

The synthesis and analysis of $\text{Ce}_{0.95-y}\text{Pr}_{0.05}\text{Gd}_y\text{O}_{2-y/2}$ pigments

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Received 9 February 2001; received in revised form 10 April 2001; accepted 17 October 2001

Abstract

The synthesis of new colourants based on CeO_2 has been investigated, the focus of which was the preparation of pigments for colouring ceramic glazes. The synthesis of these colourants involved high-temperature calcination of starting oxides and optimum conditions for their synthesis were determined. The title pigments were evaluated from the standpoint of their structure, colour and ability to dye ceramic glazes. © 2002 Elsevier Science Ltd. All rights reserved.

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

1. Introduction

The synthesis of some new inorganic pigments has been investigated, with particular respect to the preparation of thermally stable pigments that can be used for colouring ceramic glazes. Although it is known that inorganic pigments based on cerium dioxide (CeO_2) possess high-temperature stability, these colourants represent only a small, but an important part of the family of inorganic pigments [1].

Pigments based on CeO_2 in new colour hues have been described [2]. These pigments are characterised by solid solutions of $\text{Ce}_{1-x}\text{Pr}_x\text{O}_2$ having fluorite structures. They give interesting pink–orange and red–brown hues in ceramic media that are based on the incorporation of Pr ions into the host lattice of CeO_2 . CeO_2 -based pigments that utilise an admixture of other lanthanides give

various light or dark pink–orange hues [3]. In the case of the $\text{Ce}_{0.95-y}\text{Pr}_{0.05}\text{La}_y\text{O}_{2-y/2}$ pigments, increasing La content gives pink–orange to yellow hues [4]. Increasing Nd content produces pigments having dark pink–orange to light yellow–orange hues [5].

In the present study, the new pigments are of the formula $\text{Ce}_{1-(x+y)}\text{Pr}_x\text{Gd}_y\text{O}_{2-y/2}$. The goals of this study were to develop conditions for the synthesis of the CeO_2 – PrO_2 – Gd_2O_3 pigments and to determine the influence of gadolinium oxide (Gd_2O_3) on the colouring effects of $\text{Ce}_{0.95-y}\text{Pr}_{0.05}\text{Gd}_y\text{O}_{2-y/2}$ pigments. This work has merit because these pigments afford interesting hues in ceramic glazes, are heat-resistant, and represent potential alternative inorganic pigments from an environmental point of view [6].

2. Experimental

As starting materials for the preparation of the $\text{Ce}_{1-(x+y)}\text{Pr}_x\text{Gd}_y\text{O}_{2-y/2}$ pigments we used CeO_2 of

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95% purity, Pr_6O_{11} of 90% purity, and Gd_2O_3 of 99% purity (Indian Rare Earths Ltd., India).

The starting mixtures containing both basic oxides (CeO_2 and Pr_6O_{11}) with the required content of Gd_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 $10^\circ\text{C}/\text{min}$. The calcination temperature of 1300°C was maintained for 1 h. The pigments (10% w/w) were added to a middle-temperature borate-silicate (transparent leadless) glaze 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 (HunterLab, USA).

The 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. CuK_α ($\lambda = 0.154178\text{ nm}$) radiation was used for the angular range of $2\theta < 35^\circ$ and $\text{K}\alpha_1$ ($\lambda = 0.154051\text{ nm}$) for the range of $2\theta > 35^\circ$, employing a nickel filter for attenuation of the $\text{K}\beta$ radiation. A proportional detector was used.

3. Results and discussion

The effect of increasing Gd content on the colour of pigment powders themselves and pigments applied in borate-silicate glaze was deter-

mined. The results in Table 1 indicate that L^* values increased with increasing Gd content, with the pigment containing 85 mol% Gd having the highest L^* value. The powdered pigments containing 5 to 25 mol% Gd gave red-brown hues, with the powdered pigment containing 5 mol% Gd giving the darkest hue. At higher Gd content, the L^* value increased and the pigment powder was the lightest (Fig. 1). Increasing Gd content above 55 mol% decreased the red character of these pigments and the pigments became brown-yellow (Fig. 2).

Experimental data obtained when these pigments were incorporated into borate-silicate glazes indicated that increasing Gd content produced $\text{Ce}_{0.95-y}\text{Pr}_{0.05}\text{Gd}_y\text{O}_{2-y/2}$ pigments having dark orange to light yellow-orange hues (Fig. 3).

