

THERMAL SYNTHESIS OF THE CeO₂–PrO₂–La₂O₃ PIGMENTS

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Abstract

The synthesis of new compounds based on CeO₂–PrO₂–La₂O₃, 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. 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 449/C Jupiter (Netzsch, Germany).

Keywords: ceramic pigments, optical properties, solid solutions CeO₂–PrO₂, thermal analysis

Introduction

The pigments on the base of CeO₂ 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. This type of pigments also represents mixed metal oxides [1].

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. Their commercial significance is in their thermal, chemical and light stability, combined with their low toxicity. The colour of mixed metal oxide pigments results from the incorporation of cation of transition metals, so-called chromophores, into the structure of stable host oxides. Typical examples of the chromophores are transition metal ions (Fe, Cr, Mn, Ni, Co, Cu, V, etc.) and rare earth elements (Ce, Pr, Nd) [2].

The pigments of the CeO₂–PrO₂–La₂O₃ system give interesting pink-orange hues in ceramic glazes which are based on the incorporation of praseodymium and lanthanum ions (as chromophore) into the host lattice of CeO₂ [3]. These pigments are formed by a solid solution Ce_{0.95–y}Pr_{0.05}La_yO_{2–y/2} with the fluorite structure of CeO₂. This type of pigments is prepared by high-temperature calcination of the basic starting oxides CeO₂, Pr₆O₁₁ and La₂O₃.

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Experimental

As a starting material for the preparation of the Ce_{0.95-y}Pr_{0.05}La_yO_{2-y/2} pigments we have used commercial CeO₂ of 95% purity, Pr₆O₁₁ of 90% purity and La₂O₃ of 99% purity (Indian Rare Earths Ltd., India).

The starting mixtures containing basic oxides (CeO₂, Pr₆O₁₁ and La₂O₃) with the increasing content of lanthanum (y=0.05, 0.15, 0.25, 0.35, 0.45, 0.55, 0.65, 0.75 and 0.85) 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°C min⁻¹). The calcination temperature was 1350°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°C for 15 min [3]. 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 gray scale. In the L* a* b* system it is described by numbers from zero (black) to hundred (white).

The formation of these 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 same prepared starting mixtures were studied by thermal analysis in ceramic crucible in air in temperature region from 30 to 1500°C. The increase of temperature was 10°C min⁻¹. α-Al₂O₃ was used as reference material [4].

The powder pigments were studied by X-ray diffraction analysis. The X-ray diffractograms in the range of 20 to 60° 2θ 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 to 60° 2θ. CuK_α (λ=0.154178 nm) radiation was used. A proportional detector was used.

Results and discussion

The main aim was to develop conditions of the synthesis of pigments based on the fluorite structure of CeO₂ with admixture of La₂O₃. The influence of lanthanum oxide on the colouring effect of the Ce_{0.95-y}Pr_{0.05}La_yO_{2-y/2} pigments was also studied. Based on experimental data for these pigments applied in borate–silicate glaze (Table 1), it can be seen that increasing La content produces pigments having dark pink-orange to light yellow-orange hues. Lanthanum content of 5 to 25 mol% in pigments gives intense pink-orange hues. At higher lanthanum content (35–55 mol%) the colour intensity and red character of these pigments decrease. Lanthanum content of 65 to 85 mol% increases L* and b* values and pigment colour is shifted to yellow and becomes lighter.

The structure of the Ce_{0.95-y}Pr_{0.05}La_yO_{2-y/2} pigments was also investigated. Pigments having lanthanum content of 5, 15, 25, 35, 45, 55, 65, 75 and 85 mol% were

Table 1 The effect of lanthanides on the colour properties of Ce_{0.95-y}Pr_{0.05}La_yO_{2-y/2} pigments

Formula	L^*	a^*	b^*
Ce _{0.90} Pr _{0.05} La _{0.05} O _{1.975}	66.23	20.31	26.94
Ce _{0.80} Pr _{0.05} La _{0.15} O _{1.925}	71.16	17.66	26.57
Ce _{0.70} Pr _{0.05} La _{0.25} O _{1.875}	73.41	15.82	26.45
Ce _{0.60} Pr _{0.05} La _{0.35} O _{1.825}	76.34	11.31	23.54
Ce _{0.50} Pr _{0.05} La _{0.45} O _{1.775}	77.99	10.78	24.54
Ce _{0.40} Pr _{0.05} La _{0.55} O _{1.725}	79.69	7.94	22.92
Ce _{0.30} Pr _{0.05} La _{0.65} O _{1.675}	80.73	5.84	25.13
Ce _{0.20} Pr _{0.05} La _{0.75} O _{1.625}	82.71	2.02	29.98
Ce _{0.10} Pr _{0.05} La _{0.85} O _{1.575}	83.21	-0.58	34.34

studied by X-ray diffraction analyses. Diffraction lines characteristic of the fluorite structure of CeO₂ were observed. All of the pigments with $y=0.05, 0.15, 0.25, 0.35, 0.45$ and 0.55 exhibited only peaks that could be assigned to CeO₂, indicating that they were homogeneous. PrO₂ and La₂O₃ dissolved in CeO₂ at 1300°C forming a solid solution. When lanthanum content of 65, 75 and 85 mol% is used, peaks were evident that could be assigned to La₂O₃, as these pigments were heterogeneous [5].

