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The synthesis and analysis of $Ce_{0.95-y}Pr_{0.05}Sm_yO_{2-y/2}$ pigments

Petra Šulcová*, Miroslav Trojan

Department of Inorganic Technology, Faculty of Chemical Technology, University of Pardubice, Legions Sq. 565, 532 10 Pardubice, Czech Republic

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Abstract

The synthesis of new colorants based on CeO_2 has been investigated, the focus of which was the preparation of pigments for colouring ceramic glazes. The synthesis of these colorants involved high-temperature calcination of the oxides and determination of the optimum conditions for their synthesis. The pigments were evaluated in terms of their structure, colour and ability to color ceramic glazes.

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

1. Introduction

Each pigment has a defined crystal structure that is determined by the host lattice. Other oxides interdiffuse at high temperatures into the host lattice structure forming either a solid-state solution or a new compound. Most mixed metal oxide pigments contain metal cations balanced by oxygen anions with structures similar to naturally occurring minerals. Their commercial significance is in their high thermal, chemical and light stability, combined with their low toxicity. When they are employed for colouring glass enamels and ceramics, they are sometimes referred to as *colours* or *stains*; when used to colour paints and plastics, they are known as *pigments* [1].

The colour of mixed metal oxide pigments results from the incorporation of the cation of transition metals, so-called chromophores, into the structure of stable host oxides. The host can be a single oxide (e.g. SnO_2, TiO_2) or a mixed oxide (e.g. $ZrSiO_4$, $MgAl_2O_4$). Typical examples of the chromophores are transition metal ions (Fe, Cr, Mn, Ni, Co, Cu, V, etc.) and rare earth elements (Ce, Pr, Nd).

The pigments of CeO_2 belong to special inorganic pigments with high-temperature stability [2] which are characterised by solid solutions of Ce_{1-x} Pr_xO_2 pigments 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 $Ce_{0.95-y}Pr_{0.05}La_yO_{2-y/2}$ pigments, increasing the La content gives pink-orange to yellow hues [4] which increasing the Nd content produces pigments having dark pink-orange to light yellow–orange

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* Corresponding author. Fax: +420-40-603-7275.
E-mail address: petra.sulcova@upce.cz (P. Šulcová).

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hues [5]. The presence of Gd in $Ce_{0.95-y}Pr_{0.05}Gd_yO_{2-y/2}$ pigments [6] gives colours that range from dark orange (5 mol.% Gd) to yellow (85 mol.% Gd).

In the present study, pigments of formula $Ce_{1-(x+y)}Pr_xSm_yO_{2-y/2}$ were synthesised. The goals of this study were to determine the optimum conditions for the synthesis of the CeO_2–PrO_2–Sm_2O_3 pigments and to determine the influence of samarium oxide (Sm_2O_3) on the colouring effects of $Ce_{0.95-y}Pr_{0.05}Sm_yO_{2-y/2}$ pigments. This work has merit because such pigments afford interesting hues in ceramic glazes, are heat-resistant and represent potential alternative inorganic pigments from an environmental point of view.

2. Experimental

As starting materials for the preparation of the $Ce_{1-(x+y)}Pr_xSm_yO_{2-y/2}$ pigments, CeO_2 of 95% purity, Pr_6O_{11} of 90% purity, Sm_2O_3 of 99% purity were used (Indian Rare Earths Ltd.).

The starting mixtures containing both basic oxides (CeO_2 and Pr_6O_{11}) with the required content of Sm_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^{-1}. 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).

The X-ray diffractograms of pigment powders were obtained using a vertical X-ray diffractometer HZG-4B (Freiberger Präzisionsmechanik) 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

The effect of increasing Sm content on the colour of pigment powders and pigments applied in borate–silicate glaze was determined. The colour properties are described in terms of CIE $L^*a^*b^*$ system (1976). The value a^* represents the redness/greenness axis and value b^* the yellowness/blueness axis. The value L^* represents the lightness or darkness of the colour as related to a neutral gray scale. In the $L^*a^*b^*$ system it is described by numbers from 0 (black) to 100 (white).

