

Study of $\text{Ce}_{1-x}\text{Pr}_x\text{O}_2$ pigments

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Abstract

The synthesis of new compounds based on CeO_2 , which can be used as pigments for colouring of ceramic glazes, is investigated in our laboratory. The optimum conditions for the syntheses of these compounds have been estimated and the pigments prepared have been evaluated from the standpoint of their structure. The first information about the temperature region of the formation of the pigments investigated is provided by thermal analysis. The synthesis of these compounds is followed by thermal analysis using STA 449C Jupiter (NETZSCH, Germany).

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1. Introduction

The pigments on the base of CeO_2 belong to special inorganic pigments with high-temperature stability, which represent only a small, but an important part of the entire family of the inorganic pigments [1]. This type of pigments also represents mixed metal oxides.

Each pigment has a defined crystal structure that is determined by the host lattice. Other oxides interdiffuse at high temperatures into the host lattice structure forming either a solid-state solution or a new compound. Most of mixed metal oxide pigments contain metal cations balanced by oxygen anions with structures similar to naturally occurring minerals. Their commercial significance is in their thermal, chemical and light stability, combined with their low toxicity. When they are employed for colouring glass enamels

and ceramics, they are sometimes referred to as colours or stains; when used to colour paints and plastics, they are known as pigments.

The colour of mixed metal oxide pigments results from the incorporation of cation of transition metals, the so-called chromophores, into the structure of stable host oxides. The host can be a single oxide (e.g. SnO_2 , TiO_2) or a mixed oxide (e.g. ZrSiO_4 , MgAl_2O_4). Typical examples of the chromophores are transition metal ions (Fe, Cr, Mn, Ni, Co, Cu, V, etc.) and rare-earth elements (Ce, Pr, Nd).

The pigments of the $\text{CeO}_2\text{--PrO}_2$ system give interesting colour hues in ceramic glazes which are based on the incorporation of praseodymium ions (as chromophore) into the host lattice of CeO_2 . These pigments are formed by a solid solution $\text{Ce}_{1-x}\text{Pr}_x\text{O}_2$ with the fluorite structure of CeO_2 . This type of pigments is prepared by high-temperature calcination of the basic starting oxides CeO_2 and Pr_6O_{11} [2]. Their hues of colour in ceramic glazes are very interesting. They give various pink–orange hues, which represent only a

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small, but an important part of the entire family of the inorganic pigments.

2. Experimental

As a starting material for the preparation of the $\text{Ce}_{1-x}\text{Pr}_x\text{O}_2$ pigments, we have used commercial CeO_2 of 95% purity and Pr_6O_{11} of 90% purity (Indian Rare Earths Ltd., India).

The starting mixtures containing basic oxides (CeO_2 and Pr_6O_{11}) with the increasing content of praseodymium ($x = 0.05, 0.10, 0.20, 0.30, 0.40, 0.50, 0.60, 0.70, 0.80$ and 0.90) 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 K/min). The calcination temperature was $1350\text{ }^\circ\text{C}$ for the duration of 1 h . The pigments prepared were applied to a middle-temperature glaze in amounts of 10% (mass/mass) with a glazing temperature of $1050\text{ }^\circ\text{C}$ for 15 min [2]. 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 colour properties are described 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 value L^* represents the lightness or darkness of the colour as related to a neutral grey scale. In the $L^*a^*b^*$ system, it is described by numbers from zero (black) to 100 (white).

The formation of these types of pigments was followed by thermal analysis using STA 449C Jupiter (NETZSCH, Germany) which allows the evaluation of data and simultaneous registration of the thermoanalytical curves TG and DTA. The starting raw material and the some prepared starting mixtures were studied by thermal analysis in ceramic crucible in air in temperature region from 30 to $1500\text{ }^\circ\text{C}$. The increase of temperature was 10 K/min . $\alpha\text{-Al}_2\text{O}_3$ was used as reference material.

The powder pigments were studied by X-ray diffraction analysis. The X-ray diffractograms in the range $20\text{--}60^\circ 2\theta$ of the samples were obtained using a vertical X-ray diffractometer HZG-4B (Freiburger Präzisionsmechanik, Germany) equipped with a goniometer of 25 cm diameter in the range $20\text{--}60^\circ 2\theta$. $\text{Cu K}\alpha$ ($\lambda = 0.154178\text{ nm}$) radiation was used for the

angular range of $2\theta < 35^\circ$ and $\text{K}\alpha 1$ ($\lambda = 0.154051\text{ nm}$) for the range of $2\theta > 35^\circ$, employing a nickel filter for attenuation of the $\text{K}\beta$ radiation. A proportional detector was used.

