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PREPARATION AND PRACTICAL APPLICATION OF SPINEL PIGMENT $Co_{0.46}Zn_{0.55}(Ti_{0.064}Cr_{0.91})_2O_4$

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Synthesis of the green spinel pigment $Co_{0.46}Zn_{0.55}(Ti_{0.064}Cr_{0.91})_2O_4$ by a novel two-step method of preparation have been investigated. Inorganic pigments are almost always prepared by a solid state reaction. It is classical ceramic method which used oxides, hydroxides or carbonates as precursors. The reaction is performed at temperature higher than 1300°C and an agent of mineralization is usually present. The presented novel method of preparation decreases the calcining temperature necessary for reaching of bright and clear hue of the pigments prepared. Main attention was focused on the influence of two types of titanium raw materials on the temperature region of the spinel structure formation and on the colour properties of the pigments. The mixture of precursors with TiO_2 gives a one-phase system when calcining at 1100°C but the colour properties are more interesting at 1150°C. Thermal stability of this pigment is limited by temperature 1300°C. This temperature is connected with partial oxidation of Cr(III) to Cr(VI). Thermal analysis provided the first information about the temperature region of the pigment formation and determined the thermal stability of pigment.

Keywords: *ceramic pigments, optical properties, spinel pigments, thermal analysis*

Introduction

Pigments with the spinel structure belong to the group of mixed metal oxide pigments. Mixed metal oxide pigments can be considered as a subcategory of complex inorganic colour pigments. The term, i.e. the mixed metal oxides, does not represent the reality as these pigments are not mixtures but solid solutions or compounds consisting of two or more metal oxides. Each pigment has a defined crystal structure which is determined by the host lattice. Other oxides interdiffuse at high temperature into the host lattice structure by forming either a solid-state solution or a new compound [1]. Spinel pigments are widely used in ceramics for colouring of porcelain and glazes [2]. They cover a wide range of colours and many of them are thermally stable up to 1400°C. They are used not only as heat resistant pigments, but they have a great importance as catalytic materials [3] and magnetic materials [4].

The spinel pigments have a common chemical formula AB_2X_4; structurally they have a cubic symmetry. Based on the ions A, B and X, the spinels can be divided into three categories [5]. Most often the X ions represent oxygen anions. In classical spinels the A ions occupy tetrahedral sites, and the B ions occupy octahedral sites, $A^{tet}B_2^{oct}O_4$. In inverse spinels the A ions and half of the B ions swap positions to give $B^{tet}[AB]^{oct}O_4$. Between the both extremes there is a number of intermediate spinels [6]. The manners in which such sites are occupied depend on the calcination temperature [7, 8]. Spinels are most often prepared by solid state reactions [9]. Some chemical routes have been used to prepare the spinel pigments, among them, the polymeric precursor method developed by Pechini [10], the sol-gel method [11] and the hydrothermal method [12, 13].

In this work, a non-stoichiometric green spinel pigment containing Co, Zn, Ti and Cr was prepared by a novel method of preparation which consists of two steps of the calcination.

Experimental

The pigments were prepared by a two-step method. The first step represents the formation of semi-products at medium temperature. The semi-products were obtained by mixing of raw materials in suspensions in a porcelain mortar and were calcinated at 400°C on an alloy steel sheet. The second step represents a classical calcination in an electric resistance furnace with an increase of temperature 10°C min^{-1}. The calcination temperature of the second step of synthesis 1100–1300°C was maintained for 1 h. After that, the fired samples were decanted in hot water, filtrated and dried.

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The influence of precursors, especially titanium precursors, on the colour properties of the pigments was investigated. The first reaction mixture contained these precursors: $CoSO_4 \cdot 7H_2O$ and $CoCO_3$ (in ratio 0.42:0.04), $ZnSO_4 \cdot 7H_2O$, $Na_2Cr_2O_7 \cdot 2H_2O$ and TiO_2. The second reaction mixture contained the same precursors $CoSO_4 \cdot 7H_2O$ and $CoCO_3$ (in ratio 0.42:0.04), $ZnSO_4 \cdot 7H_2O$, $Na_2Cr_2O_7 \cdot 2H_2O$ only the titanium precursor was changed to $Na_2Ti_4O_9$. Both mixtures contained foaming agents, i.e. fumaric acid and urea.

Simultaneous TG/DTA measurements were performed by STA Jupiter 449 equipment (NETZSCH, Germany) in the temperature range 50–1200°C (1400°C) at heating rate 10°C min^{-1}. The analysis was carried out in a ceramic crucible under air and α-Al_2O_3 was used as a reference material.

The X-ray diffractograms of the samples in the range 2Θ of 10–80° were obtained using the diffractometer D8 (Bruker, GB), CuK_α radiation, scintillation detector.

The colour properties of the pigments were measured after their application into a transparent ceramic glaze P 07491 free of lead oxide (Glazura s.r.o., Roudnice nad Labem, Czech Republic) in the amount of 10 mass%. Colour properties were measured in the visible region (400–700 nm) with MiniScan MS/S (Hunter Lab, USA). The measurement conditions were following: Illuminant D65 (6500 K), 10° complementary observer and geometry of measurements d/8°, colour space CIE L^* a^* b^* and chroma C.

Results and discussion

The main aim of the present work was to prepare the spinel pigment $Co_{0.46}Zn_{0.55}(Ti_{0.064}Cr_{0.91})_2O_4$ with good application properties. The composition of reaction mixture can affect the temperature of pigment formation.