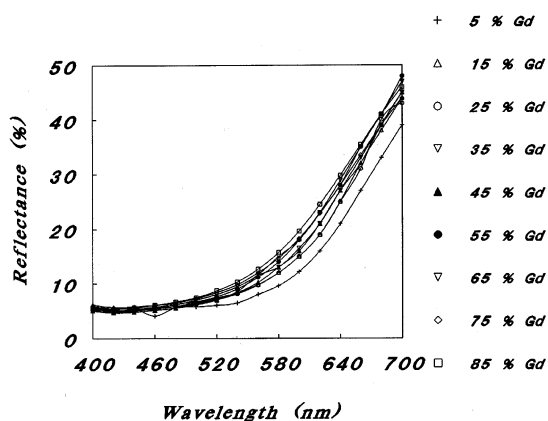


Fig. 1. The effect of Gd content on the colour of the $\text{Ce}_{0.95-y}\text{Pr}_{0.05}\text{Gd}_y\text{O}_{2-y/2}$ pigment powders.

Table 1

The effect of Gd content on the colour properties of $\text{Ce}_{0.95-y}\text{Pr}_{0.05}\text{Gd}_y\text{O}_{2-y/2}$ pigments

Formula	Powder pigments			Pigments applied in glaze		
	L^*	a^*	b^*	L^*	a^*	b^*
$\text{Ce}_{0.90}\text{Pr}_{0.05}\text{Gd}_{0.05}\text{O}_{1.975}$	35.79	16.35	12.72	64.35	20.33	27.23
$\text{Ce}_{0.80}\text{Pr}_{0.05}\text{Gd}_{0.15}\text{O}_{1.925}$	38.81	17.71	16.71	70.66	16.27	26.07
$\text{Ce}_{0.70}\text{Pr}_{0.05}\text{Gd}_{0.25}\text{O}_{1.875}$	39.01	18.22	18.54	72.22	14.81	26.04
$\text{Ce}_{0.60}\text{Pr}_{0.05}\text{Gd}_{0.35}\text{O}_{1.825}$	39.61	18.97	20.78	73.98	12.08	26.58
$\text{Ce}_{0.50}\text{Pr}_{0.05}\text{Gd}_{0.45}\text{O}_{1.775}$	39.92	19.41	21.72	74.04	11.46	26.94
$\text{Ce}_{0.40}\text{Pr}_{0.05}\text{Gd}_{0.55}\text{O}_{1.725}$	41.12	19.73	23.21	74.52	9.46	30.21
$\text{Ce}_{0.30}\text{Pr}_{0.05}\text{Gd}_{0.65}\text{O}_{1.675}$	41.69	19.11	23.51	74.56	9.31	30.32
$\text{Ce}_{0.20}\text{Pr}_{0.05}\text{Gd}_{0.75}\text{O}_{1.625}$	42.01	18.59	23.75	75.83	7.43	35.37
$\text{Ce}_{0.10}\text{Pr}_{0.05}\text{Gd}_{0.85}\text{O}_{1.575}$	43.11	17.89	22.11	78.16	3.05	39.45

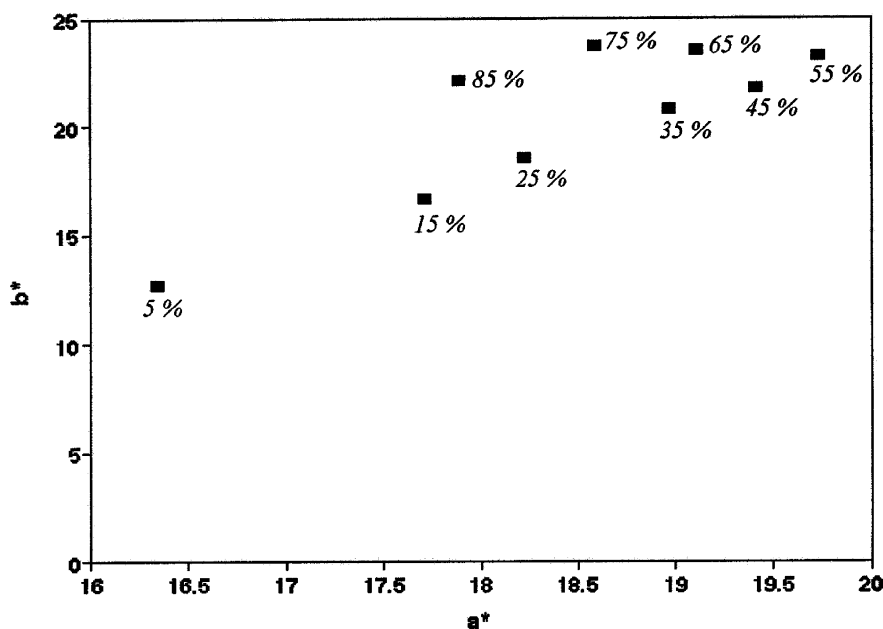


Fig. 2. The effect of Gd content on the colour co-ordinates of $\text{Ce}_{0.95-y}\text{Pr}_{0.05}\text{Gd}_y\text{O}_{2-y/2}$ pigment powders.

