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

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Abstract

The synthesis of some new inorganic pigments has been investigated. In this regard, emphasis was placed on the preparation of heat-resistant pigments. The synthesis of the title pigments is based on high-temperature calcination of CeO_2 and Pr_6O_{11}, and the optimum conditions for pigment formation have been determined The pigments were evaluated from the standpoint of their structure, colour and ability to dye ceramic glazes. © 2000 Elsevier Science Ltd. All rights reserved.

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1. Introduction

The goal of this study was to develop conditions for the synthesis of pigments based on a fluorite structure of CeO_2 with admixed La_2O_3. The influence of La_2O_3 on the colouring effects of $Ce_{0.95-y}Pr_{0.05}La_yO_{2-y/2}$ pigments was also studied.

The pigments for colouring ceramics, usually inorganic products composed of metal oxides or compounds capable of forming metal oxides, must possess thermal and chemical stability at high temperature 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 have dominated research and development in this area in recent years.

Our approach in the present investigation focused on the preparation of pigments based on cerium dioxide (CeO_2) that are stable at very high temperatures. Pigments based on CeO_2 are known to give various pink–orange hues in ceramic glazes [2]. This type of pigment is prepared by high temperature calcination of CeO_2 and Pr_6O_{11}. In this process, Pr_6O_{11}, dissolves in hot CeO_2 forming a $Ce_{1-X}Pr_XO_2$ solid solution.

In the present study, the new pigments are of the formula $Ce_{1-(x+y)}Pr_xLa_yO_{2-y/2}$. Lanthanum oxide ($La_2O_3$) and praseodymium dioxide (PrO_2) dissolve in cerium oxide at 1300°C forming a solid solution of the three oxides. CeO_2–PrO_2–La_2O_3 pigments give very interesting red hues in the ceramic glaze. These heat-resistant, chemical-resistant pigments have a fluorite structure and represent potential environmentally friendly inorganic colorants [2]. They are insoluble in concentrated sulfuric acid and hydrochloric acid while the starting oxides are soluble. This solubility behavior can be

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used to detect the strength of the crystal lattice of pigments prepared.

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2. Experimental

As starting materials for the preparation of the $Ce_{1-(x+y)}Pr_xLa_yO_{2-y/2}$ pigments, we used CeO_2 of 95% purity, and Pr_6O_{11}, of 90% purity, and La_2O_3 of 99% purity (Indian Rare Earths Ltd., India).

The starting mixtures of CeO_2 and Pr_6O_{11} containing La_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 to 1300°C at 10°C/min, and holding there for a period of 1 h. The pigments (10%, w/w) were added to a middle-temperature borate-silicate glaze at a glazing temperature of 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. Cu K_α ($\lambda=0.154178$ run) radiation was used for the angular range of $2\theta<35°$ and $K_{\alpha1}$ ($\lambda=0.154051$ mn) 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 effects of increasing La content on the colour of pigment powders and pigments mixed with borate–silicate glaze were determined. From Table 1 it is seen that L^* values increased with increasing La content, with the pigment containing 85 mol% La having the highest L^* value. The powdered pigments containing 5 to 55 mol% La have red-brown hues, with the pigment containing 5 mol% La giving the darkest hues. At higher La the L^* value increased and the pigment powder became the lightest (Fig. 1). Increasing La content above 55 mol% decreased 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 La content produced $Ce_{0.95-y}Pr_{0.05}La_yO_{2-y/2}$ pigments having dark pink–orange to light yellow–orange hues (Fig. 3). Increasing La content

