr_{0.05}Nd_{0.15}O_{1.925}$	45.42	11.51	9.41	64.61	19.61	25.87
$Ce_{0.70}Pr_{0.05}Nd_{0.25}O_{1.875}$	47.76	11.25	11.33	68.13	16.33	24.68
$Ce_{0.60}Pr_{0.05}Nd_{0.35}O_{1.825}$	46.47	11.59	10.91	69.74	13.84	23.26
$Ce_{0.50}Pr_{0.05}Nd_{0.45}O_{1.775}$	47.38	10.16	11.52	70.86	11.14	22.35
$Ce_{0.40}Pr_{0.05}Nd_{0.55}O_{1.725}$	47.59	9.26	11.58	71.63	8.19	20.99
$Ce_{0.30}Pr_{0.05}Nd_{0.65}O_{1.675}$	46.71	8.08	12.57	70.66	7.15	20.97
$Ce_{0.20}Pr_{0.05}Nd_{0.75}O_{1.625}$	49.77	8.67	13.05	70.66	4.47	21.32
$Ce_{0.10}Pr_{0.05}Nd_{0.85}O_{1.575}$	56.57	7.21	14.21	65.95	3.02	24.42

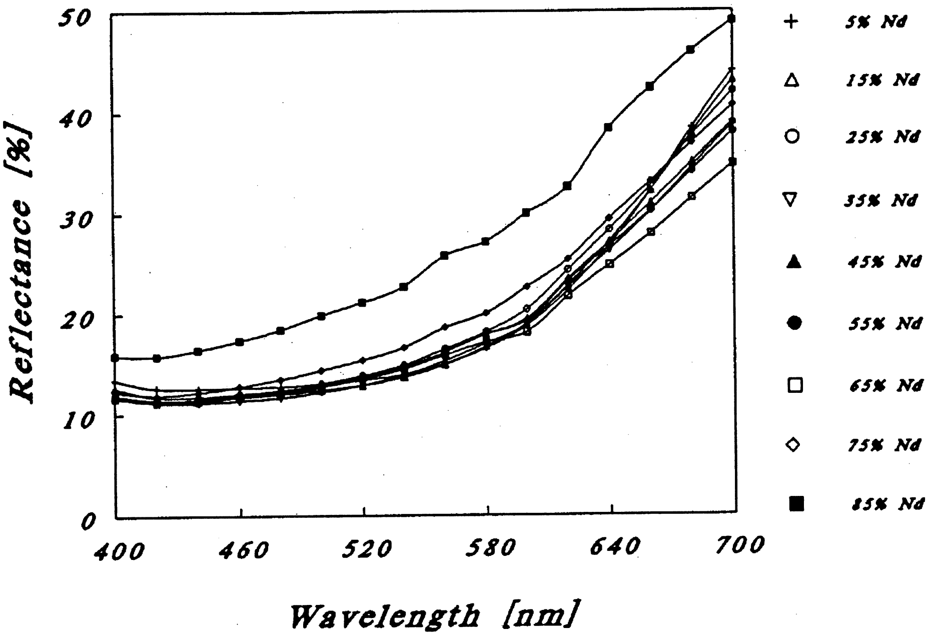

Fig. 1. The effects of Nd content on the colour of the $Ce_{0.95-y}Pr_{0.05}Nd_yO_{2-y/2}$ pigment powders.