Praseodymium atoms replace cerium atoms in the crystal lattice forming uncharged substitutional defects Pr_{Ce}^x in the solid solution of Ce_{0.95-y}Pr_{0.05}La_yO_{2-y/2} pigments. Praseodymium enters into CeO₂ as substitutional defects because the tetravalent Pr ion ($r(\text{Pr}^{4+})=0.092$ nm) has a smaller radius than the tetravalent Ce ion ($r(\text{Ce}^{4+})=0.101$ nm). Ions of lanthanum ($r(\text{La}^{3+})=0.115$ nm), that enter to the fluorite structure, have a little larger than Ce⁴⁺ ions, which are substituted. The formation of these defects is associated with an increase of the volume of the elementary CeO₂ cell (Table 2).

The raw material of Pr was mixed oxide Pr₆O₁₁ [6]. Pr ions are available in two oxidation states in this mixed oxide Pr₆O₁₁ (4PrO₂·Pr₂O₃). In the temperature range from 250 to 400°C mixed oxide Pr₆O₁₁ is reduced to Pr₂O₃. On the base of results of DTA it

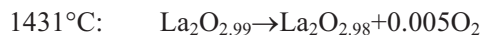
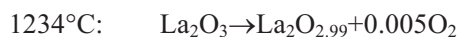
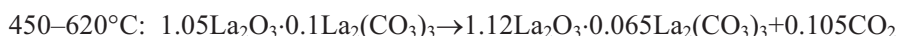
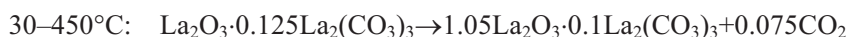
Table 2 Lattice parameters of Ce_{0.95-y}Pr_{0.05}La_yO_{2-y/2} pigments and CeO₂

Formula	a/nm	V/nm^3	$\Delta 2\nu^a$
CeO ₂	0.54221	0.15941	0.004
Ce _{0.90} Pr _{0.05} La _{0.05} O _{1.975}	0.54486	0.16175	0.005
Ce _{0.80} Pr _{0.05} La _{0.15} O _{1.925}	0.55021	0.16656	0.003
Ce _{0.70} Pr _{0.05} La _{0.25} O _{1.875}	0.55424	0.17025	0.005
Ce _{0.60} Pr _{0.05} La _{0.35} O _{1.825}	0.55759	0.17328	0.006
Ce _{0.50} Pr _{0.05} La _{0.45} O _{1.775}	0.55984	0.17547	0.001
Ce _{0.40} Pr _{0.05} La _{0.55} O _{1.725}	0.56102	0.17658	0.005

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

follows that process of reduction is represented by endothermic effect on the DTA curve (350°C). Crystal lattice of Pr₂O₃ is characterized by excess of oxygen. From DTA curve it follows that the content of oxygen is decreased with increasing temperature. This loss of oxygen is represented by several endothermic effects on DTA curve [7].

The next raw oxide for synthesis was La₂O₃. On the base of results of thermal analysis (Fig. 1) it follows that this oxide is mixture of oxide and carbonate with formula La₂O₃·0.125La₂(CO₃)₃. This formula was evaluated on the base of mass loss (TG curve). This raw material is changed to La₂O₃ with increasing temperature (Table 3). This process is represented by three endothermic effect on the DTA curve and the sequence of these changes is described by following schemes. From DTA curve it follows that the content of oxygen in La₂O₃ is decreased at temperature above 1200°C. This loss of oxygen is represented by two endothermic effects on DTA curve.



The mixture from starting oxides (CeO₂, Pr₆O₁₁ and La₂O₃) containing 5 mol% of Pr and 25 mol% of La was homogenized in agate mortar. This mixture was also studied by DTA (Fig. 2). From DTA curve of mixture for synthesis of Ce_{0.7}Pr_{0.05}La_{0.25}O_{1.875} it follows that the endothermic effect of reduction of Pr₆O₁₁ is shifted to lower temperature (311°C). Next endothermic effect with minimum at 397°C corresponds to partial decomposition of La₂O₃·0.125La₂(CO₃)₃. This decomposition follows in temperature range from 500 to 800°C (Table 4). These endothermic effects are characterized by the decrease of mass on TG curve.