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

	Pigment powders			Pigments in glaze		
Formula	L^*	a^*	b^*	L^*	a^*	b^*
$Ce_{0.90}Pr_{0.05}La_{0.05}O_{1.975}$	47.35	12.12	9.77	66.23	20.31	26.94
$Ce_{0.80}Pr_{0.05}La_{0.15}O_{1.925}$	50.87	14.43	15.88	71.16	17.66	26.57
$Ce_{0.70}Pr_{0.05}La_{0.25}O_{1.875}$	52.79	15.61	18.52	73.41	15.82	26.45
$Ce_{0.60}Pr_{0.05}La_{0.35}O_{1.825}$	59.45	15.24	23.56	76.34	11.31	23.54
$Ce_{0.50}Pr_{0.05}La_{0.45}O_{1.775}$	60.97	14.76	23.95	77.99	10.78	24.54
$Ce_{0.40}Pr_{0.05}La_{0.55}O_{1.725}$	63.09	14.36	24.18	79.69	7.94	22.92
$Ce_{0.30}Pr_{0.05}La_{0.65}O_{1.675}$	70.61	11.32	22.01	80.73	5.84	25.13
$Ce_{0.20}Pr_{0.05}La_{0.75}O_{1.625}$	78.77	7.84	18.71	82.71	2.02	29.98
$Ce_{0.10}Pr_{0.05}La_{0.85}O_{1.575}$	85.42	4.85	14.64	83.21	−0.58	34.34

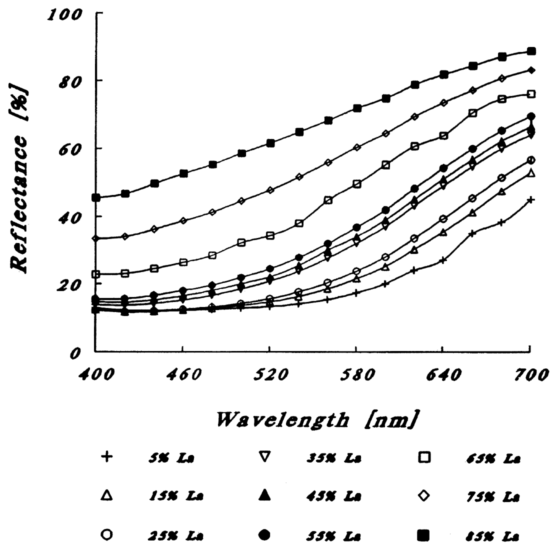

Fig. 1. The effect of La content on the colour of $Ce_{0.95-y}Pr_{0.05}La_yO_{2-y/2}$ pigment powders.

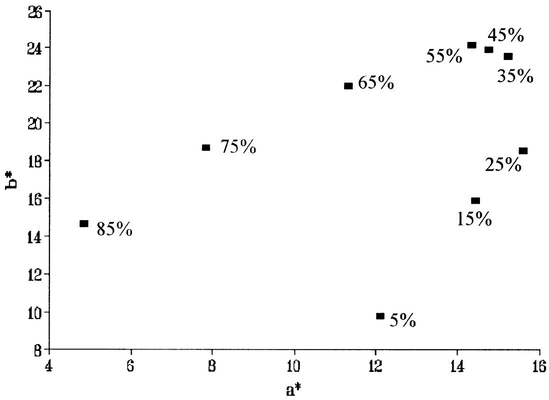

Fig. 2. The effect of La content on the colour coordinates of $Ce_{0.95-y}Pr_{0.05}La_yO_{2-y/2}$ pigment powders.

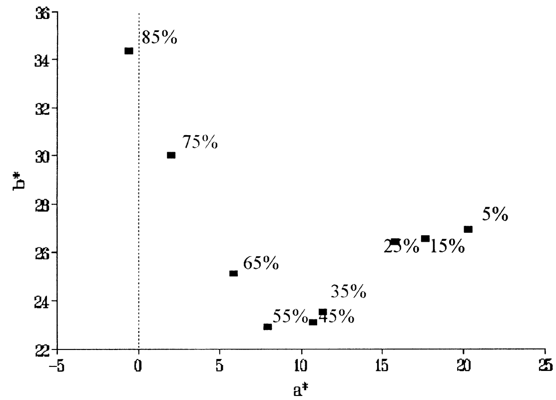

Fig. 4. The effect of La content on a* and b* values of $Ce_{0.95-y}Pr_{0.05}La_yO_{2-y/2}$ pigments applied to glazes.

