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**THE SYNTHESIS  
OF THE  $\text{CeO}_2\text{-PrO}_2\text{-Ln}_2\text{O}_3$  PIGMENTS**

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*The synthesis of new inorganic pigments based on  $\text{CeO}_2\text{-PrO}_2\text{-Ln}_2\text{O}_3$  has been investigated. The main attention is directed to the preparation of these pigments which can be used for colouring ceramic glazes. The synthesis of these pigments is based on high-temperature calcination of starting oxides. The optimum conditions for the syntheses of pigments have been estimated and the pigments prepared have been evaluated from the standpoint of their structure, colour hue and ability to dye ceramic glazes.*

### **Introduction**

The pigments based on cerium dioxide,  $\text{CeO}_2$ , are less known ceramic pigments and belong to special inorganic pigments with high-temperature stability [1].

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The pigments based on cerium dioxide,  $\text{CeO}_2$ , in new colour hues have now been synthesised in our laboratory. The new pigments are based on the fluorite structure of cerium dioxide with an admixture of oxides of other lanthanides. This type of pigment is formed by a solid solution  $\text{Ce}_{1-(x+y)}\text{Pr}_x\text{Ln}_y\text{O}_{2-y/2}$  where  $\text{Ln} = \text{La}, \text{Nd}, \text{Y}, \text{Sm}, \text{Gd}, \text{Eu}, \text{Er}$  and  $\text{Tb}$ . Lanthanide oxide ( $\text{Ln}_2\text{O}_3$ ) and praseodymium dioxide ( $\text{PrO}_2$ ) dissolve in cerium dioxide during the heat treatment of the starting mixtures at the temperature of  $1350\text{ }^\circ\text{C}$  forming the solid solution of all the oxides.

The pigments of the  $\text{CeO}_2\text{-PrO}_2\text{-Ln}_2\text{O}_3$  system are high-temperature pigments with fluorite structure which represent new inorganic pigments from the environmental point of view. Their colour hues in ceramic glazes are very interesting. They give various pink-orange hues, which represent only a small, but an important part of the entire family of the inorganic pigments.

## Experimental

As starting material for the preparation of the  $\text{Ce}_{1-(x+y)}\text{Pr}_x\text{Ln}_y\text{O}_{2-y/2}$  (where  $x = 0.05$  and  $y = 0.7$ ) pigments we have used  $\text{CeO}_2$  of 95% purity and  $\text{Pr}_6\text{O}_{11}$  of 90% purity,  $\text{La}_2\text{O}_3$ ,  $\text{Nd}_2\text{O}_3$ ,  $\text{Sm}_2\text{O}_3$ ,  $\text{Gd}_2\text{O}_3$ ,  $\text{Y}_2\text{O}_3$ ,  $\text{Eu}_2\text{O}_3$ ,  $\text{Er}_2\text{O}_3$  and  $\text{Tb}_2\text{O}_3$  of 99% purity (Indian Rare Earths Ltd., India).

The starting mixtures containing the both basic oxides ( $\text{CeO}_2$  and  $\text{Pr}_6\text{O}_{11}$ ) 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 (the increase of the temperature  $10\text{ }^\circ\text{C min}^{-1}$ ). The calcination temperature was  $1350\text{ }^\circ\text{C}$  for the duration of one hour. The pigments prepared were applied to a middle-temperature glaze in amounts of 10% (w/w) with a glazing temperature of  $1000\text{ }^\circ\text{C}$  applied for 15 min. The final glazes were evaluated with regard to their colour hues by measurements of spectral reflectance in the visible region of light using a MiniScan (HunterLab, 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  $20^\circ$  to  $60^\circ 2\theta$ .  $\text{Cu } K_\alpha$  ( $\lambda = 0.154178\text{ nm}$ ) radiation was used for the angular range of  $2\theta < 35^\circ$  and  $K_{\alpha 1}$  ( $\lambda = 0.154051\text{ nm}$ ) for the range of  $2\theta > 35^\circ$ , employing a nickel filter for attenuation of the  $K_\beta$  radiation. A proportional detector was used. Powder silicon ( $a = 0.543055\text{ nm}$ ) served as an internal standard.

