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Cerium Dioxide Fluorite Type Pigments

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ABSTRACT

Pigments of cerium-praseodymium type have not been well known. They are of interest with respect to their colour hues in ceramic glazes, and are based on the incorporation of praseodymium ions into the host lattice of cerium dioxide. We have now studied possibilities for the preparation of $Ce_{1-x}Pr_xO_2$ *pigments, their properties, structure, quality and possible applications for ceramic glazes.* © *1998 Elsevier Science Ltd*

Keywords: ceramic pigments, solid solutions CeO_2–PrO_2, optical properties.

INTRODUCTION

Pigments based on cerium dioxide CeO_2 with an admixture of praseodymium are lesser known ceramic pigments. This type of pigment gives interesting pink–orange and red–brown hues in ceramic glazes. These pigments are characterized by high heat stability and chemical resistance. Pigments of cerium-praseodymium type are formed by a solid solution $Ce_{1-x}Pr_xO_2$ with the fluorite structure of CeO_2 and are prepared by high-temperature calcination of the basic starting oxides CeO_2 and Pr_6O_{11}.

EXPERIMENTAL

As starting materials for the preparation of the $Ce_{1-x}Pr_xO_2$ pigments we used CeO_2 of 95% purity and Pr_6O_{11} of 90% purity (Indian Rare Earths Ltd). The starting mixtures containing both basic oxides were homogenized in an agate mortar. The mixtures were then calcinated at chosen temperatures in corundum crucibles in an electric resistance furnace (the rate of temperature increase was 10°C min^{-1}). The calcination temperatures were in the range from 1250–1350°C for one hour. When the mineralizers were used, the calcinates were extracted with hot hydrochloric acid (100 ml 0.3 M HCl/10 g pigments, 20 min boiling) to remove soluble residues of the mineralizers. The extracted and dried pigments were applied to a middle-temperature borate-silicate glaze in amounts of 10% (w/w) with a glazing temperature of 1000°C for 15 min. The final glazes were evaluated with regard to their colour hues by measurements of spectral reflectance in the visible region using a MiniScan (HunterLab, USA).

The powder pigments were studied by X-ray diffraction analysis (X-ray diffractometer HZG4B, Freiberger Pracisionsmechanic, Germany).

RESULTS AND DISCUSSION

Initially studied were the calcination conditions of the pigment preparation and the effect of the praseodymium content in the starting mixtures on the colour hue of the pigment.

The starting mixtures containing an increasing content of praseodymium (5, 9, 17, 33, 40 and 50 mol% Pr) were homogenized in an agate mortar. The mixtures were calcinated at three chosen temperatures (1250, 1300 and 1350°C) for one hour. From Fig. 1 it follows that the most intensive pink–orange hues of the $Ce_{1-x}Pr_xO_2$ pigments are obtained at a calcination temperature of

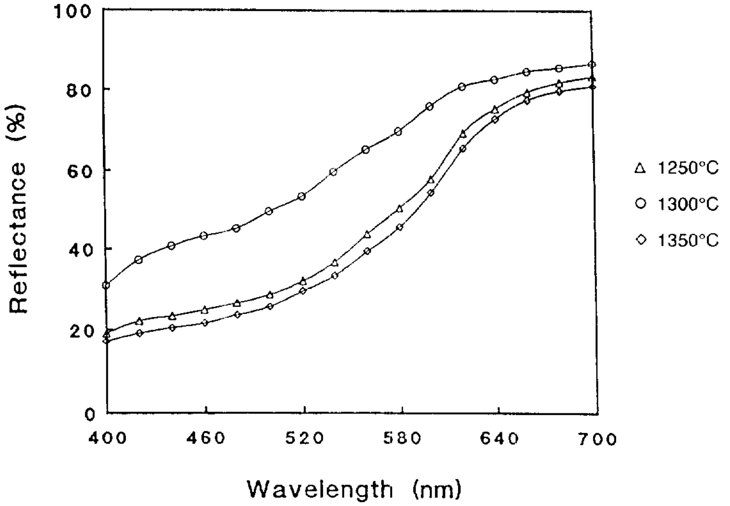

Fig. 1. The effect of the calcination temperature on the colour hue of the $Ce_{0.91}Pr_{0.09}O_2$ pigment.

1300°C. At higher temperature the colour intensity increases only a little, but the colour hue does not differ from the pigments calcinated at 1300°C. At a calcination temperature of 1250°C the *L** values increase and these pigments become the lightest.

