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**THE HIGH TEMPERATURE  
PIGMENTS BASED ON CeO<sub>2</sub>**

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*The synthesis of new inorganic pigments is investigated in our laboratory. The main attention is directed to the preparation of high-temperature colour pigments which can be used for colouring of 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. The pigments prepared have been evaluated from the standpoint of their structure, colour hue and ability to dye ceramic glazes.*

**Introduction**

The pigments on the basis of cerium dioxide CeO<sub>2</sub> belong to special inorganic pigments with high thermal stability, and represent a small but important part of the entire family of the inorganic pigments [1]. They are suspended in glass matrixes which require the highest degree of heat stability and chemical resistance to

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withstand the attack of molten glass in glazes and enamels.

The pigments based on cerium dioxide  $\text{CeO}_2$  with an admixture [2] of praseodymium are less known ceramic pigments. They seem to be interesting as to their colour hue in ceramic glazes. These pigments give interesting pink-orange and red-brown hues in ceramic glazes which are based on the incorporation of praseodymium ions into the host lattice of cerium dioxide. The pigments of cerium-praseodymium type are formed by a solid solution  $\text{Ce}_{1-x}\text{Pr}_x\text{O}_2$  with the fluorite structure of  $\text{CeO}_2$ . This type of pigments is prepared by high-temperature calcination of the basic starting oxides  $\text{CeO}_2$  and  $\text{Pr}_6\text{O}_{11}$ .

The main attention has been directed [3] to the preparation of the  $\text{Ce}_{1-x}\text{Pr}_x\text{O}_2$  pigments, their properties, structure and possible application for ceramic glazes.

## Experimental

As starting materials for the preparation of the  $\text{Ce}_{1-x}\text{Pr}_x\text{O}_2$  pigments we have used  $\text{CeO}_2$  of 95% purity and  $\text{Pr}_6\text{O}_{11}$  of 90% purity (Indian Rare Earths Ltd.).

The starting mixtures containing the both basic oxides were homogenized in an agate mortar. The mixtures were then calcinated at a chosen temperatures in corundum crucibles in an electric resistance furnace (the temperature increase of  $10\text{ }^\circ\text{C min}^{-1}$ ). The calcination temperatures were in the range from 1200 to 1350  $^\circ\text{C}$  for the duration of one hour. The pigments prepared were applied to a middle-temperature borate-silicate glaze in amounts of 10% (w/w) with a glazing temperature of 1000  $^\circ\text{C}$  for 15 min. The final glazes were evaluated with regard to their colour hues by measurements of spectral reflectance in the visible light region using a MiniScan (HunterLab, USA).

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

## Results and Discussion

The main aim was to find such a pigment as to give an intensive pink-orange colour and, at the same time, have a low content of praseodymium, because praseodymium dioxide is more expensive than cerium dioxide.

First our investigation was focused on 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 the increasing content of praseodymium (5, 10, 17, 33, 40 and 50 mol.% Pr) were homogenized in an agate mortar. The mixtures were calcinated at four chosen temperatures (1200, 1250, 1300 and 1350  $^\circ\text{C}$ ) for a period of one hour. The most intensive pink-orange hues of  $\text{Ce}_{1-x}\text{Pr}_x\text{O}_2$

pigments were obtained at the calcination temperature of 1300 °C. At higher temperatures, the colour intensity increases only little but the colour hue does not differ from that of the pigments calcinated at 1300 °C. At the calcination temperature of 1250 °C (1200 °C) the values  $L^*$  increase and the pigments become lighter.

The ceramic industry describes colour in terms of CIE  $L^*a^*b^*$  system (1976). The values  $a^*$  (the axis red-green) and  $b^*$  (the axis yellow-blue) indicate the colour hue. The four principal colours are red, yellow, green and blue. 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 number from zero (black) to hundred (white).

From Table I it follows that the chromacity  $C \left[ C = \sqrt{a^2 + b^2} \right]$  increases with increasing temperature. The chromacity of the pigment calcinated at 1300 °C does not differ from that of the pigment calcinated at 1350 °C. On the basis of colouring properties of these pigments it follows that intensive pink-orange hues can be prepared by calcination of starting mixtures at the temperature of 1300 °C.