The results in Table 1 show that L^* values increased with increasing Sm content, with the pigment containing 85 mol.% Sm having the highest L^*. The powdered pigments containing 5–25 mol.% Sm gave from brown to brown-red hues, with the powder pigment containing 5 mol.% Sm giving the darkest hue. At higher Sm content, the L^* value increased and the pigment powder was palest (Table 1). The presence of 35–55 mol.% Sm produced pigments having red-brown hues. Increasing Sm content above 45 mol.% reduced the red character of the pigments and the pigments changed from orange-brown color (65–75 mol.% Sm) to brown-yellow in case of 85 mol.% Sm (Fig. 1).

Experimental data obtained when these pigments were incorporated into borate-silicate glazes indicated that increasing Sm content produced $Ce_{0.95-y}Pr_{0.05}Sm_yO_{2-y/2}$ pigments having intense pink–orange to light yellow-orange hues (Fig. 2). Increasing Sm content increased the L^* value while the a^* decreased and b^* increased. Sm content from 5 to 35 mol.% in pigment gave an intense pink-orange colour, and the pigments containing 45 and 55 mol.% Sm gave yellow-orange hues. At higher Sm content (65–75 mol%) value a^* of these pigments decreased, values L^* and b^* increased and they became lighter (Table 1). These pigments are characterised by light yellow-orange colour. However, the presence of 85 mol.% Sm increased L^* and b^* values and pigment colour was shifted to yellow (Fig. 2). Sm content of 85 mol.% also produced yellow colour.

The $Ce_{0.95-y}Pr_{0.05}Sm_yO_{2-y/2}$ pigments having Sm contents of 5, 15, 25, 35, 45 and 55 mol.% were studied by X-ray diffraction. In this regard,

Table 1
The effect of Sm content on the colour properties of $Ce_{0.95-y}Pr_{0.05}Sm_yO_{2-y/2}$ pigments

Formula	Powder pigments			Pigments applied in glaze		
	*L**	*a**	*b**	*L**	*a**	*b**
$Ce_{0.90}Pr_{0.05}Sm_{0.05}O_{1.975}$	36.06	18.07	14.24	65.27	19.18	25.72
$Ce_{0.80}Pr_{0.05}Sm_{0.15}O_{1.925}$	37.11	18.51	17.06	69.81	16.77	25.74
$Ce_{0.70}Pr_{0.05}Sm_{0.25}O_{1.875}$	37.61	18.71	17.68	72.19	14.71	25.47
$Ce_{0.60}Pr_{0.05}Sm_{0.35}O_{1.825}$	38.06	19.04	19.05	73.62	13.46	26.01
$Ce_{0.50}Pr_{0.05}Sm_{0.45}O_{1.775}$	38.65	19.31	21.05	75.01	11.51	26.71
$Ce_{0.40}Pr_{0.05}Sm_{0.55}O_{1.725}$	38.67	19.08	22.06	75.15	10.41	27.45
$Ce_{0.30}Pr_{0.05}Sm_{0.65}O_{1.675}$	38.91	18.91	22.91	75.35	9.54	30.45
$Ce_{0.20}Pr_{0.05}Sm_{0.75}O_{1.625}$	39.64	18.86	23.04	75.97	8.91	33.11
$Ce_{0.10}Pr_{0.05}Sm_{0.85}O_{1.575}$	42.53	18.43	24.41	76.63	7.19	42.67