The structure of these pigments of cerium-praseodymium type was then investigated. The samples with increasing praseodymium content (5, 9, 17, 33, 40 and 50 mol%) were studied by X-ray diffraction analysis. The observed diffraction lines corresponded with the characteristic lines of the fluorite structure of cerium dioxide. The samples with the highest content of praseodymium (50 mol%) exhibited only peaks which could be assigned to cerium dioxide. This means that all samples are homogeneous. Praseodymium dioxide, PrO_2, dissolves in cerium dioxide during the heat treatment of the starting mixture at the temperature of 1300°C, forming a solid solution of both oxides. The values of the lattice parameters of cerium dioxide (Table 1) show that parameter *a* decreases with increasing content of praseodymium (Fig. 2). Praseodymium atoms substitute cerium atoms in

TABLE 1

Lattice Parameters of Samples of the $Ce_{1-x}Pr_xO_2$ Pigments

mol% Ce	*mol% Pr*	*a (nm)*	*V (nm³)*
100	0	0.54111	0.15843
95	5	0.54105	0.15839
91	9	0.054097	0.15831
83	17	0.54081	0.15817
75	25	0.54068	0.15806
67	33	0.54054	0.15794
60	40	0.54044	0.15785
50	50	0.54043	0.15784

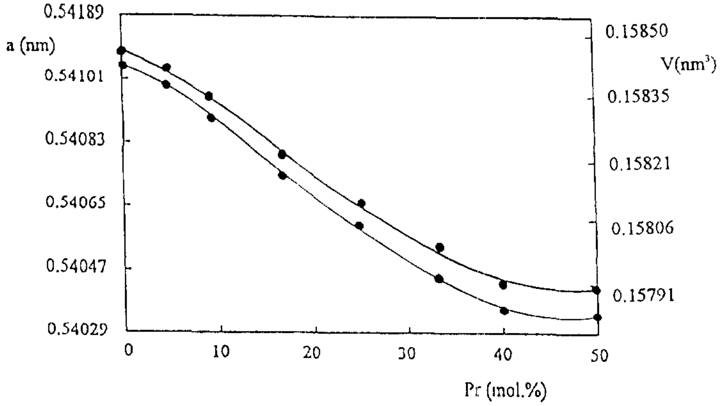

Fig. 2. The dependence of the crystal lattice parameter *a* and the volume of the elementary cell V on the increasing content of praseodymium.

their crystal lattice, forming uncharged substitutional defects $\mathrm{Pr}^{x}_{\mathrm{Ce}}$ in the solid solution $\mathrm{Ce}_{1-x}\mathrm{Pr}_x\mathrm{O}_2$.

The formation of these defects is associated with the decrease of the volume of the elementary cell of cerium dioxide (Fig. 2). Praseodymium enters into cerium dioxide as substitutional defects instead of cerium, because the tetravalent praseodymium ion [r(Pr4+) = 0.092 nm] has a smaller radius than the tetravalent cerium ion [$r(\mathrm{Ce}^{4+}) = 0.101$ nm].

The effect of the praseodymium content in the mixtures on the colour hue of these pigments is demonstrated in Figs 3 and 4. The increasing content of

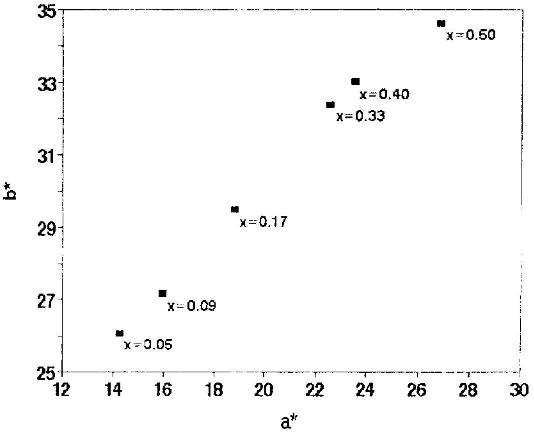

Fig. 3. The effect of the increasing content of praseodymium on the colour hue of the $\mathrm{Ce}_{1-x}\mathrm{Pr}_x\mathrm{O}_2$ pigment in a^*, b^* coordinates.

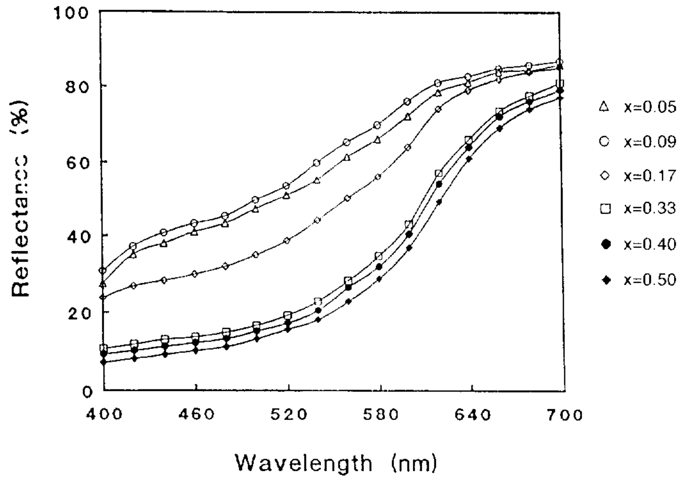

Fig. 4. The effect of the increasing content of praseodymium on the colour hue of the $\mathrm{Ce}_{1-x}\mathrm{Pr}_x\mathrm{O}_2$ pigments.

praseodymium increases the red hue of these pigments. The intensive pink–orange colour with the acceptably low content of praseodymium was found with the pigment containing 9 mol% of praseodymium. This pigment can be described by the formula $Ce_{0.91}Pr_{0.09}O_2$. When 50 mol% of praseodymium is used, the hue of the pigment shifted to red–brown (Table 2).