## Results and Discussion

The main aim was to propose conditions of the synthesis of this type of pigments based on the fluorite structure of cerium dioxide with admixture of other lanthanides. The influence of the lanthanide oxides on the colouring effect of the  $\text{Ce}_{0.70}\text{Pr}_{0.05}\text{Ln}_{0.25}\text{O}_{1.875}$  pigments (where Ln = La, Nd, Y, Sm, Gd, Eu, Er and Tb) were studied.

In ceramic industry, colour is described in terms of CIE  $L^*a^*b^*$  system (1976). The values  $a^*$  (the red-green axis) and  $b^*$  (the yellow-blue axis) indicate the colour hue. 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 zero (black) to hundred (white).

From Fig. 1 it follows that the highest values of colour coordinates  $L^*$ ,  $a^*$ ,  $b^*$  of powder pigments are exhibited by the pigments containing Gd and Eu. The presence of Tb as admixture shifts the colour of powder pigment to the centre of the axis cross of the colour coordinates  $L^*$ ,  $a^*$ ,  $b^*$ . This powder pigment is the darkest from all the pigments prepared (Table I).

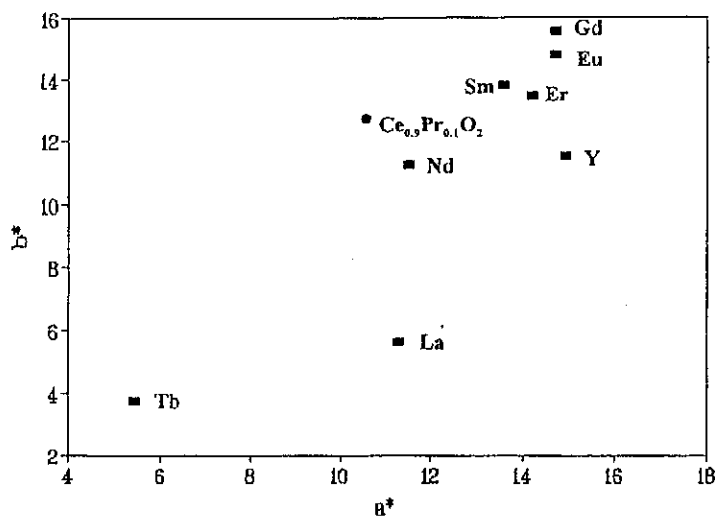


Fig. 1 The effect of lanthanides on the colour hue of the  $\text{Ce}_{0.70}\text{Pr}_{0.05}\text{Ln}_{0.25}\text{O}_{1.875}$  powder pigments ( $L^*$ ,  $a^*$ ,  $b^*$  coordinates)

The pigment with the highest values of colour coordinates  $a^*$  and  $b^*$  was selected on the basis of the measured colour coordinates  $L^*a^*b^*$  of pigments applied in borate-silicate glaze (Fig. 2). When lanthanum was used as admixture, the colour coordinate  $a^*$  increased (Table II). The colour hue of the pigments con-

Table I The effect of lanthanides on the colour properties of the  $Ce_{1-(x+y)}Pr_xLn_yO_{2-y/2}$  pigments (powder pigments)