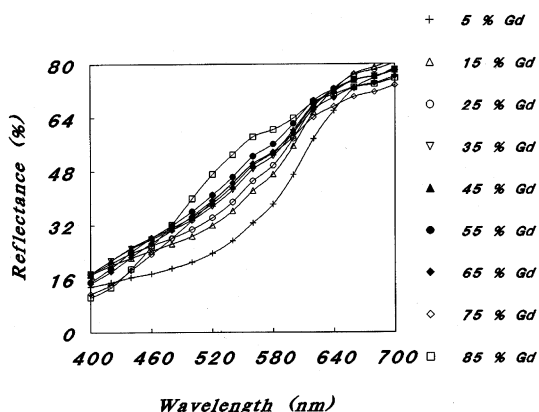


Fig. 3. The effect of Gd content on the colour of $\text{Ce}_{0.95-y}\text{Pr}_{0.05}\text{Gd}_y\text{O}_{2-y/2}$ pigments applied to glazes.

Increasing Gd content increased the L^* value while the colour co-ordinate a^* decreased. Gd content of 5 mol% in the pigment gave an intense orange colour, and the pigments containing 15 and 45 mol% Gd gave pink–orange hues. At higher Gd content (55–65 mol%), the colour intensity and red character of these pigments decreased and they became lighter (Fig. 4). These pigments were yellow–orange. However, the presence of 75 mol%

Gd increased L^* and b^* values and pigment colour was shifted to yellow. Gd content of 85 mol% also produced a yellow colour.

The $\text{Ce}_{0.95-y}\text{Pr}_{0.05}\text{Gd}_y\text{O}_{2-y/2}$ pigments having Gd contents of 5, 15, 25, 35, 45, 55 and 65 mol% were studied by X-ray diffraction. In this regard, diffraction lines that were characteristic of the fluorite structure of CeO_2 were observed. All of the pigments exhibited only peaks that could be assigned to CeO_2 , indicating that they were homogeneous. Praseodymium dioxide (PrO_2) and gadolinium oxide (Gd_2O_3), dissolved in CeO_2 at 1300 °C, forming a solid solution. When Gd contents of 75 and 85 mol% were used, diffraction lines were evident that could be assigned to Gd_2O_3 , as these pigments were heterogeneous.

Pr atoms replaced Ce atoms in the crystal lattice, forming uncharged substitutional defects Pr_{Ce}^x in the solid solution of $\text{Ce}_{0.95-y}\text{Pr}_{0.05}\text{Gd}_y\text{O}_{2-y/2}$ pigments. Pr entered the CeO_2 matrix as substitutional defects because the tetravalent Pr ion [$r(\text{Pr}^{4+}) = 0.092 \text{ nm}$] has a smaller radius than the tetravalent Ce ion [$r(\text{Ce}^{4+}) = 0.101 \text{ nm}$]. Ions of gadolinium [$r(\text{Gd}^{3+}) = 0.102 \text{ nm}$] that enter into the fluorite structure are a little larger than Ce^{4+} ions that were substituted. The formation of these defects is

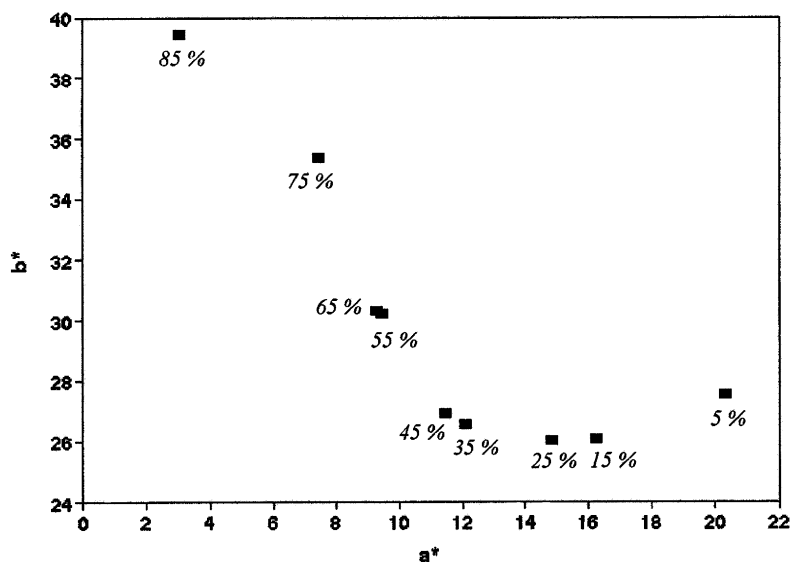


Fig. 4. The effect of Gd content on a^* and b^* values of $\text{Ce}_{0.95-y}\text{Pr}_{0.05}\text{Gd}_y\text{O}_{2-y/2}$ pigments applied to glazes.