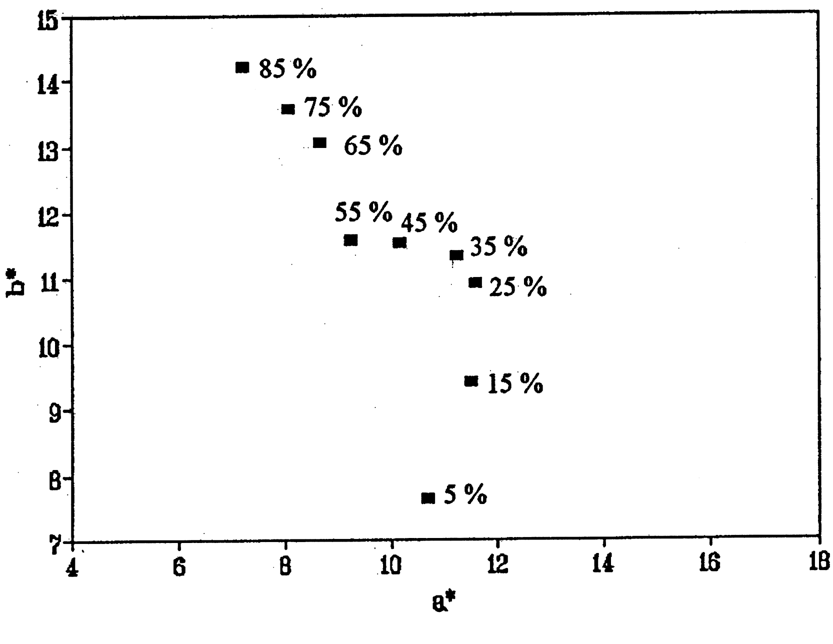

Fig. 2. The effects of Nd content on the colour coordinates of $Ce_{0.95-y}Pr_{0.05}Nd_yO_{2-y/2}$ pigment powders.

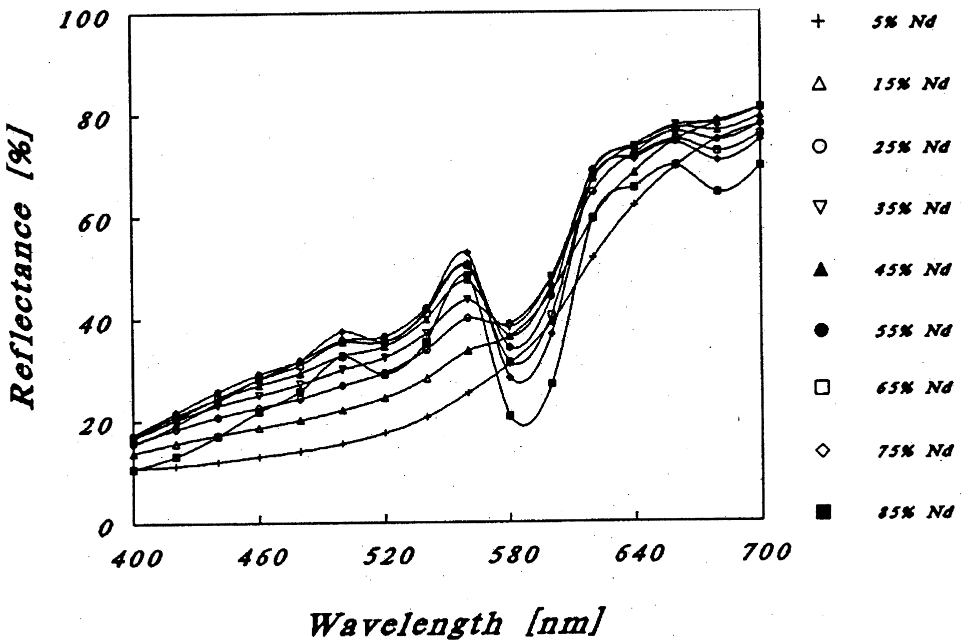

Fig. 3. The effects of Nd content on the colour of $Ce_{0.95-y}Pr_{0.05}Nd_yO_{2-y/2}$ pigments applied to glazes.

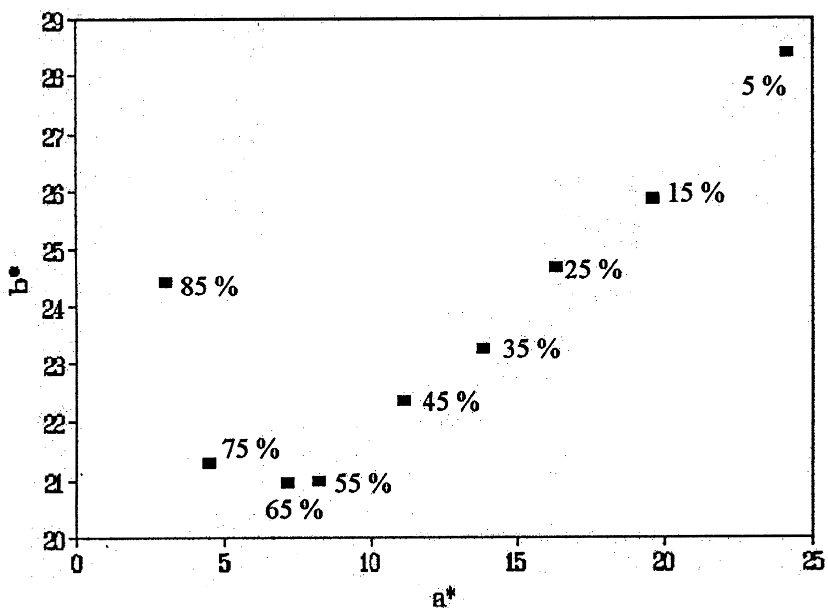

Fig. 4. The effects of Nd content on a^* and b^* values of $Ce_{0.95-y}Pr_{0.05}Nd_yO_{2-y/2}$ pigments applied to glazes.

exhibited peaks that could be assigned exclusively to CeO_2, indicating that they were homogeneous. This means that PrO_2 and Nd_2O_3 had dissolved in CeO_2 at 1300°C to form a solid solution. When Nd contents of 75 and 85 mol% were used, peaks were observed that could be assigned to Nd_2O_3, as the resultant pigments were heterogeneous.

