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THERMAL SYNTHESIS OF THE CeO_2–PrO_2–Nd_2O_3 PIGMENTS

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The synthesis of new compounds based on the CeO_2–PrO_2–Nd_2O_3 system, 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 methods of thermal analysis provided first information about the temperature region of the formation of the pigments investigated. The synthesis of these compounds was followed by thermal analysis using STA 449/C Jupiter (Netzsch, Germany).

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

Introduction

Ceramic pigments are used for colouring of ceramic glazes, ceramic materials and enamels [1]. It is possible thanks to their high thermal stability and chemical resistance. Last ten years they are used not only for high-temperature purposes but more and more often for colouring of paints, plastic or building materials (façades, interpavers, roof coverings).

Research of our workplace is concentrated not only on well-known types of ceramic pigments (for instance spinel, zircon, rutile, etc.) but also on preparation of new inorganic compounds which would obtain interesting colours and could be applicable as pigments. Growing demands for thermal stability and ecological purity of pigments make difficulties to compile a colour range of available pigments and their colour hues. The most requisite hues are yellow, pink, orange and red. Their presence in the ceramic field is insufficient. The main reason is the fact that most of applied pigments contain elements which are found at present time as ecologically and hygienically problematical and even unacceptable.

Especially elements like Pb, Cr^{6+}, Cd, Sb and Se belonging to inorganic pigments are undesirable [2]. More than that, great difficulties in an area of ceramic pigments make elements like lead and antimony. Both together create the yellow pyrochlore pigment $Pb_2Sb_2O_7$. Antimony is also included in many rutile pigments of yellow, ochre, brown and black hues. Hexavalent chromium is absolutely unacceptable.

The new direction for pigment research started because of ecological pressure. Compounds unacceptable in the past for their high prices have been at present time investigated. These compounds contain elements of the rare earth. Such pigments are either compounds of lanthanides (oxide or sulfide compounds) or compounds created by the host crystal structure (ZrO_2, Al_2O_3) where ions of lanthanides work like chromophores [3, 4].

Pigments whose basis are supporting structures of the fluorite lattice CeO_2 and ions of praseodymium like a chromophore look interesting [5]. The pigment is created by the solid solution of $Ce_{1-x}Pr_xO_2$. This compound is created during the high-temperture calcination (1300°C) when praseodymium dioxide is dissolved in CeO_2. The colour hue depends on the praseodymium content, begins at pink–orange, goes on to red–brown and ends at brown. The brown requires high content of praseodymium ($x>0.6$). Final colour pigment hue can be influenced by adding of another lanthanides (Ln), the results are compounds created by the system CeO_2–PrO_2–Ln_2O_3, i.e. it is characterized by the partial dissolving of Ln_2O_3 together with the praseodymium dioxide into CeO_2 forming a solid solution of $Ce_{1-(x+y)}Pr_xLn_yO_{2-2/y}$.

The submitted work investigates conditions of the synthesis of compounds $Ce_{0.95-y}Pr_{0.05}Nd_yO_{2-y/2}$, structural, applied and colour properties of pigments are measured, their using for colouring of ceramic glazes is evaluated.

Experimental

As a starting material for the preparation of the $Ce_{0.95-y}Pr_{0.05}Nd_yO_{2-y/2}$ pigments we have used commercial CeO_2 of 95% purity, Pr_6O_{11} of 90% purity and Nd_2O_3 of 99% purity (Indian Rare Earths Ltd., India). The starting mixtures containing basic oxides (CeO_2,

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Pr_6O_{11} and Nd_2O_3) with the increasing content of neodymium (*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 one hour. 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 [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 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 some prepared starting mixtures were studied by thermal analysis in corundum crucible in air in temperature region from 30 to 1500°C. The increase of temperature was 10°C $\min^{-1}$. α-Al_2O_3 was used as reference material [6, 7].

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_λ (λ=0.154178 nm) radiation was used. A proportional detector was used.

Results and discussion

The attention was concentrated on the research how much the growing content of neodymium is able to influence colour properties of pigment types $Ce_{0.95-y}Pr_{0.05}Nd_yO_{2-y/2}$. The starting mixtures corresponding to the formula $Ce_{0.95-y}Pr_{0.05}Nd_yO_{2-y/2}$ with *y*=0.05, 0.15, 0.25, 0.35, 0.45, 0.55, 0.65, 0.75 and 0.85 were prepared. Fired pigments were blended in an agate mortar and applied into the ceramic glaze.

It can be seen after pigment application in the borate–silicate glaze (Table 1) that increasing content of neodymium makes gradual declining of the colour value a^*. Red character of these pigments is decreased and give pink–orange colour of the glaze application. The same tendency, i.e. the slow declining is seen even at the colour values b^* up to *y*=0.65. Higher content of neodymium rises at the value b^* and produces a higher yellow hue having yellow–orange tint. Growing neodymium content increases brightness at the value L^* and pigment hues became lighter.