Formula	$L^*$	$a^*$	$b^*$
$Ce_{0.70}Pr_{0.05}La_{0.25}O_{1.875}$	48.29	14.17	12.04
$Ce_{0.70}Pr_{0.05}Eu_{0.25}O_{1.875}$	50.15	14.72	14.79
$Ce_{0.70}Pr_{0.05}Nd_{0.25}O_{1.875}$	47.51	11.51	11.23
$Ce_{0.70}Pr_{0.05}Sm_{0.25}O_{1.875}$	49.37	13.56	13.83
$Ce_{0.70}Pr_{0.05}Gd_{0.25}O_{1.875}$	51.01	14.71	15.55
$Ce_{0.70}Pr_{0.05}Tb_{0.25}O_{1.875}$	40.98	5.41	3.76
$Ce_{0.70}Pr_{0.05}Er_{0.25}O_{1.875}$	49.04	14.18	13.46
$Ce_{0.70}Pr_{0.05}Y_{0.25}O_{1.875}$	46.16	19.94	11.51

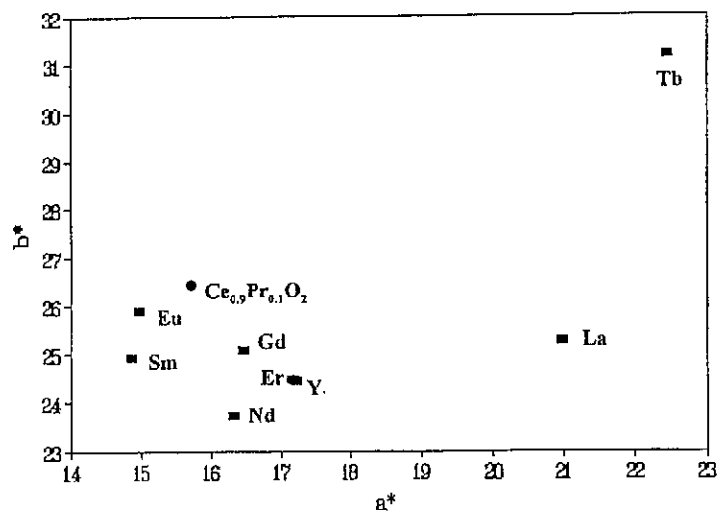


Fig. 2 The effect of lanthanides on the colour hue of the  $Ce_{0.70}Pr_{0.05}Ln_{0.25}O_{1.875}$  pigments applied in glaze (in  $L^*$ ,  $a^*$ ,  $b^*$  coordinates)

taining Nd, Y, Er, Gd, Sm and Eu as admixture does not differ from the pigment [2]  $Ce_{0.9}Pr_{0.1}O_2$  calcinated at 1300 °C. The presence of Tb as admixture increases the red hue of this pigment (i.e. decreases the  $L^*$  value and increases the  $a^*$  and  $b^*$  values).

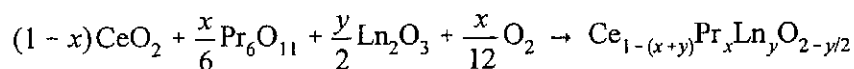
The structure of the pigments of the  $Ce_{0.70}Pr_{0.05}Ln_{0.25}O_{1.875}$  type was also investigated. The samples with the content of other lanthanides (La, Nd, Y, Sm, Gd,

Table II The effect of lanthanides on the colour properties of the  $Ce_{1-(x+y)}Pr_xLn_yO_{2-y/2}$  pigments (application in glaze G70)

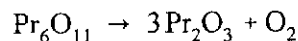
Formula	$L^*$	$a^*$	$b^*$
$Ce_{0.70}Pr_{0.05}La_{0.25}O_{1.875}$	65.43	20.78	23.87
$Ce_{0.70}Pr_{0.05}Eu_{0.25}O_{1.875}$	73.55	14.97	25.89
$Ce_{0.70}Pr_{0.05}Nd_{0.25}O_{1.875}$	66.98	16.31	23.71
$Ce_{0.70}Pr_{0.05}Sm_{0.25}O_{1.875}$	73.16	14.87	24.92
$Ce_{0.70}Pr_{0.05}Gd_{0.25}O_{1.875}$	70.21	16.45	25.09
$Ce_{0.70}Pr_{0.05}Tb_{0.25}O_{1.875}$	61.62	22.43	31.18
$Ce_{0.70}Pr_{0.05}Er_{0.25}O_{1.875}$	69.66	17.17	24.47
$Ce_{0.70}Pr_{0.05}Y_{0.25}O_{1.875}$	69.59	17.21	24.45

