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Synthesis of $Ce_{1-x}Pr_xO_2$ pigments with other lanthanides

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Abstract

The synthesis of some new inorganic pigments has been investigated, with particular respect to the preparation high-temperature colour pigments which can be used for colouring ceramic glazes. The synthesis of these pigments based on high-temperature calcination of the starting oxides. The optimum conditions for the syntheses of these pi ments have been estimated and the pigments prepared have been evaluated from the standpoint of their structu colour hue and ability to colour ceramic glazes. © 1998 Elsevier Science Ltd. All rights reserved.

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

1. Introduction

Pigments based on cerium dioxide are inorganic pigments with a high-temperature [1] stability, but which represent only a small, but an important part of the range of inorganic pigments. When suspended in glass matrixes, which require the highest degree of heat stability and chemical resistance, they withstand the attack of molten glass in glazes and enamels.

Pigments based on cerium dioxide are lesser known ceramic pigments, but their hues are very interesting. They give various pink–orange hues, which are based on the incorporation of praseodymium ions into the host lattice of cerium dioxide. This type of pigment is prepared by high-temper ture calcination of the basic starting oxides Ce and Pr_6O_{11} which dissolve in CeO_2 during the he treatment, forming a $Ce_{1-x}Pr_xO_2$ solid solution.

Pigments based of cerium dioxide in new colo hues are now described. These pigments are bas on the fluorite structure of cerium dioxide with a admixture of other lanthanides. This type of pi ment is formed by a solid solution, i. $Ce_{1-(x+y)}Pr_xLn_yO_{2-y/2}$ where Ln = La, Nd, Sm, Gd, Eu, Er and Tb. Lanthanide oxide (Ln_2 and praseodymium dioxide (PrO_2) dissolve in ce ium dioxide during the heat treatment of t starting mixtures at 1350°C, forming the sol solution of all oxides.

The CeO_2–PrO_2–Ln_2O_3 pigments are high-ter perature pigments with a fluorite structure a which represent new inorganic pigments from t environmental point of view.

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2. Experimental

As starting materials for the preparation of the $Ce_{1-(x+y)}Pr_xLn_yO_{2-y/2}$ pigments we have used CeO_2 of 95% purity and Pr_6O_{11} of 90% purity, La_2O_3, Nd_2O_3, Sm_2O_3, Gd_2O_3, Y_2O_3, Eu_2O_3, Er_2O_3 and Tb_2O_3 of 99% purity (Indian Rare Earths Ltd., India) were used.

The starting mixtures containing both basic oxides (CeO_2 and Pr_6O_{11}), with the required content of admixture (other oxides of lanthanides), were homogenised in an agate mortar. The mixtures were then calcinated in corundum crucibles in an electric resistance furnace (increase of the temperature 10°C/min). The calcination temperature was 1350°C for the duration of 1 h. The pigments prepared 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 (Hunter Lab, USA).

The powder pigments were studied by X-ray diffraction analysis. The X-ray diffractograms of the samples were obtained using a vertical X-ray diffractometer HZG-4B (Freiberger Präzisionsmechanik, Germany) equipped with a goniometer of 25 cm diameter in the range of 20–60°2ϑ Cu K ($\lambda = 0.154178$ nm) radiation was used for t angular range of $2\vartheta < 35°$ and $K_{\alpha 1}$ ($\lambda = 0.154051$ nm for the range of $2\vartheta > 35°$, employing a nick filter for attenuation of the $K\beta$ radiation. A pr portional detector was used. Powder silic ($a = 0.543055$ nm) served as an internal standard

3. Results and discussion

The principal objective of this investigation w to evaluate conditions for the synthesis of the ty of pigments based on the fluorite structure of ceriu dioxide with admixture of other lanthanides. T influence of the lanthanide oxides on the colour the $Ce_{0.70}Pr_{0.05}Ln_{0.25}O_{1.875}$ pigments (where Ln La, Nd, Y, Sm, Gd, Eu, Er and Tb) were al studied.