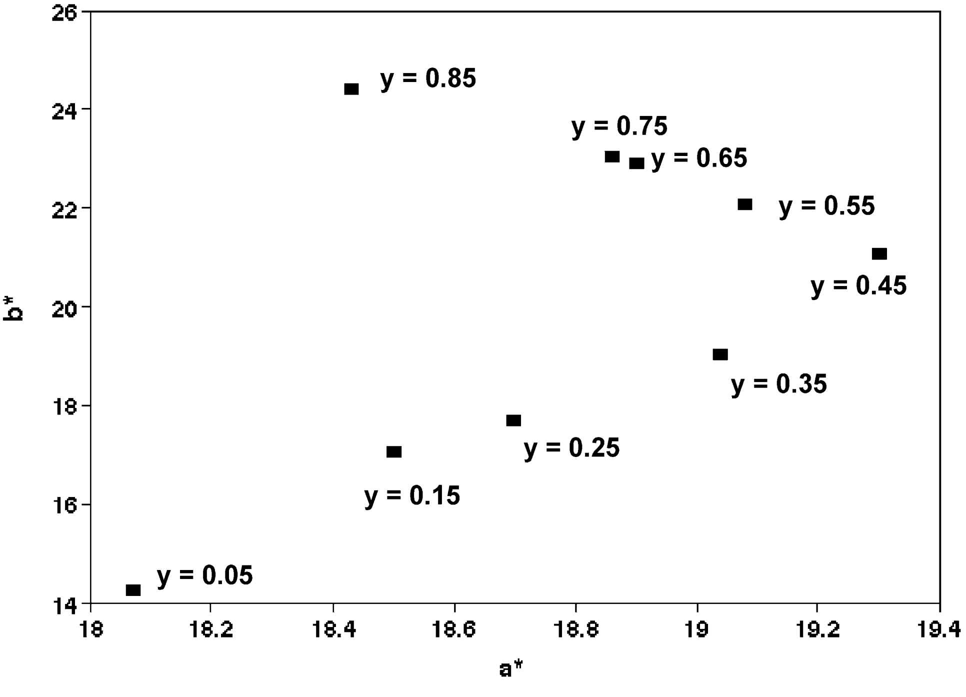

Fig. 1. The effect of Sm content on the colour co-ordinates *a** and *b** of $Ce_{0.95-y}Pr_{0.05}Sm_yO_{2-y/2}$ pigment powders.

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 samarium oxide (Sm_2O_3), dissolved in CeO_2 at 1300 °C, forming a solid solution. When Sm contents of 65, 75 and 85 mol.% were used, diffraction lines were evident that could be assigned to free Sm_2O_3, as these pigments were heterogeneous. The lattice parameter for cubic lattice of Sm_2O_3, which was presented in sample with higher Sm content (85 mol.%), was determined and is 1.089 nm.

Pr atoms replaced Ce atoms in the crystal lattice, forming uncharged substitutional defects Pr_{Ce}^{X} in the solid solution of $Ce_{0.95-y}Pr_{0.05}Sm_yO_{2-y/2}$ pigments. Pr entered the CeO_2 matrix as substitutional defects because the tetravalent Pr ion