Eu, Er and Tb) were studied by X-ray diffraction analyses. The observed diffraction lines corresponded with characteristic lines of fluorite structure of cerium dioxide. The samples of all the prepared pigments exhibited only peaks that have been assigned to cerium dioxide. This means that all the samples are homogeneous.

Praseodymium dioxide,  $PrO_2$ , and other lanthanide oxides,  $Ln_2O_3$ , dissolve in cerium dioxide during the heat treatment of the starting mixtures at the temperature of 1350 °C forming a solid solution of all oxides. The formation of solid solution is described by the following scheme



Praseodymium ions are available in two oxidation states in the raw material mixed oxide  $Pr_6O_{11}$  ( $4PrO_2 \cdot Pr_2O_3$ ). In the temperature range from 260 to 300 °C mixed oxide  $Pr_6O_{11}$  is reduced to  $Pr_2O_3$



Praseodymium ions are oxidized to the tetravalent state at the moment of pigment formation

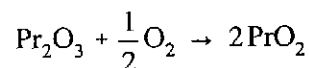
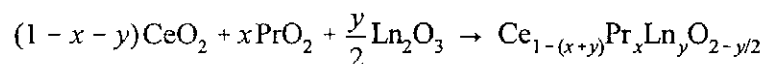


Table III Lattice parameters of samples of the  $\text{Ce}_{1-(x+y)}\text{Pr}_x\text{Ln}_y\text{O}_{2-y/2}$  pigments

Formula	$a$ , nm	$V$ , nm <sup>3</sup>	$\Delta 2\nu$ <sup>a)</sup>	$r(\text{Ln}^{3+})$ , nm
$\text{Ce}_{0.70}\text{Pr}_{0.05}\text{La}_{0.25}\text{O}_{1.875}$	0.55424(6)	0.17025(6)	0.003	0.115
$\text{Ce}_{0.70}\text{Pr}_{0.05}\text{Eu}_{0.25}\text{O}_{1.875}$	0.55127(1)	0.16753(1)	0.002	0.112
$\text{Ce}_{0.70}\text{Pr}_{0.05}\text{Nd}_{0.25}\text{O}_{1.875}$	0.54577(2)	0.16257(2)	0.005	0.108
$\text{Ce}_{0.70}\text{Pr}_{0.05}\text{Sm}_{0.25}\text{O}_{1.875}$	0.54414(4)	0.16111(4)	0.001	0.104
$\text{Ce}_{0.70}\text{Pr}_{0.05}\text{Gd}_{0.25}\text{O}_{1.875}$	0.54371(3)	0.16073(1)	0.002	0.102
$\text{Ce}_{0.70}\text{Pr}_{0.05}\text{Tb}_{0.25}\text{O}_{1.875}$	0.54322(2)	0.16029(7)	0.006	0.100
$\text{Ce}_{0.70}\text{Pr}_{0.05}\text{Er}_{0.25}\text{O}_{1.875}$	0.54221(2)	0.15940(5)	0.003	0.096
$\text{Ce}_{0.70}\text{Pr}_{0.05}\text{Y}_{0.25}\text{O}_{1.875}$	0.54162(2)	0.15889(2)	0.007	0.093

<sup>a)</sup>  $\Delta 2\nu = N^{-1}(2\nu_{\text{exp}} - 2\nu_{\text{calc}})$ , 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