On the base of objective colour rating, pigments can be divided in two groups. First group are represented by pigments with *y*=0.05–0.65 and give deep pink–orange hues. Second group are pigments with *y*=0.75 and 0.85 and give yellow–orange hues.

The identification of compounds having $Ce_{0.95-y}Pr_{0.05}Nd_yO_{2-y/2}$ with *y*=0.05, 0.15, 0.25, 0.35, 0.45, 0.55, 0.65, 0.75 and 0.85 were studied by X-ray diffraction analyses. Samples with *y*=0.05–0.65 are single-phase because obtained diffraction lines exhibited only peaks that could be assigned to CeO_2. Diffraction lines of samples with the higher content of neodymium (*y*=0.75 and 0.85) exhibited even other diffraction peaks corresponding with diffraction of the plane of crystal lattice Nd_2O_3. These samples are two-phase and created by solid solution of $Ce_{0.95-y}Pr_{0.05}Nd_yO_{2-y/2}$ and by free Nd_2O_3 (hexagonal) whose the most intensive zone was situated at the range of 2θ approximately 30.7°.

This inquiry is also in accordance with colour properties of prepared compounds $Ce_{0.95-y}Pr_{0.05}Nd_yO_{2-y/2}$. This type provides the glazes of deep pink–orange colour hues in the area of mutual solubility of all three oxides (*y*=0.05–0.65). On the other hand, higher content of neodymium (*y*=0.75 and 0.85) created at second phase Nd_2O_3, moves the pigment colour up to yellow–orange.

Growing content of neodymium increases value of the lattice parameter *a* and also volume of elementary cell in the crystal lattice CeO_2 (Table 2). Ions of neodymium incorporated into the crystal lattice of cerium dioxide are accompanied by significant deformation of elementary cell in the crystal lattice CeO_2 because incorporation of Nd^{3+} results at volume extension made by its higher ion radius ($r(Ce^{4+})$=0.101 nm, $r(Pr^{4+})$=0.092 nm, $r(Nd^{3+})$=0.108 nm).

Table 1 The effect of Nd content on the colour properties of $Ce_{0.95-y}Pr_{0.05}Nd_yO_{2-y/2}$ pigments

y	L^*	a^*	b^*
0.05	58.71	24.16	28.39
0.15	64.61	19.61	25.87
0.25	68.13	16.33	24.68
0.35	69.74	13.84	23.26
0.45	70.86	11.14	22.35
0.55	71.63	8.19	20.99
0.65	72.66	7.15	20.97
0.75	73.66	4.47	21.32
0.85	75.95	3.02	24.42

Table 2 Lattice parameters of $Ce_{0.95-y}Pr_{0.05}Nd_yO_{2-y/2}$ pigments and CeO_2

Formula	*a*/nm	*V*/nm^3	$\Delta 2\upsilon^a$
CeO_2	0.54221	0.15941	0.003
$Ce_{0.90}Pr_{0.05}Nd_{0.05}O_{1.975}$	0.54279	0.15992	0.005
$Ce_{0.80}Pr_{0.05}Nd_{0.15}O_{1.975}$	0.54427	0.16121	0.003
$Ce_{0.70}Pr_{0.05}Nd_{0.25}O_{1.875}$	0.54577	0.16257	0.003
$Ce_{0.60}Pr_{0.05}Nd_{0.35}O_{1.875}$	0.54725	0.16389	0.004
$Ce_{0.50}Pr_{0.05}Nd_{0.45}O_{1.775}$	0.54836	0.16489	0.003
$Ce_{0.50}Pr_{0.05}Nd_{0.55}O_{1.725}$	0.54955	0.16597	0.005
$Ce_{0.40}Pr_{0.05}Nd_{0.65}O_{1.675}$	0.55022	0.16626	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.

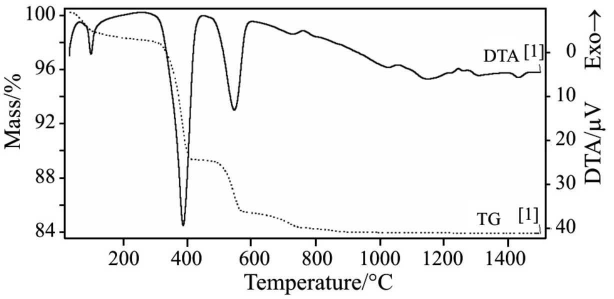

Fig. 1 TG and DTA curves of Nd_2O_3 (mass of sample: 183.50 mg, atmosphere: air, heating rate: 10°C min^{-1})

The pigment syntheses $Ce_{0.95-y}Pr_{0.05}Nd_yO_{2-y/2}$ type were studied with help of the thermal analysis (TG-DTA). Starting oxides, i.e. Nd_2O_3 and mixed oxide Pr_6O_{11} [7] followed by starting mixture for pigment preparation with $y=0.25$ were measured.