Table I The effect of the temperature on the colour properties of the  $Ce_{0.90}Pr_{0.10}O_2$  pigment (application in glaze G70)

$T, ^\circ C$	$L^*$	$a^*$	$b^*$	$C$
1200	76.52	10.37	19.22	21.84
1250	72.71	17.22	29.21	33.91
1300	62.71	26.96	33.17	42.74
1350	60.23	27.09	34.17	43.96

The effect of the praseodymium content in the mixtures on the colour hue of these pigments is demonstrated in Fig. 1. Increasing Praseodymium content increases the red hue of these pigments. An intensive pink-orange colour with acceptable low praseodymium content was found with the pigment containing 10 mol.% of praseodymium. This pigment can be described by the formula  $Ce_{0.90}Pr_{0.10}O_2$ . When 50 mol.% of praseodymium is used, the colour hue of the pigment is shifted to red-brown hue (Table II).

The structure of the pigments of cerium-praseodymium type was also investigated. The samples with the increasing content of praseodymium (10, 20, 30, 40, 50 and 60 mol.%) were studied by X-ray diffraction analysis. The observed diffraction lines corresponded with characteristic lines of fluorite structure of cerium dioxide. The samples with the highest content of praseodymium (60 mol.%) exhibited only peaks assigned to cerium dioxide. This means that all the samples are homogeneous.

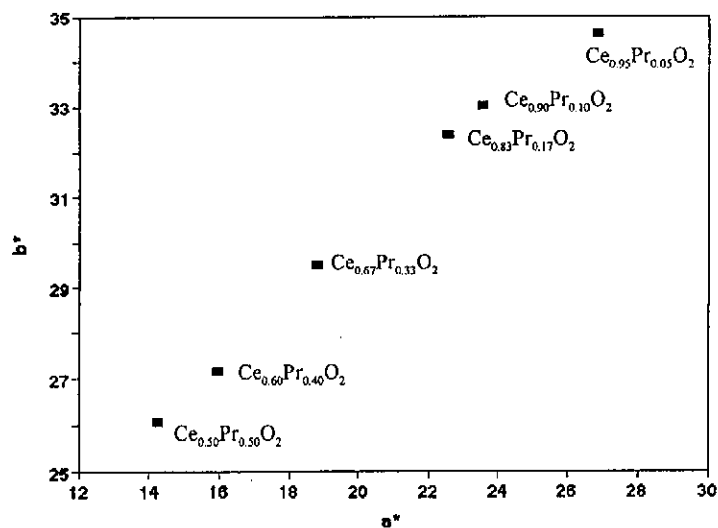
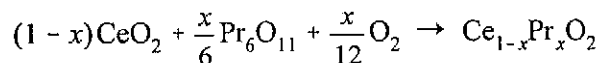


Fig. 1 The effect of the praseodymium content on the colour properties of the  $Ce_{1-x}Pr_xO_2$  pigments (application in glaze G70)

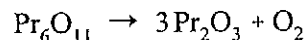
Table II The effect of the praseodymium content on the colour properties of the  $Ce_{1-x}Pr_xO_2$  pigments (application in glaze G70)

Formula	$L^*$	$a^*$	$b^*$
$Ce_{0.95}Pr_{0.05}O_2$	52.71	26.87	34.59
$Ce_{0.90}Pr_{0.10}O_2$	62.41	23.55	34.01
$Ce_{0.83}Pr_{0.17}O_2$	65.34	22.56	32.41
$Ce_{0.67}Pr_{0.33}O_2$	67.78	18.81	29.51
$Ce_{0.60}Pr_{0.40}O_2$	72.71	15.96	27.17
$Ce_{0.50}Pr_{0.50}O_2$	73.52	14.26	26.08

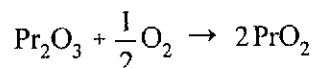
Praseodymium dioxide  $PrO_2$  dissolves in cerium dioxide during the heat treatment of the starting mixtures forming a solid solution of both oxides. The formation of solid solution is described by the following scheme



Praseodymium ions are present in two oxidation states in the raw material mixed oxide  $\text{Pr}_6\text{O}_{11}$  ( $4\text{PrO}_2 \cdot \text{Pr}_2\text{O}_3$ ). In the temperature range from 260 to 300 °C, the mixed oxide  $\text{Pr}_6\text{O}_{11}$  is reduced to  $\text{Pr}_2\text{O}_3$



At the moment of pigment formation praseodymium ions are oxidized to the tetravalent state



The pigment crystals are formed during pigment preparation by high temperature reaction of  $\text{CeO}_2$  and  $\text{PrO}_2$ .  $\text{PrO}_2$  dissolves in  $\text{CeO}_2$  during the heat treatment of the starting mixtures forming the solid solution of both oxides  $\text{Ce}_{1-x}\text{Pr}_x\text{O}_2$

