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THERMAL ANALYSIS OF PIGMENTS BASED ON CeO_2

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Abstract

The synthesis of new compounds based on CeO_2 is investigated in our laboratory. The main attention is directed to the preparation of these compounds which can be used as pigments for colouring of ceramic glazes. The synthesis of these compounds is based on high-temperature calcination of starting oxides. The optimum conditions for the syntheses of compounds have been estimated and the pigments prepared have been evaluated from the standpoint of their structure.

Keywords: ceramic pigments, optical properties, solid solutions CeO_2–PrO_2

Introduction

The pigments on the base of cerium dioxide 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 inorganic pigments [1].

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. These pigments are formed by a solid solution $Ce_{1-x}Pr_xO_2$ 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}.

Experimental

As a starting material for the preparation of $Ce_{1-x}Pr_xO_2$ 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}) 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 one hour. The pigments prepared were applied to a middle-temperature borate-silicate glaze in amounts of 10% (mass/mass) with a glazing temperature of 1000°C for 15 min [2].

The formation of these types of pigments was followed by thermal analysis using TA Instruments Co. apparatus (USA) which allows the evaluation of data and simultaneous registration of the thermoanalytical curves TG and DTA. The starting

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raw material and some prepared starting mixtures were studied by thermal analysis in ceramic crucible in air. The increase of temperature was 5°C $\min^{-1}$ [3].

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 Zeiss HZG-4B (Freiberger Präzisionsmechanik, Germany) equipped with a goniometer of 25 cm diameter.

Results and discussion

The main aim was to find such a pigment that 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 Fig. 1. The increasing content of praseodymium decreases the red hue of these pigments. The intensive pink-orange colour with the acceptable low content of praseodymium was attributed to 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.

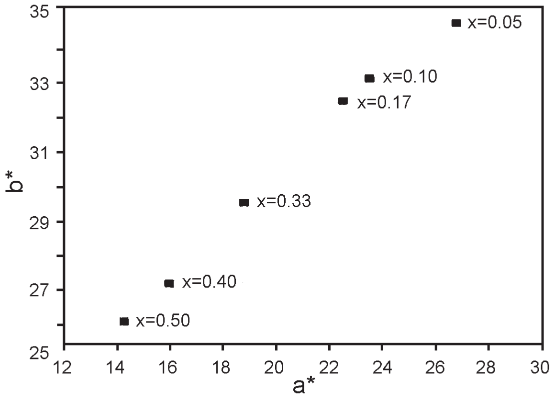

Fig. 1 The effect of the praseodymium content on the colour properties of the $Ce_{1-x}Pr_xO_2$ pigments (application in glaze)

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, 60, 70, 80 and 90 mol%) were studied by X-ray diffraction analyses. The observed diffraction lines corresponded with characteristic lines of fluorite structure of cerium dioxide. The samples with the highest content of praseodymium (70, 80 and 90 mol%) exhibited additional peaks, which have been assigned to PrO_2. Praseodymium dioxide, PrO_2, dissolves in CeO_2 forming thus $Ce_{1-x}Pr_xO_2$ solid solutions up to x=0.6.

Table 1 Lattice parameters of samples of the $Ce_{1-x}Pr_xO_2$ pigments and CeO_2

Formula	a/nm	V/nm^3	$\Delta 2\upsilon$[a]
CeO_2	0.54221(6)	0.15941(6)	0.002
$Ce_{0.90}Pr_{0.10}O_2$	0.54205(2)	0.15927(2)	0.007
$Ce_{0.80}Pr_{0.20}O_2$	0.54178(2)	0.15902(2)	0.003
$Ce_{0.70}Pr_{0.30}O_2$	0.54163(4)	0.15889(4)	0.005
$Ce_{0.60}Pr_{0.40}O_2$	0.54145(5)	0.15873(1)	0.004
$Ce_{0.50}Pr_{0.50}O_2$	0.54137(3)	0.15866(2)	0.005
$Ce_{0.40}Pr_{0.60}O_2$	0.54122(1)	0.15853(1)	0.002

[a] $\Delta 2\upsilon = N^{-1}(2\upsilon_{exp} - 2\upsilon_{calc})$, where $2\upsilon_{exp}$ is the experimental diffraction angle, $2\upsilon_{calc}$ 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 1) show that 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 $Ce_{1-x}Pr_xO_2$. The formation of these defects is associated with the decrease of the volume of the elementary cell of CeO_2. Praseodymium enters into cerium dioxide as substitutional defects instead of cerium because the tetravalent praseodymium ion ($r(Pr^{4+})=0.092$ nm) has a smaller radius than the tetravalent cerium ion ($r(Ce^{4+})=0.101$ nm).