The effect of the lanthanides on the colour h both of powder pigments and pigments applied borate-silicate glaze was initially studied. Fro Fig. 1 (Table 1) it is apparent that the highe values of the colour coordinates L_*, a_*, b_* perta to pigments containing Gd and Eu. The presence Tb as admixture component results in this pigme being the darkest of all pigments prepared (Fig. 2

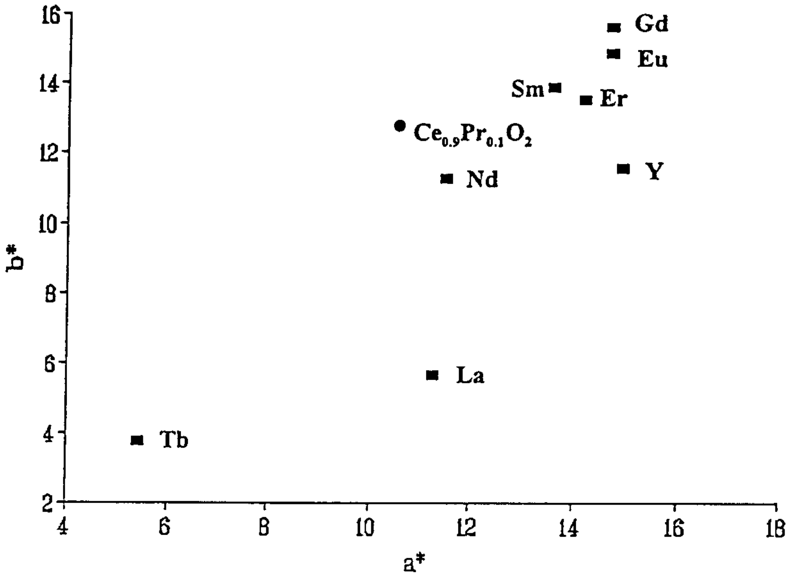

Fig. 1. The effect of lanthanides on the colour hue of the $Ce_{0.70}Pr_{0.05}Ln_{0.25}O_{1.875}$ powders pigments (L^*, a^*, b^* coordinates).

The pigment which had the highest values of colour coordinates ($a*$ and $b*$) was selected on the basis of the measured colour coordinates of the pigments applied in borate–silicate glaze (Fig. 3, Table 1). When lanthanum as admixture was used, the colour coordinates $a*$ and $b*$ decreased. The colour hue of the pigments containing Nd, Y, Er, Gd, Sm and Eu as admixture did not differ from the pigment [2] $Ce_{0.9}Pr_{0.1}O_2$ calcinated at 1300°C.

The structure of the pigments of the $Ce_{0.70}Pr_{0.05}Ln_{0.25}O_{1.875}$ type was also investigated. Samples

Table 1
The effect of lanthanides on the colour hue of the $Ce_{0.70}Pr_{0.05}Ln_{0.25}O_{1.875}$ pigments in L^*, a^*, b^* coordinates

	Powder pigments			Pigments applied in glaze		
Ln	L^*	a^*	b^*	L^*	a^*	b^*
Y	46.16	14.94	11.51	69.59	17.21	24.45
La	48.29	14.17	12.04	65.43	20.78	23.87
Nd	47.51	11.51	11.23	66.98	16.31	23.71
Sm	49.37	13.56	13.83	73.16	14.87	24.92
Gd	51.01	14.71	15.55	70.21	16.45	25.09
Er	49.04	14.18	13.46	69.66	17.17	24.47
Eu	50.15	14.72	14.79	73.55	14.97	25.89
Tb	40.98	5.41	3.76	61.62	22.46	31.18

with a content of other lanthanides (La, Nd, Sm, Gd, Eu, Er and Tb) were studied by X-r diffraction analyses (Fig. 4). The observed diffra tion lines corresponded with the characterist lines of fluorite structure of cerium dioxide. T samples of all the prepared pigments exhibit only peaks that have been assigned to ceriu dioxide. This means that all the samples are hom geneous. Praseodymium dioxide PrO_2 and oth lanthanide oxide Ln_2O_3 dissolve in cerium dioxi during the heat treatment of the starting mixtur at 1350°C, forming a solid solution of all oxides

Praseodymium atoms substitute cerium ator in their crystal lattice, forming uncharged su stitutional defects Pr_{Ce}^{x} in the solid soluti $Ce_{1-(x+y)}Pr_xLn_yO_{2-y/2}$. Praseodymium enters in cerium dioxide as substitutional defects [2] inste of cerium, because the tetravalent praseodymiu ion ($r(Pr^{4+}) = 0.092$ nm) has a smaller radius th the tetravalent cerium ion ($r(Ce^{4+}) = 0.101$ nm Ions of other lanthanides, which enter the fluori structure, are a little larger than Ce^{4+} ions, whi are substituted. Ions of lanthanides enter the pi ment structure as negatively charged defects Ln_C The strongly negative charge of these defects compensated by the positively charged substituti