Table 2
Lattice parameters for $\text{Ce}_{0.95-y}\text{Pr}_{0.05}\text{Gd}_y\text{O}_{2-y/2}$ pigments

Formula	a (nm)	V (nm ³)	$\Delta 2\nu$
CeO_2	0.54221	0.15941	0.002
$\text{Ce}_{0.90}\text{Pr}_{0.05}\text{Gd}_{0.05}\text{O}_{1.975}$	0.54306	0.16016	0.002
$\text{Ce}_{0.80}\text{Pr}_{0.05}\text{Gd}_{0.15}\text{O}_{1.925}$	0.54337	0.16043	0.001
$\text{Ce}_{0.70}\text{Pr}_{0.05}\text{Gd}_{0.25}\text{O}_{1.875}$	0.54371	0.16073	0.003
$\text{Ce}_{0.60}\text{Pr}_{0.05}\text{Gd}_{0.35}\text{O}_{1.825}$	0.54395	0.16094	0.002
$\text{Ce}_{0.50}\text{Pr}_{0.05}\text{Gd}_{0.45}\text{O}_{1.775}$	0.54416	0.16113	0.001
$\text{Ce}_{0.50}\text{Pr}_{0.05}\text{Gd}_{0.55}\text{O}_{1.725}$	0.54432	0.16127	0.003
$\text{Ce}_{0.40}\text{Pr}_{0.05}\text{Gd}_{0.65}\text{O}_{1.675}$	0.54446	0.16139	0.002

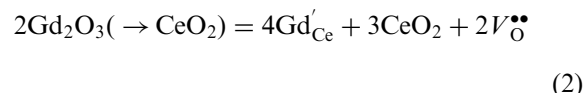
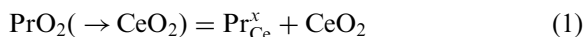
$\Delta 2\nu = N^{-1}(2\nu_{\text{exp}} - 2\nu_{\text{calc}})$, where $2\nu_{\text{exp}}$ is the experimental diffraction angle, $2\nu_{\text{calc}}$ is the angle calculated from lattice parameters, and N is the number of investigated diffraction lines.

associated with an increase in the volume of the elementary CeO_2 cell (Table 2).

The values for the lattice parameters of the $\text{Ce}_{0.95-y}\text{Pr}_{0.05}\text{Gd}_y\text{O}_{2-y/2}$ pigments are given in Table 2 and show that the lattice parameter “ a ” increased with increasing Gd_2O_3 content. The volume of the elementary cell of CeO_2 also increased with increasing Gd_2O_3 content.

Ions of Gd entered the pigment structure as negatively charged defects (Gd'_{Ce}). The strongly negative charge of these defects was compensated by the positively charged substitution defects ($\text{V}_{\text{O}}^{\bullet\bullet}$). It is anticipated that the variations in the

lattice parameters of CeO_2 are associated with the formation of a solid solution of CeO_2 , PrO_2 and Gd_2O_3 . Such a solution is probably of the substitutional type, where Pr^{4+} and Gd^{3+} cations were substituted in Ce^{4+} lattice positions forming uncharged electrically neutral defects (Pr^x_{Ce}) and negatively charged defects (Gd'_{Ce}) that were compensated for by oxygen vacancies ($\text{V}_{\text{O}}^{\bullet\bullet}$). The formation of these defects can be described using Eqs. (1)–(2):



In other experiments, the $\text{Ce}_{0.95-y}\text{Pr}_{0.05}\text{Gd}_y\text{O}_{2-y/2}$ pigments were added to high temperature glazes that are used for sanitary ceramics. The glazing temperature was above 1250 °C and the pigments were found to be heat and chemical stable under these conditions. Their colour and hiding power were unchanged.

4. Conclusion

The title $\text{Ce}_{0.95-y}\text{Pr}_{0.05}\text{Gd}_y\text{O}_{2-y/2}$ pigments have fluorite structures. They are heat and chemical

resistant and can be used even in high temperature glazes for sanitary ceramics. These pigments have very good hiding power and intense colours in glazes. Increasing the Gd content produces pigments having dark orange (5 mol% Gd) to yellow hues (85 mol% Gd) in middle-temperature transparent leadless glazes. These pigments are insoluble in concentrated H_2SO_4 and HCl while the starting oxides are soluble. This property demonstrates the strength of their crystal lattice.

Acknowledgements

The preparation of the title of pigments was investigated within the framework of a grant project dealing with new ecologically friendly coloured

inorganic pigments. This work was supported by the grant No. 104/98/P227 from the Grant Agency of Czech Republic.

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