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

$$(1-x)CeO_2 + x/6Pr_6O_{11} + x/12O_2 \rightarrow Ce_{1-x}Pr_xO_2 \tag{1}$$

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. On the basis of results of thermal analysis it follows that process of reduction is represented by endothermic effect in the DTA curve (Fig. 2). The mass loss corresponding to the temperature range of the first endothermic effect is in good agreement with theoretical value calculated on the base of the reaction equation. From Fig. 3 (DTA curve of mixture $Ce_{0.9}Pr_{0.1}O_2$) it follows that this endothermic effect is shifted to lower temperature (261°C).

$$Pr_6O_{11} \rightarrow 3Pr_2O_3 + O_2 \tag{2}$$

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

$$Pr_2O_3 + 1/2O_2 \rightarrow 2PrO_2 \tag{3}$$

The pigment crystals are formed during its preparation by high temperature reaction of 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 $Ce_{1-x}Pr_xO_2$.

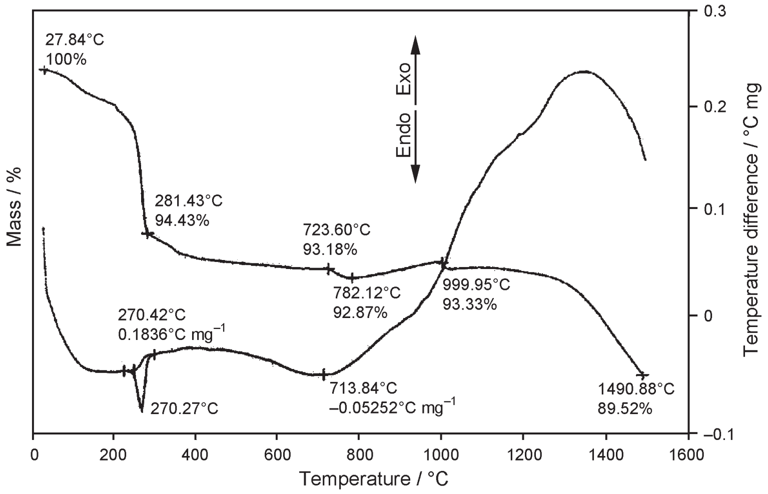

Fig. 2 TG and DTA curves of mixed oxide Pr_6O_{11}

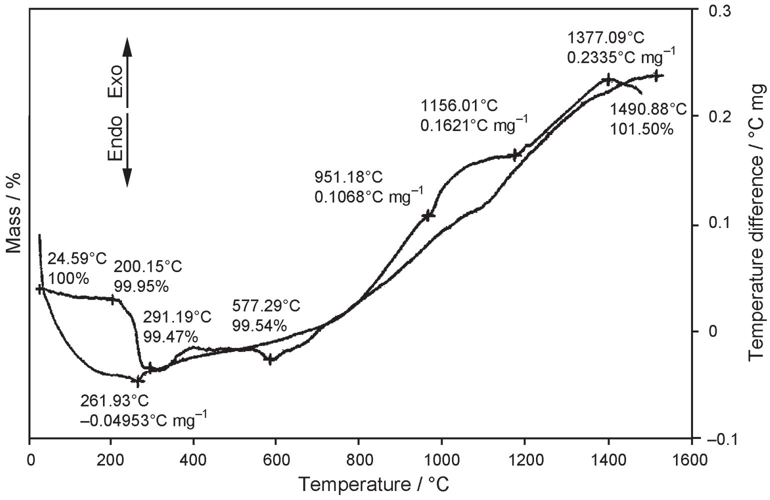

Fig. 3 TG and DTA curves of mixture $Ce_{0.9}Pr_{0.1}O_2$

Conclusions

The compounds based on CeO_2 are characterised by heat stability, 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. Unlike the starting oxides, the pigments are insoluble in concentrated H_2SO_4 and HCl. This property reflects the strength of the crystal lattice of the pigments prepared.

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

References

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