TG curve of starting oxide Nd_2O_3 indicates the mass loss at the temperature range from 30 to 120°C (Fig. 1). This process is represented by endothermic effect on the DTA curve with minimum at temperature 98°C and corresponds with the loss of oxide moisture. Temperature interval from 120 to 800°C makes the significant mass loss (Table 3) corresponding to decomposition of the carbonate $Nd_2(CO_3)_3$ which is included in the starting oxide. On the base of the mass loss, formula of the starting compound $Nd_2O_3{\cdot}0.1Nd_2(CO_3)_3$ was determined and decomposition of the carbonate was then represented on the DTA curve by three endothermic effects. At temperature 1028°C the endothermic effect on the DTA curve corresponds with the modification change of cubic Nd_2O_3 (C-type) for hexagonal modification Nd_2O_3 (A-type).

The process is accompanied by a small mass loss connected with the partial oxygen loss. Final oxide is being characterized by the formula $Nd_2O_{2.75}$. DTA curve at temperature above 1200°C is associated by a slight exothermic effect with maximum at temperature 1245°C connected with the repeated oxygen receiving. DTA curve at temperature above 1400°C is characterized by endothermic effect with minimum at temperature 1430°C connected with the reversible change of hexagonal modification Nd_2O_3 for cubic modification.

Table 3 Thermal decomposition of Nd_2O_3 (Fig. 1)

T_{range}/°C	T_{peak}/°C	Mass loss/%
30–120	98	1.58
120–400	386	9.15
400–600	546	3.87
600–800	729	1.17
800–1050	1028	0.34
1050–1500	1245 1430	0.07

Starting mixture for the pigment preparation with composition $Ce_{0.70}Pr_{0.05}Nd_{0.25}O_{1.875}$ was homogenized in an agate mortar and studied with using of DTA. The thermogravimetric curve (TG) indicates that significant mass loss develops at temperature interval from 30 to 400°C (Table 4). This loss is associated by the endothermic effect with minimum at temperature 374°C. This process is connected with the range of mixed oxide Pr_6O_{11} for Pr_2O_3 [8] and with decomposition of $Nd_2(CO_3)_3$. In comparison with the mixed oxide Pr_6O_{11} (350°C), the process moves 24°C higher and the starting oxide of neodymium (386°C) about 12°C lower. Another mass loss is made at temperature interval from 400 to 820°C and associates with the partial oxygen loss from Pr_2O_3 and with ending of decomposition of the carbonate presented at starting Nd_2O_3.

Growing temperature indicates another endothermic effect at the DTA curve with minimum at temperature 958°C which is connected with continual oxygen loss from Pr_2O_3 or Nd_2O_3 what is characterized by slight mass loss at the TG curve (Fig. 2). Above 1000°C from the DTA curve it follows that significant exothermic process with maximum at temperature 1039°C is connected with the creation of PrO_2 and at the same time with the partial oxygen loss from CeO_2. The endothermic peak with minimum at temperature 1306°C corresponds to modification change of cubic

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

T_{range}/°C	T_{peak}/°C	Mass loss/%
30–400	374	2.73
400–600	547	0.83
600–820	804	0.51
820–1000	958	0.10
1000–1500	1039 1306 1437	0.07

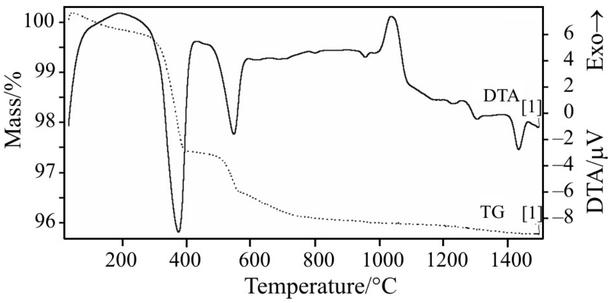

Fig. 2 TG and DTA curves of mixture for synthesis $Ce_{0.7}Pr_{0.05}Nd_{0.25}O_{1.875}$ (mass of sample: 250.25 mg, atmosphere: air, heating rate: 10°C min^{-1})

Nd_2O_3 for A-type what is in accordance with results of X-ray diffraction analysis. Last endothermic process at the DTA curve with minimum at temperature 1437°C then corresponds with dissolving of PrO_2 and Nd_2O_3 in CeO_2 forming a solid solution of $Ce_{0.7}Pr_{0.05}Nd_{0.25}O_{1.875}$.

Conclusions

Compounds $Ce_{0.95-y}Pr_{0.05}Nd_yO_{2-y/2}$ type with y=0.05, 0.15, 0.25, 0.35, 0.45, 0.55, 0.65, 0.75 and 0.85 were studied. It was determined that the area of solubility Nd_2O_3 and PrO_2 in CeO_2 at temperature 1350°C forming a solid solution $Ce_{0.95-y}Pr_{0.05}Nd_yO_{2-y/2}$ is with y=0.05 up to 0.65. These compounds provide the glazes of deep pink–orange colour hues. Higher content of neodymium (y=0.75 and 0.85) besides the solid-state solution indicates second phase, i.e. free Nd_2O_3 which moves the colour from pink–orange for yellow–orange. These compounds can be used for colouring of ceramic glazes and are ecologically friendly.

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