It was also found that Pr atoms replace Ce atoms in the crystal lattice, forming uncharged substitutional defects (Pr^x_{Ce}) in the solid solution of $Ce_{0.95-y}Pr_{0.05}NdyO_{2-y/2}$ pigments. It is believed that Pr generates substitutional defects [3] because the tetravalent Pr ion [$r(Pr^{4+})=0.092$ nm] has a smaller radius than the tetravalent Ce ion [$r(Ce^{4+})=0.101$ nm]. The lanthanum ions [$r(Nd^{3+})=0.108$ nm] that enter the fluorite structure are a little larger than the Ce^{4+} ions that are substituted. The formation of these defects is responsible for the increase in the CeO_2 cell volume (Table 2).

The values of the lattice parameters of $Ce_{0.95-y}Pr_{0.05}Nd_yO_{2-y/2}$ pigments are given in Table 2 and show that the lattice parameter a increases with increasing Nd_2O_3 content. The volume of the elementary cell of CeO_2 also increases with increasing Nd_2O_3 content.

Nd ions enter the pigment structure as negatively charged defects Nd'_{Ce}. The strongly negative charge of these defects is compensated by the positively charged substitution defects ($V^{\bullet}_{O}$). The variations in the lattice parameters of CeO_2 are believed to be associated with the formation of a solid solution of CeO_2, PrO_2 and Nd_2O_3 [4]. Such a solution is probably of the substitutional type, where Pr^{4+} and Nd^{3+} cations are substituted in Ce^{4+} lattice positions, forming uncharged electrically neutral defects (Pr^x_{Ce}) and negatively charged defects (Nd'_{Ce}) that are compensated for by oxygen vacancies ($V^{\bullet}_{O}$). The formation of these defects can be described by Eqs. (1) and (2):

$$PrO_2(\rightarrow\ CeO_2) \Longleftrightarrow Pr^x_{Ce} + CeO_2 \quad (1)$$

$$2Nd_2O_3(\rightarrow\ CeO_2) \rightleftarrows 4Nd'_{Ce} + 3CeO_2 + 4V^{\bullet}_{O} \quad (2)$$

Table 2
Lattice parameters for $Ce_{0.95-y}Pr_{0.05}Nd_yO_{2-y/2}$ pigments

Formula	a (nm)	V (nm^3)	$\Delta 2\upsilon^a$
CeO_2	0.54221	0.15941	0.003
$Ce_{0.90}Pr_{0.05}Nd_{0.05}O_{1.975}$	0.54279	0.15992	0.005
$Ce_{0.80}Pr_{0.05}Nd_{0.15}O_{1.925}$	0.54427	0.16121	0.003
$Ce_{0.70}Pr_{0.05}Nd_{0.25}O_{1.875}$	0.54577	0.16257	0.003
$Ce_{0.60}Pr_{0.05}Nd_{0.35}O_{1.825}$	0.54725	0.16389	0.004
$Ce_{0.50}Pr_{0.05}Nd_{0.45}O_{1.775}$	0.54836	0.16489	0.003
$Ce_{0.50}Pr_{0.05}Nd_{0.55}O_{1.725}$	0.54955	0.16597	0.005
$Ce_{0.40}Pr_{0.05}Nd_{0.65}O_{1.675}$	0.55022	0.16626	0.002

[a] $\Delta 2\upsilon = N^{-1}(2\upsilon_{exp} - 2\upsilon_{calc})$, where $2\upsilon_{exp}$ is the experimental diffraction angle, $2\upsilon_{calc}$ is the angle calculated from lattice parameters, and N is the number of investigated diffraction lines.

4. Conclusions

$Ce_{0.95-y}Pr_{0.05}Nd_yO_{2-y/2}$ type pigments are characterised by heat stability, intense colours and very good hiding power. Due to their high resistance to degradation by molten glazes and enamels, these pigments may be classified as high-temperature pigments. They are suitable for all types of ceramic glazes. In addition, these pigments give interesting pink-orange hues in ceramic glazes.

Acknowledgements

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