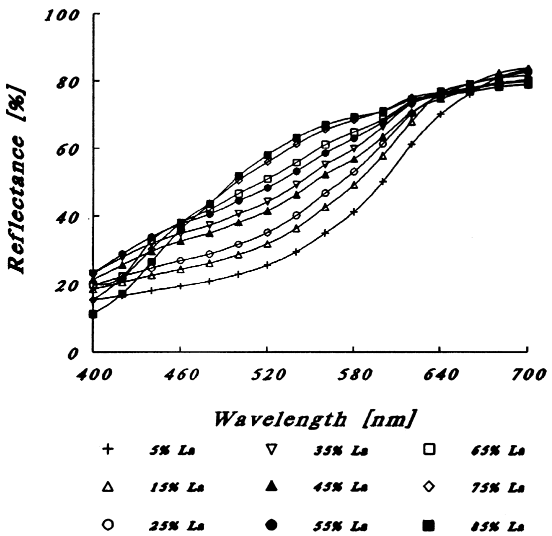

Fig. 3. The effect of La content on the colour of the $Ce_{0.95-y}Pr_{0.05}La_yO_{2-y/2}$ pigments applied to glazes.

increased the L^* value while the colour coordinate a^* decreased. La content of 5 to 25 mol% in pigments gave intense pink–orange hues. At La content of 35–55 mol% the colour intensity and red character of these pigments decreased (Fig. 4). La content of 65 to 85 mol% increased L^* and b^* values, and pigment colour was shifted to yellow and becames lighter.

The structure of the $Ce_{0.95-Y}$ $Pr_{0.05}La_yO_{2-y/2}$ pigments was also investigated. Pigments having La content of 5, 15, 25, 35, 45 and 55 mol% were studied by X-ray diffraction analysis. Diffraction lines 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. PrO_2 and La_2O_3, dissolved in CeO_2 at 1300°C, to form a solid solution. When La content of 65, 75 and 85 mol% was used, peaks were evident that could be assigned to La_2O_3, as these pigments were heterogeneous.

Pr atoms replace Ce atoms in the crystal lattice forming unchanged substitutional defects (Pr_{Ce}^{X}) in a solid solution of $Ce_{0.95-y}Pr_{0.05}La_yO_{2-y/2}$. Pr enters into CeO_2 as substitutions defects 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] [3]. Ions of lanthanum [$r(La^{3+}) = 0.115$ nm], that enter the fluorite structure are a little larger than the Ce^{4+} ions, which are substituted. 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 $Ce_{0.95-Y}Pr_{0.05}La_yO_{2-y/2}$ pigments are given in Table 2 and show that the lattice parameter a increased with increasing La_2O_3 content. The volume of the elementary cell of CeO_2 also increased with increasing La_2O_3 content.

Ions of La enter the pigment structure as negatively charged defects Ln_{Ce}'. The strongly negative charge of these defects is compensated by the

Table 2
Lattice parameters of $Ce_{0.95-y}Pr_{0.05}La_yO_{2-y/2}$ pigments

Formula	*a* (nm)	*V* (nm^3)	$\Delta 2\nu^a$
CeO_2	0.54221	0.15941	0.004
$Ce_{0.90}Pr_{0.05}La_{0.05}O_{1.975}$	0.54486	0.16175	0.005
$Ce_{0.80}Pr_{0.05}La_{0.15}O_{1.925}$	0.55021	0.16656	0.003
$Ce_{0.70}Pr_{0.05}La_{0.25}O_{1.875}$	0.55424	0.17025	0.005
$Ce_{0.60}Pr_{0.05}La_{0.35}O_{1.825}$	0.55759	0.17328	0.006
$Ce_{0.50}Pr_{0.05}La_{0.45}O_{1.775}$	0.55984	0.17547	0.001
$Ce_{0.40}Pr_{0.05}La_{0.55}O_{1.725}$	0.56102	0.17658	0.005

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

positively charged substitution defects (V_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 La_2O_3 [4]. Such a solution is probably of the substitutional type, where Pr^{4+} and La^{3+} cations are substituted in Ce^{4+} lattice positions, forming uncharged electrically neutral defects (Pr^x_{ce}) and negatively charged defects (La_{Ce}') that are compensated for by oxygen vacancies ($V_o^\bullet$) The formation of these defects can be described by Eqs. (1) and (2).

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

$$2La_2O_3(\rightarrow\ CeO_2) \Longleftrightarrow 4La'_{Ce} + 3CeO_2 + 4V^\bullet_o \quad (2)$$

4. Conclusion

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

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