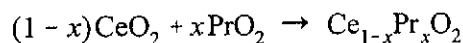


Table III Lattice parameters of samples of the  $\text{Ce}_{1-x}\text{Pr}_x\text{O}_2$  pigments and  $\text{CeO}_2$

Formula	$a$ , nm	$V$ , nm <sup>3</sup>	$\Delta 2\nu$ <sup>a)</sup>
$\text{CeO}_2$	0.54221(6)	0.15941(6)	0.002
$\text{Ce}_{0.90}\text{Pr}_{0.10}\text{O}_2$	0.54205(2)	0.15927(2)	0.007
$\text{Ce}_{0.80}\text{Pr}_{0.20}\text{O}_2$	0.54178(2)	0.15902(2)	0.003
$\text{Ce}_{0.70}\text{Pr}_{0.30}\text{O}_2$	0.54163(4)	0.15889(4)	0.005
$\text{Ce}_{0.60}\text{Pr}_{0.40}\text{O}_2$	0.54145(5)	0.15873(1)	0.004
$\text{Ce}_{0.50}\text{Pr}_{0.50}\text{O}_2$	0.54137(3)	0.15866(2)	0.005
$\text{Ce}_{0.40}\text{Pr}_{0.60}\text{O}_2$	0.54122(1)	0.15853(1)	0.002

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

The values of lattice parameters of cerium dioxide (Table III) show that the parameter  $a$  decreases with increasing content of praseodymium. Praseodymium atoms substitute cerium atoms in their crystal lattice forming uncharged substitutional defects  $\text{Pr}_{\text{Ce}}^x$  in the solid solution  $\text{Ce}_{1-x}\text{Pr}_x\text{O}_2$ . The formation of these defects is associated with a decrease in volume of the elementary cell of cerium dioxide (Fig. 2). Praseodymium enters cerium dioxide as substitutional defects instead of cerium because the tetravalent praseodymium ion ( $r(\text{Pr}^{4+}) = 0.092 \text{ nm}$ ) has a smaller radius than the tetravalent cerium ion ( $r(\text{Ce}^{4+}) = 0.101 \text{ nm}$ ).

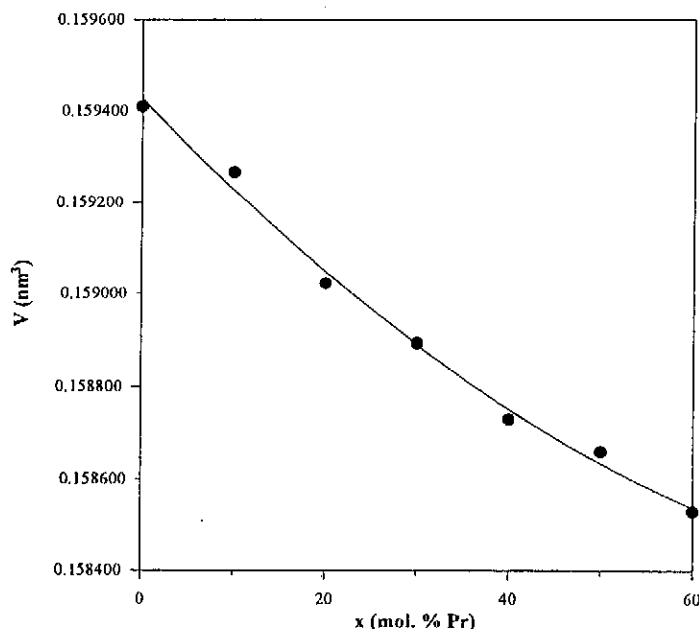


Fig. 2 The effect of the increasing content of praseodymium on the volume of the elementary cell of  $\text{CeO}_2$

## Conclusion

The  $\text{Ce}_{1-x}\text{Pr}_x\text{O}_2$  pigments are interesting as to their various pink-orange and red-brown hues in ceramic glaze. They are characterized by heat stability, intensive colour and great hiding power. The pigments of cerium-praseodymium type are environmentally friendly and therefore very progressive too. In addition, the colour of these pigments is pleasant and interesting. The intensive colour hues were obtained with an acceptably low praseodymium content in the pigments. They could complete the basic assortment of colour of ceramic pigments.

## References

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3. Grant No. 104/98/P227, the Grant Agency of the Czech Republic.