The pigment crystals are formed during pigment preparation by high temperature reaction of  $\text{CeO}_2$ ,  $\text{PrO}_2$  and  $\text{Ln}_2\text{O}_3$ .  $\text{PrO}_2$  and  $\text{Ln}_2\text{O}_3$  dissolve in  $\text{CeO}_2$  during the heat treatment of the starting mixtures, forming the solid solution of all the oxides  $\text{Ce}_{1-(x+y)}\text{Pr}_x\text{Ln}_y\text{O}_{2-y/2}$

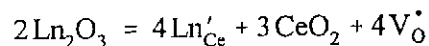
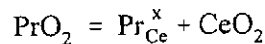


Praseodymium atoms replace cerium atoms in their crystal lattice, forming uncharged substitutional defects,  $\text{Pr}_{\text{Ce}}^x$ , in the solid solution  $\text{Ce}_{1-(x+y)}\text{Pr}_x\text{Ln}_y\text{O}_{2-y/2}$ . Praseodymium enters cerium dioxide as substitutional defects [2] instead of cerium because the tetravalent praseodymium ion [ $r(\text{Pr}^{4+}) = 0.092$  nm] has a smaller radius than the tetravalent cerium ion [ $r(\text{Ce}^{4+}) = 0.101$  nm]. Ions of other lanthanides, which enter the fluorite structure, are a little larger than  $\text{Ce}^{4+}$  ions substituted.

The values of lattice parameters of cerium dioxide (Table III) show that the parameter  $a$  increases with the increasing radius of trivalent ions of other lanthanides. The formation of substitutional defects is associated with the increase in the volume of the elementary cell of  $\text{CeO}_2$ .

Ions of lanthanides [3] enter the pigment structure as negatively charged defects  $\text{Ln}'_{\text{Ce}}$ . The highly negative charge of these defects is compensated by the positively charged substitution defects  $\text{V}_\text{O}^\bullet$ . The variations of the lattice parameters of  $\text{CeO}_2$  are supposed to be associated with the formation of solid solution of  $\text{CeO}_2$ ,  $\text{PrO}_2$  and  $\text{Ln}_2\text{O}_3$  where Ln = La, Nd, Y, Sm, Gd, Eu, Er and Tb. Such a

solution is most probably of the substitutional type, where  $\text{Pr}^{4+}$  and  $\text{Ln}^{3+}$  cations are substituted in lattice positions of  $\text{Ce}^{4+}$ , forming uncharged electrically neutral defects,  $\text{Pr}_{\text{Ce}}^x$ , and negatively charged defects,  $\text{Ln}'_{\text{Ce}}$ , which are compensated by oxygen vacancies  $V_{\text{O}}^{\bullet}$ . The formation of all these defects can be described by



## Conclusion

The pigments of the  $\text{CeO}_2$ - $\text{PrO}_2$ - $\text{Ln}_2\text{O}_3$  system are characterised by heat stability, intensive colour and high opacity. Due to their high resistance to the attack of molten glass in glazes and enamels, these pigments belong to high-temperature pigments. They are suitable for all types of ceramic glazes and can be used even in the sanitary ceramics. The pigments of the  $\text{Ce}_{1-(x+y)}\text{Pr}_x\text{Ln}_y\text{O}_{2-y/2}$  type are environmentally friendly and therefore very progressive too. In addition, the colour of these pigments is pleasant and interesting. They could complete the basic assortment of colours of ceramic pigments.

The preparation of this pigment type was investigated within the framework of a grant project dealing with new environmentally friendly coloured inorganic pigments [4].

## References

- [1] Trojan M., Šolc Z., Novotny M.: *Pigments*, Kirk-Othmer Encyclopedia of Chem. Technol., Vol. 17, J. Wiley and Sons Inc., New York 1995.
- [2] Šulcová P., Trojan M., Šolc Z.: *Dyes and Pigments* **37**, 65 (1998).
- [3] Šulcová P., Trojan M.: *Dyes and Pigments* **40**, 87 (1998).
- [4] Grant No. 104/98/P227, Grant Agency of Czech Republic.