3. Results and discussion

The main aim was to found such a pigment, which would give the intensive pink–orange colour and at the same time being of the low content of praseodymium. The effect of the praseodymium content in the starting mixtures on the colour hue of the pigments was studied.

The effect of the praseodymium content in the mixtures on the colour hue of these pigments applied in glaze is demonstrated in Table 1. The increasing content of praseodymium decreases the red hue (coordinate a^*) and yellow hue (coordinate b^*) of these pigments. The intensive pink–orange colour with the acceptable low content of praseodymium was attributed to the pigment containing $10\text{ mol}\%$ of praseodymium. This pigment can be described by the formula $\text{Ce}_{0.90}\text{Pr}_{0.10}\text{O}_2$. When $50\text{ mol}\%$ of praseodymium is used, the colour hue of the pigment is shifted to red–brown hue. Higher content of praseodymium increases value L^* and a^* and shifts colour to brown–yellow (Fig. 1). This effect corresponds with the fact that these samples are heterogeneous because free PrO_2 exists next solid solution of both oxides (PrO_2 in CeO_2).

The structure of the pigments of $\text{Ce}_{1-x}\text{Pr}_x\text{O}_2$ type was also investigated. The samples with the increasing content of praseodymium ($x = 0.05, 0.10, 0.20, 0.30, 0.40, 0.50, 0.60, 0.70, 0.80$ and 0.90) were studied by

Table 1

The effect of Pr content on the colour properties of the $\text{Ce}_{1-x}\text{Pr}_x\text{O}_2$ pigments applied to glaze G07091

Formula	L^*	a^*	b^*
$\text{Ce}_{0.95}\text{Pr}_{0.05}\text{O}_2$	62.71	26.96	33.17
$\text{Ce}_{0.90}\text{Pr}_{0.10}\text{O}_2$	60.21	23.53	33.21
$\text{Ce}_{0.80}\text{Pr}_{0.20}\text{O}_2$	56.82	22.62	32.61
$\text{Ce}_{0.70}\text{Pr}_{0.30}\text{O}_2$	56.36	18.51	29.61
$\text{Ce}_{0.60}\text{Pr}_{0.40}\text{O}_2$	55.27	16.06	27.06
$\text{Ce}_{0.50}\text{Pr}_{0.50}\text{O}_2$	55.02	14.02	26.01
$\text{Ce}_{0.40}\text{Pr}_{0.60}\text{O}_2$	50.51	8.64	21.62
$\text{Ce}_{0.30}\text{Pr}_{0.70}\text{O}_2$	56.72	4.96	25.85
$\text{Ce}_{0.20}\text{Pr}_{0.80}\text{O}_2$	61.35	4.21	30.21
$\text{Ce}_{0.10}\text{Pr}_{0.90}\text{O}_2$	62.21	3.52	39.21

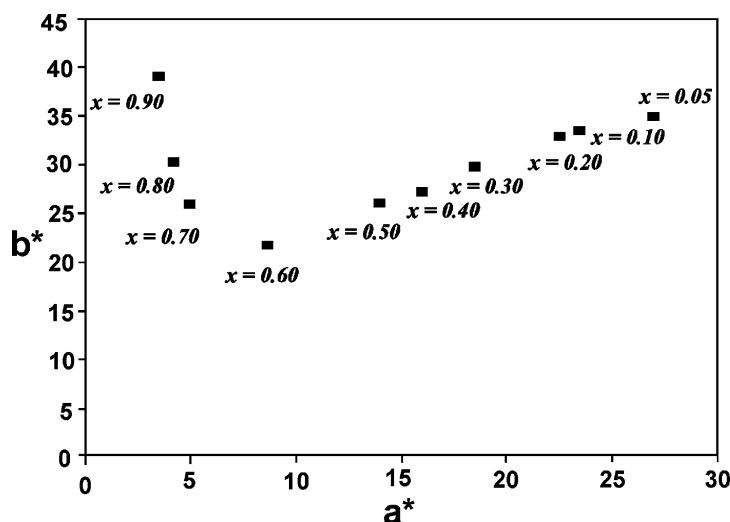


Fig. 1. The effect of Pr content on the colour properties of the $\text{Ce}_{1-x}\text{Pr}_x\text{O}_2$ pigments applied to glaze G07091.

X-ray diffraction analyses. The observed diffraction lines corresponded with characteristic lines of fluorite structure of CeO_2 . The samples with the highest content of praseodymium ($x = 0.70, 0.80$ and 0.90) exhibited additional peaks, which have been assigned to PrO_2 . PrO_2 dissolves in CeO_2 forming thus $\text{Ce}_{1-x}\text{Pr}_x\text{O}_2$ solid solutions up to $x = 0.6$.