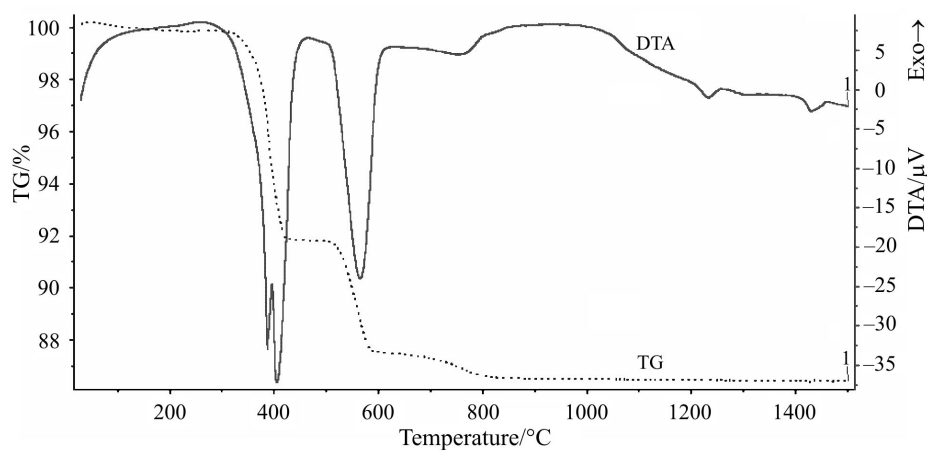
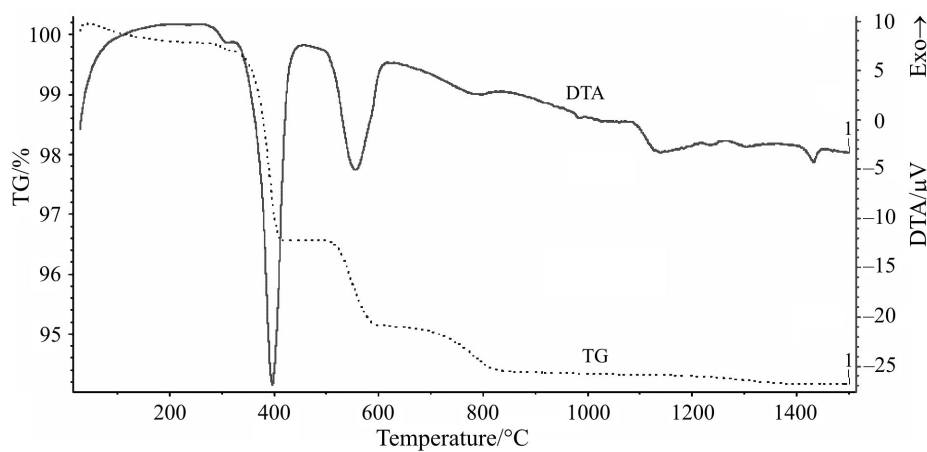
Exothermic effect about 1087°C attributes to partial oxidation of trivalent praseodymium ions to tetravalent ions. This effect is ended at temperature above 1300°C. Last endothermic peak on DTA curve with minimum at 1432°C belongs to dissolving of PrO₂ and La₂O₃ into CeO₂. This fact corresponds with results of X-ray

Table 3 Thermal decomposition of La₂O₃ (Fig. 1)

Temperature range/°C	Peak temperature/°C	Mass loss/%
30–450	388 406	8.18
450–620	566	4.32
620–850	752	0.97
850–1500	1234 1431	0.11

Table 4 Thermal decomposition of the mixture for synthesis Ce_{0.7}Pr_{0.05}La_{0.25}O_{1.875}La₂O₃ (Fig. 2)

Temperature range/°C	Peak temperature/°C	Mass loss/%
30–420	312 397	3.28
420–600	557	1.42
600–850	798	0.78
850–1500	1087 1432	0.36

**Fig. 1** TG and DTA curves of La₂O₃ (mass of sample: 200.45 mg, atmosphere: air, heating rate: 10°C min⁻¹)**Fig. 2** TG and DTA curves of the mixture for synthesis Ce_{0.7}Pr_{0.05}La_{0.25}O_{1.875}La₂O₃ (mass of sample: 253.00 mg, atmosphere: air, heating rate: 10°C min⁻¹)

diffraction analysis. It means that the pigment crystals are formed during the high temperature reaction between CeO₂, PrO₂ and La₂O₃. PrO₂ and La₂O₃ dissolve in CeO₂ during the heat treatment of the starting mixtures forming the solid solution of all oxides Ce_{1-(x+y)}Pr_xLa_yO_{2-y/2}. The formation of solid solution is described by the following scheme:



Conclusions

Ce_{0.95-y}Pr_{0.05}La_yO_{2-y/2} type pigments are characterised by heat stability, intense colour and very good hiding power. Due to their high resistance to degradation by molten glass in glazes and enamels, these pigments may be classified as high-temperature pigments. They are suitable for all types of ceramic glazes and are environmentally friendly. In addition, these pigments give interesting pink-orange hues in ceramic glazes.

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The preparation of this type of pigment was investigated within the framework of a grant project dealing with new ecological high-temperature inorganic pigments. This work was supported by the grant No. 104/02/1443 from the Grant Agency of Czech Republic.

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