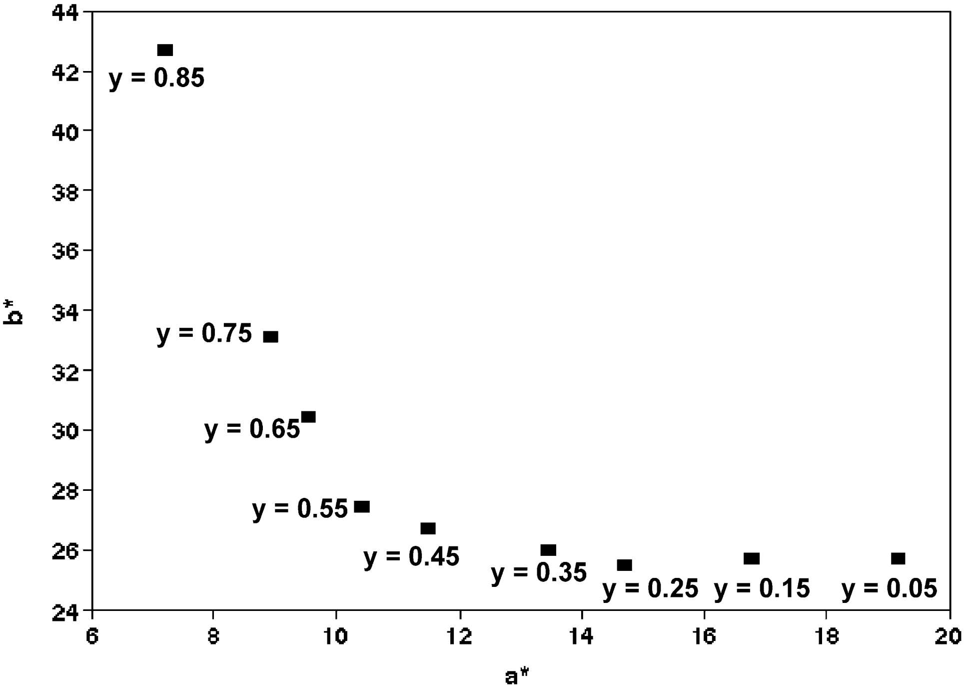

Fig. 2. The effect of Sm content on the colour co-ordinates a^* and b^* of $Ce_{0.95-y}Pr_{0.05}Sm_yO_{2-y/2}$ pigments applied to glaze.

[$r(Pr^{4+}) = 0.092$ nm] has a smaller radius than the tetravalent Ce ion [$r(Ce^{4+}) = 0.101$ nm]. Ions of samarium [$r(Sm^{3+}) = 0.104$ nm] have a little larger radius than Ce^{4+} ions. Sm^{3+} ions enter the fluorite structure where substitute Ce^{4+} ions. The formation of these defects is associated with an increase in the volume of the elementary CeO_2 cell (Table 2).

The values of the lattice parameters of the $Ce_{0.95-y}Pr_{0.05}Sm_yO_{2-y/2}$ pigments are given in Table 2 and show that the lattice parameter a increased with increasing Sm_2O_3 content. The volume of the elementary cell of CeO_2 also increased with increasing Sm_2O_3 content.

Ions of Sm entered the pigment structure as negatively charged defects Sm'_{Ce}. The strongly negative charge of these defects was compensated by the positively charged substitution defects $V_O^{\bullet\bullet}$. 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 Sm_2O_3. Such a solution is probably of the substitutional

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

Formula	a (nm)	V (nm^3)	$\Delta 2\upsilon$
CeO_2	0.54221	0.15941	0.002
$Ce_{0.90}Pr_{0.05}Sm_{0.05}O_{1.975}$	0.54417	0.16114	0.002
$Ce_{0.80}Pr_{0.05}Sm_{0.15}O_{1.925}$	0.54421	0.16118	0.001
$Ce_{0.70}Pr_{0.05}Sm_{0.25}O_{1.875}$	0.54427	0.16123	0.001
$Ce_{0.60}Pr_{0.05}Sm_{0.35}O_{1.825}$	0.54435	0.16131	0.002
$Ce_{0.50}Pr_{0.05}Sm_{0.45}O_{1.775}$	0.54436	0.16131	0.002
$Ce_{0.40}Pr_{0.05}Sm_{0.55}O_{1.675}$	0.54445	0.16139	0.002

$\Delta\upsilon = N^{-1}(2\upsilon_{exp} - \upsilon_{calc})$, 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.

type, where Pr^{4+} and Sm^{3+} cations were substituted in Ce^{4+} lattice positions forming uncharged electrically neutral defects (Pr^{x}_{Ce}) and negatively charged defects (Sm'_{Ce}) that were compensated for by oxygen vacancies ($V^{\bullet\bullet}_{O}$). The formation of these defects can be described by Eqs. (1)–(2):

$$PrO_2(\rightarrow\ CeO_2) = Pr^{x}_{Ce} + CeO_2 \qquad (1)$$

$$2Sm_2O_3(\rightarrow\ CeO_2) = 4Sm'_{Ce} + 3CeO_2 + 2V^{\bullet\bullet}_{O} \qquad (2)$$

In other experiments, the $Ce_{0.95-y}Pr_{0.05}Sm_yO_{2-y/2}$ pigments were added to high temperature glazes that are used for sanitary ceramics. The glazing temperature was above 1250 °C and the pigments were heat and chemical stable under these conditions. Their colour and hiding power were unchanged.

4. Conclusions

The $Ce_{0.95-y}Pr_{0.05}Sm_yO_{2-y/2}$ pigments with fluorite structures 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 Sm content produces pigments having pink-orange (5–35 mol% Gd), yellow-orange (45–55 mol.%) to light yellow hues (85 mol.% Gd) in middle-temperature transparent leadless glazes.

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