The values of lattice parameters of cerium dioxide (Table 2) show that the parameter a decreases with the increasing content of praseodymium. Praseodymium atoms substitute cerium atoms in their crystal lattice forming uncharged substitutional defects Pr_{Ce}^x in the solid solution $\text{Ce}_{1-x}\text{Pr}_x\text{O}_2$. The formation of these

defects is associated with the decrease of the volume of the elementary cell of CeO_2 . Praseodymium enters into CeO_2 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 ($r[\text{Ce}^{4+}] = 0.101 \text{ nm}$).

The raw material for the preparation of the $\text{Ce}_{1-x}\text{Pr}_x\text{O}_2$ pigments was mixed oxide Pr_6O_{11} . Praseodymium ions are available in two oxidation states in this mixed oxide Pr_6O_{11} ($4\text{PrO}_2 \cdot \text{Pr}_2\text{O}_3$). In the temperature range from 250 to 400°C , mixed oxide Pr_6O_{11} is reduced to Pr_2O_3 [3]. On the base of results of thermal analysis (Fig. 2), it follows that process of reduction is represented by endothermal effect on the DTA curve (350°C).



Crystal lattice of Pr_2O_3 is characterised by excess of oxygen. From DTA curve (Fig. 2), it follows that the content of oxygen is decreased with increasing temperature. This loss of oxygen is represented by several endothermal effects on DTA curve (Fig. 2). The formula of praseodymium oxides was evaluated on the base of mass loss. The sequence of these changes is described by following schemes (2)–(5):

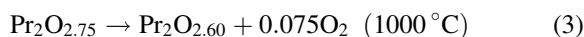
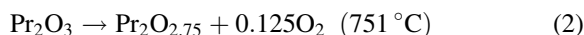


Table 2

Structural parameters of samples of $\text{Ce}_{1-x}\text{Pr}_x\text{O}_2$ pigments and CeO_2

Formula	a (nm)	V (nm ³)	$\Delta 2v^a$
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 $\Delta 2v = N^{-1}(2v_{\text{exp}} - 2v_{\text{calc}})$, where $2v_{\text{exp}}$ is the experimental diffraction angle, $2v_{\text{calc}}$ the angle calculated from lattice parameters and N the number of investigated diffraction lines.

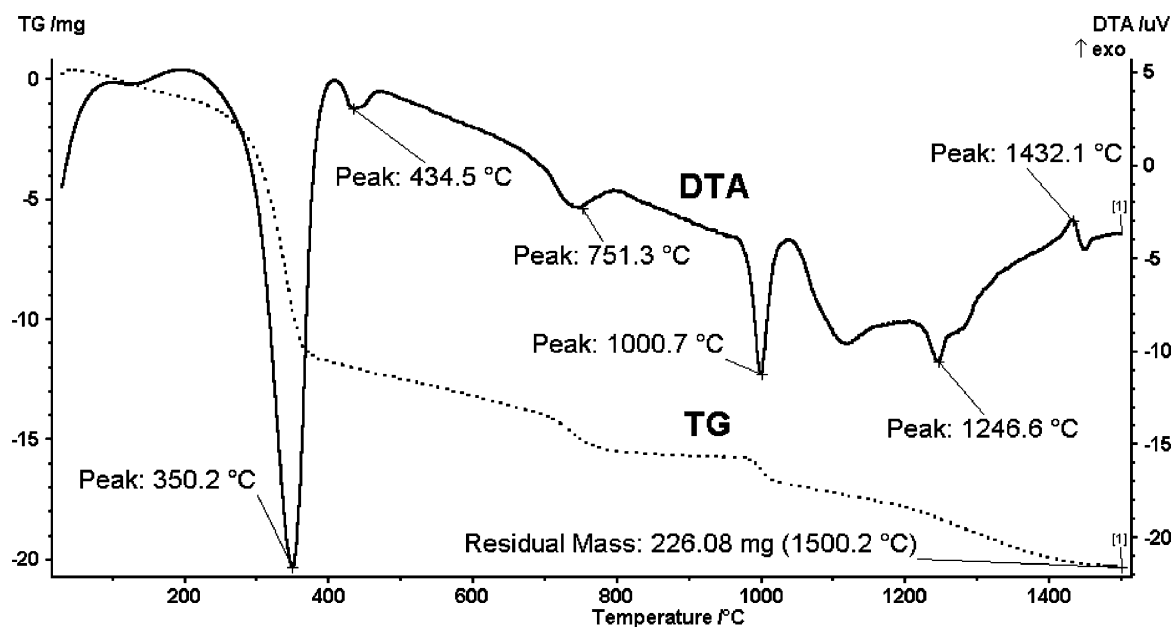


Fig. 2. TG and DTA curves of mixed oxide Pr_6O_{11} (mass of sample: 246.40 mg; atmosphere: air; heating rate: 10 K/min).