The effect of mineralizers on the hue of the $Ce_{0.91}Pr_{0.09}O_2$ pigment was then studied. All mineralizers were added to the starting mixtures in an amount of 10% by weight. The pigments were synthesised at a temperature of 1300°C for one hour.

The presence of LiF, Li_2CO_3, MgF_2, Na_2CO_3 and K_2CO_3 as mineralizers was shown to be markedly effective on the colour hue of the $Ce_{0.91}Pr_{0.09}O_2$ pigment. With these mineralizers, the pigments become a darker colour, viz., from pink–orange to red–brown. Their presence increases the red hue of these pigments (i.e. decrease of the L^* value and increase of the a^* value). When Li_2CO_3 and K_2CO_3 are used, the pigment colours were shifted to a red–brown hue and the tendency to sintering was increased (Fig. 5).

TABLE 2

The Effect of the Increasing Content of Praseodymium on the Colour Hue of the $Ce_{1-x}Pr_xO_2$ Pigment in L^*, a^*, b^* coordinates

$Ce_{1-x}Pr_xO_2$	L^*	a^*	b^*
x = 0.05	73.71	14.26	26.08
x = 0.09	72.71	15.96	27.17
x = 0.17	67.78	18.81	29.51
x = 0.33	62.34	22.56	32.41
x = 0.40	61.41	23.55	33.01
x = 0.50	52.86	26.87	34.59

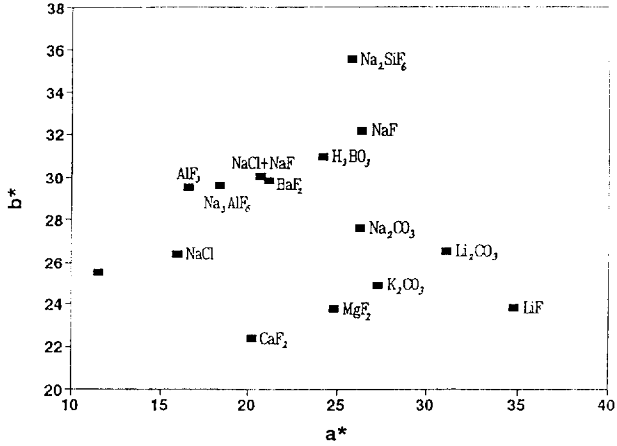

Fig. 5. The effect of the mineralizers on the colour hue of the $Ce_{0.91}Pr_{0.09}O_2$ pigment in a^*, b^* coordinates.

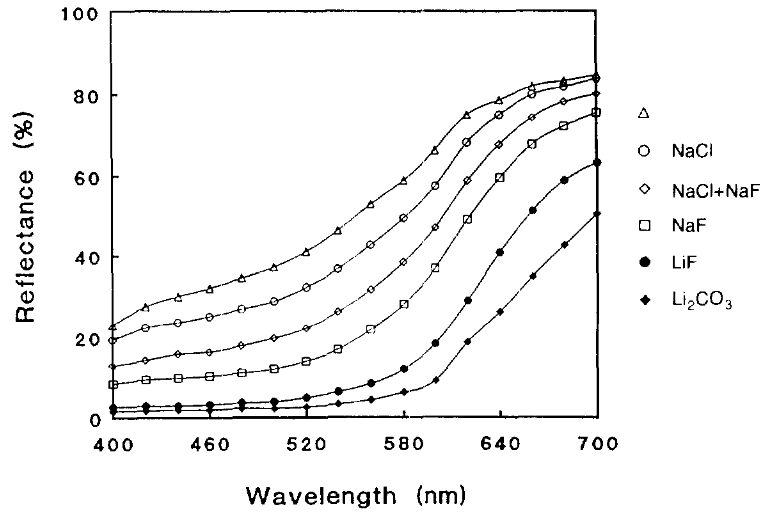

Fig. 6. The effect of the mineralizers on the colour hue of the $Ce_{0.91}Pr_{0.09}O_2$ pigment.

With the use of NaF , Na_2SiF_6 ,BaF_2 ,CaF_2 and H_3BO_3 the colour hue of the pigments also shifted to red, but the colour changes were not so marked (Fig. 6). The mineralizers NaCl, Na_3AlF_6 , AlF_3 and the combination of NaCl + NaF (1:1) very slightly influenced the colour hue of the $Ce_{0.91}Pr_{0.09}O_2$ pigment.

On the basis of the colouring properties of all these pigments applied in ceramic glaze, it follows that the presence of the mineralizers influences the colour hue of the $Ce_{1-x}Pr_xO_2$ pigments from light pink–orange hues to dark red–brown hues.

CONCLUSION

The $Ce_{1-x}Pr_xO_2$ pigments are interesting for their various pink–orange and red–brown hues in ceramic glaze. They are characterized by heat stability, intensive colour and great hiding power. The cerium-praseodyminm type pigments are environmentally friendly, and the colour of these pigments is pleasant and interesting. Intensive colour hues were obtained with an acceptably low content of praseodymium in the pigments.

The preparation of this type of pigment was investigated within the framework of a grant project dealing with new ecological coloured inorganic pigments.