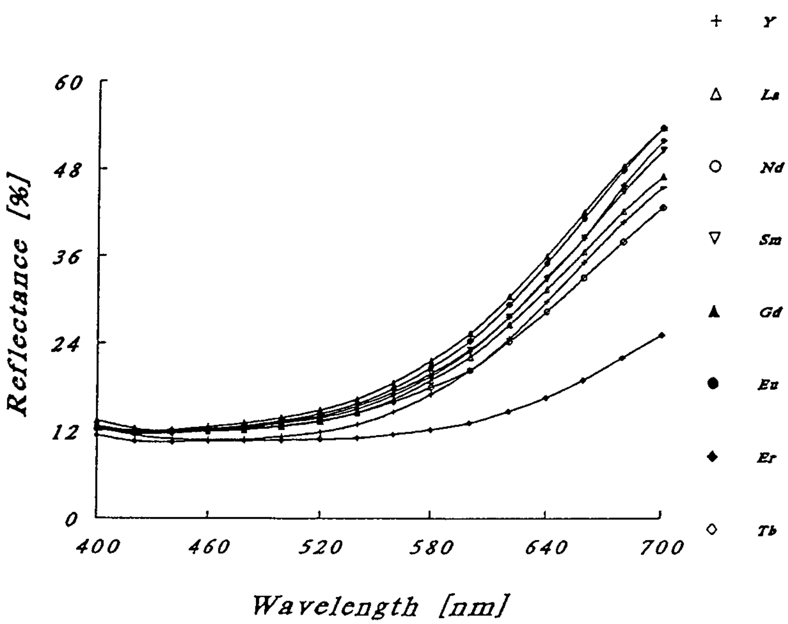

Fig. 2. The effect of lanthanides on the colour hue of the $Ce_{0.70}Pr_{0.05}Ln_{0.25}O_{1.875}$ powder pigments.

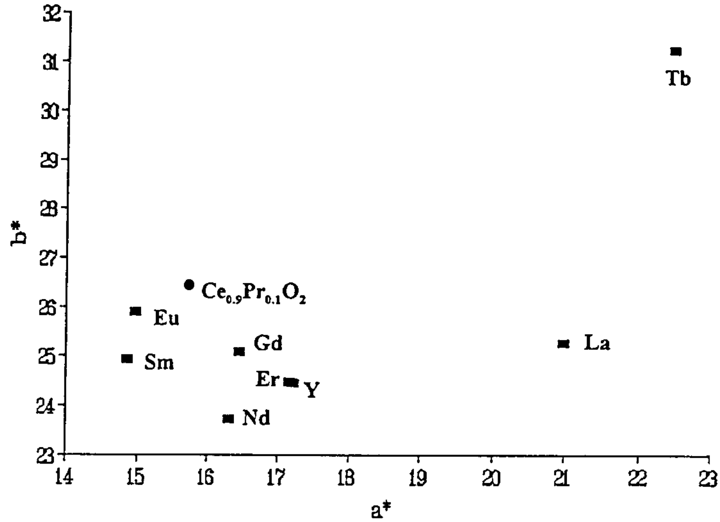

Fig. 3. The effect of lanthanides on the colour hue of the $Ce_{0.70}Pr_{0.05}Ln_{0.25}O_{1.875}$pigments applied in glaze (L^*, a^*, b^* coordinates