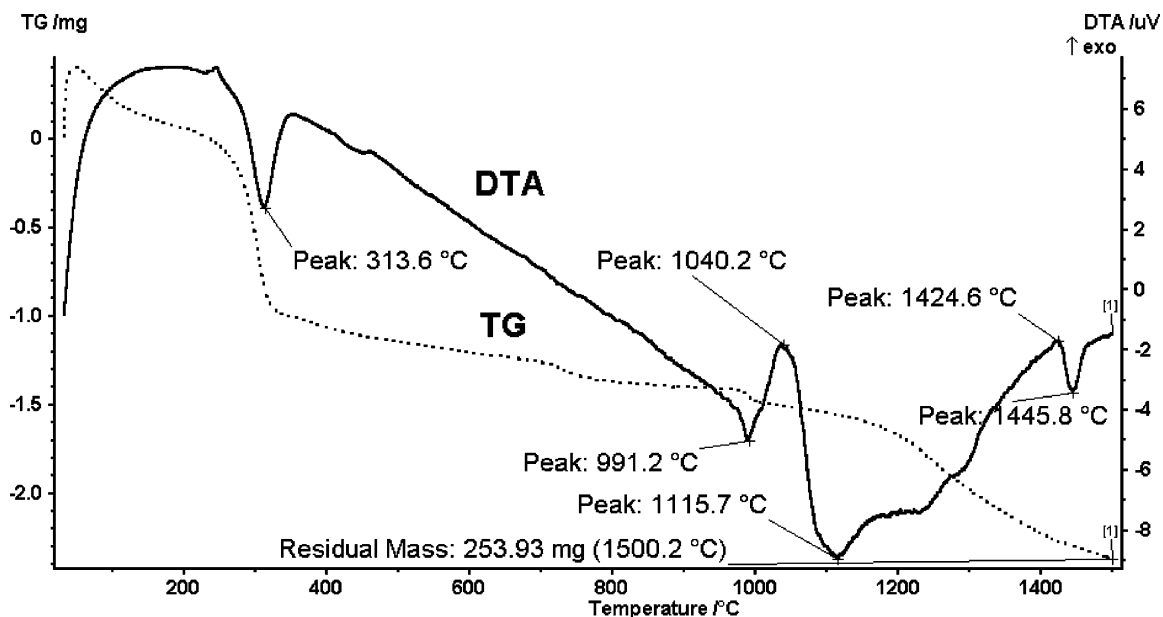
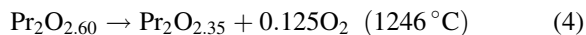


Fig. 3. TG and DTA curves of mixture for synthesis $\text{Ce}_{0.90}\text{Pr}_{0.10}\text{O}_2$ (mass of sample: 256.30 mg; atmosphere: air; heating rate: 10 K/min).



From the DTA curve (Fig. 2) it follows that the last peak, which is exothermal, belongs to the oxidation of trivalent praseodymium ions to tetravalent ions. This effect is not characterised by an increasing of sample weight, because the content of oxygen is still decreased. For oxide PrO_2 (scheme (5)), it can be used better formula $\text{PrO}_{2-\delta}$, where parameter δ characterises loss of oxygen [4].

The mixture from starting oxides (CeO_2 and Pr_6O_{11}) containing 10 mol% of Pr was homogenised in agate mortar. This mixture was also studied by DTA. From DTA curve of mixture for synthesis of $\text{Ce}_{0.9}\text{Pr}_{0.1}\text{O}_2$ (Fig. 3), it follows that the endothermal effect of reduction of Pr_6O_{11} is shifted to lower temperature (313°C). Exothermal effect above 1400°C attributes to oxidation of trivalent praseodymium ions. Last peak on DTA curve belongs to dissolving of PrO_2 into CeO_2 . This fact corresponds with the results of X-ray diffraction analyses. It means that the pigment crystals are formed during the high-temperature reaction between CeO_2 and PrO_2 . PrO_2 dissolves in CeO_2 during the heat treatment of the starting mixtures forming the solid solution of both oxides $\text{Ce}_{1-x}\text{Pr}_x\text{O}_2$. The dissolving of PrO_2 in CeO_2 is characterised by endothermic effect on the DTA curve of mixture for synthesis of $\text{Ce}_{0.9}\text{Pr}_{0.1}\text{O}_2$ with minimum at 1445°C . The formation of solid solution is described by the following scheme:



4. Conclusion

The compounds based on CeO_2 are heat- and chemical-resistant. They have intensive colour and great hiding power. 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. The pigments are insoluble in concentrated H_2SO_4 and HCl [4]. This property reflects the strength of the crystal lattice of the pigments prepared. These pigments 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.

Acknowledgements

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