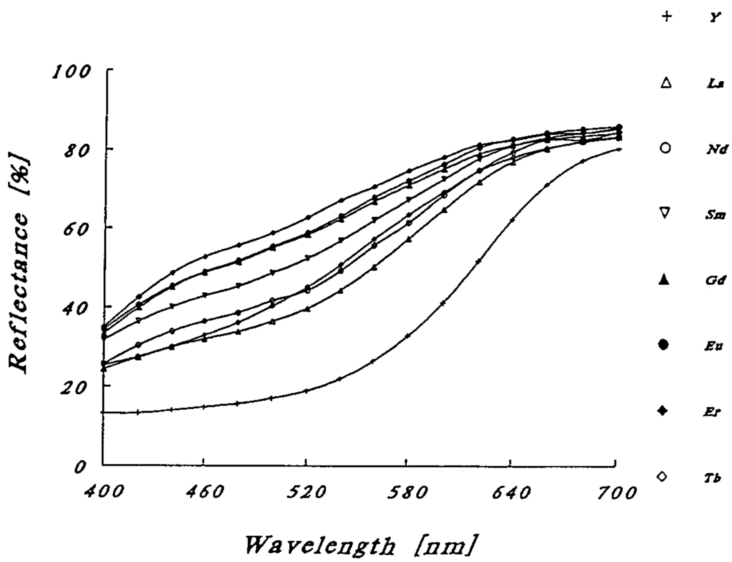

Fig. 4. The effect of lanthanides on the colour hue of the $Ce_{0.70}Pr_{0.05}Ln_{0.25}O_{1.875}$pigments applied in glaze.

defects $V_O^{\bullet}$. Variations of the lattice parameters of CeO_2 are presumed to be associated with the formation of a solid solution of CeO_2, PrO_2 and Ln_2O_3 where Ln = La, Nd, Y, Sm, Gd, Eu, Er and Tb. Such a solution is most probably of the substitutional type, where Pr^{4+} and Ln^{3+} cations are substituted in the lattice positions of Ce^{4+}, forming uncharged electrically neutral defects $Pr_{Ce}{}^{x}$ and negatively charged defects $Ln_{Ce}{}'$, which are compensated by oxygen vacancies $V_O^{\bullet}$. The fo mation of all these defects can be described l Eqs. (1) and (2):

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

$$2Ln_2O_3 \Longleftrightarrow 4Ln'_{Ce} + 3CeO_2 + 4V_O^{\bullet}(\rightarrow CeO_2) \quad ($$

Table 2
Lattice parameters of samples of the $Ce_{0.70}Pr_{0.05}Ln_{0.25}O_{1.875}$ pigments

Formula	a (nm)	V (nm^3)	$\Delta 2\nu^a$	Density (g.cm^{-3})
$Ce_{0.70}Pr_{0.05}La_{0.25}O_{1.875}$	0.55424(6)	0.17025(6)	0.003	6.6264
$Ce_{0.70}Pr_{0.05}Nd_{0.25}O_{1.875}$	0.54577(2)	0.16257(2)	0.005	6.9942
$Ce_{0.70}Pr_{0.05}Y_{0.25}O_{1.875}$	0.54162(2)	0.15889(2)	0.007	6.5778
$Ce_{0.70}Pr_{0.05}Sm_{0.25}O_{1.875}$	0.54414(4)	0.16111(4)	0.001	7.1203
$Ce_{0.70}Pr_{0.05}Gd_{0.25}O_{1.875}$	0.54371(3)	0.16073(1)	0.002	7.0009
$Ce_{0.70}Pr_{0.05}Eu_{0.25}O_{1.875}$	0.55127(1)	0.16753(1)	0.002	6.8177
$Ce_{0.70}Pr_{0.05}Er_{0.25}O_{1.875}$	0.54221(2)	0.15940(5)	0.003	6.7812
$Ce_{0.70}Pr_{0.05}Tb_{0.25}O_{1.875}$	0.54322(2)	0.16029(7)	0.006	6.9811

[a] $\Delta 2\nu = N^{-1}\{\rightsquigarrow\}(2\nu_{exp} - 2\nu_{calc})$, 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.

4. Conclusion

Pigments based on cerium dioxide in admixture other lanthanides are characterised by heat stabilit intense colour and great hiding power. Due to the high resistance to attack of molten glass in glaz and enamels, these pigments are high-temperatu pigments. They are suitable for all types of ceram glazes. They can be used even in sanitary ceramic Pigments of the $Ce_{1-(x+y)}Pr_xLn_y\ O_{2-y/2}$ type a environmentally friendly, and their colour cou complement the current range of ceramic pigment

References

[1] Grant No 104/96/1236. Grant Agency of Czech Republ
[2] Šuulcová P, Trojan M, Šolc Z. Cerium dioxide fluor type pigments. Dyes and Pigments 1998;37:65–70.