On DTA curve (Fig. 1) there were identified few effects that correspond to decomposition of the raw materials in the mixture No. 1. From the TG curve it follows that the marked mass loss occurs in the temperature range 30–300°C. The endothermic effect

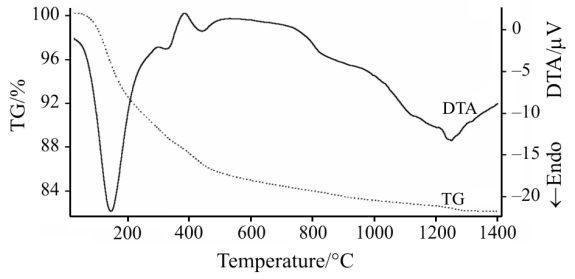

Fig. 1 DTA and TG curves of the reaction mixture No. 1 (sample mass 221.150 mg)

Table 1 Thermal decomposition of the reaction mixture No. 1 for the synthesis of $Co_{0.46}Zn_{0.55}(Ti_{0.064}Cr_{0.91})_2O_4$ (Fig. 1)

Temp. range/°C	Peak temp./°C	Mass loss/%
30–300	146	10.38
300–500	386	4.00
500–1000	–	2.53
1000–1400	1250	1.03

with a minimum at 146°C is connected with removal of crystalline water of the precursors (Table 1). The decomposition of sulfates and also sodium dichromate is finished within 300–500°C. This temperature range is also associated with the formation of black oxide Co_3O_4 (386°C) which loses oxygen and forms CoO in higher temperatures, i.e. 500–1000°C. The endothermic effect with minimum at 1250°C indicates the formation of the product. This fact was documented by X-ray diffraction analysis. The formation of spinel compound is connected with the endothermic effect on the DTA curve because the solid solution is formed. The last almost indiscernible exothermic peak (1307°C) probably corresponds to partial oxidation of Cr(III) to Cr(VI). This peak was detected also on the DTA curve of the pure product.

Several peaks corresponding to the decomposition of starting materials were also identified on the DTA curve of the reacting mixture No. 2. (Fig. 2). Thermoanalytical measurements of the sample No. 2 were carried out after the first step of synthesis. The first mass loss 0.53% is connected with the loss of remaining moisture (Table 2). Among others, the tem-

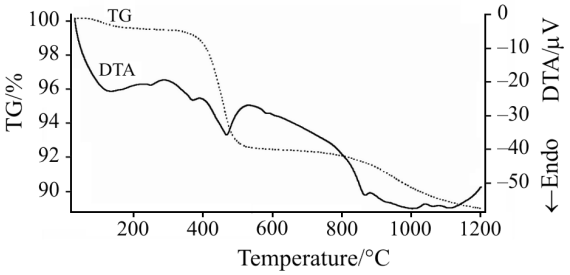

Fig. 2 DTA and TG curves of the reaction mixture No. 2 (sample mass 300.300 mg)

Table 2 Thermal decomposition of the reaction mixture No. 2 for the synthesis of $Co_{0.46}Zn_{0.55}(Ti_{0.064}Cr_{0.91})_2O_4$ (Fig. 2)

Temp. range/°C	Peak temp./°C	Mass loss/%
30–200	138	0.53
200–530	371 468	6.93
530–1200	867 1040 1077	3.56

perature range 300–500°C covers the formation of Co_3O_4. The next endothermic effect of this range (486°C) corresponds to the reversible transformation of Na_2CO_3. The endothermic effect with a minimum at 867°C is connected with the oxygen loss from Co_3O_4 to CoO and this effect also covers the thermal decomposition of Na_2CO_3. The temperature of pigment formation is characterized on the DTA curve by an exothermic effect with a maximum at 1077°C. One unidentifiable exothermic peak occurs on the DTA curve at 1040°C but this peak was also identified on the DTA curve of the pure product $Co_{0.46}Zn_{0.55}(Ti_{0.064}Cr_{0.91})_2O_4$.

The product of calcination of the reaction mixture No. 1 (1200°C) was also subjected to thermal analysis to determine the thermal stability of the new compound. Few endothermic and exothermic effects occur on the DTA curve of the fired product and some of them are identical with the effect on DTA curves of reaction mixtures (Fig. 3, Table 3). Since the total mass loss is only 0.29% the product of calcination can be marked as a pigment of good thermal stability. The indiscernible exothermic peak (1307°C) probably corresponds to partial oxidation of Cr(III) to Cr(VI). This peak was also detected on the DTA curve of the mixture No. 1 which was measured to 1400°C.

The prepared samples were subjected to X-ray diffraction analysis. Only the phase of spinel was identified in the diffraction pattern of the product prepared by calcining the mixture No. 1 at 1100°C (Fig. 4). The compound has a cubic symmetry and the value of lattice parameter *a* is 8.3280 Å.

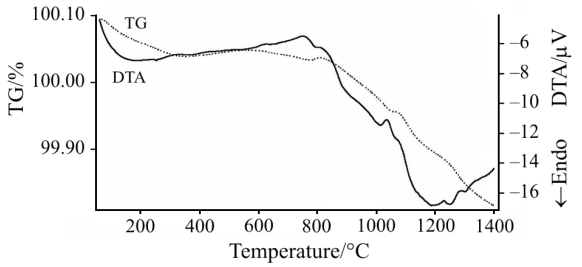

Fig. 3 DTA and TG curves of $Co_{0.46}Zn_{0.55}(Ti_{0.064}Cr_{0.91})_2O_4$ obtained by calcination of the mixture No. 1 at 1100°C (sample mass 400.700 mg)

Table 3 Thermal decomposition of $Co_{0.46}Zn_{0.55}(Ti_{0.064}Cr_{0.91})_2O_4$ obtained by calcination of the mixture No. 1 (Fig. 3)

Temp. range/°C	Peak temp./°C	Mass loss/%
60–350	–	0.06
350–780	751	0.01
780–1050	804	0.08
1050–1160	1037	0.08
1160–1400	1231 1302	0.09

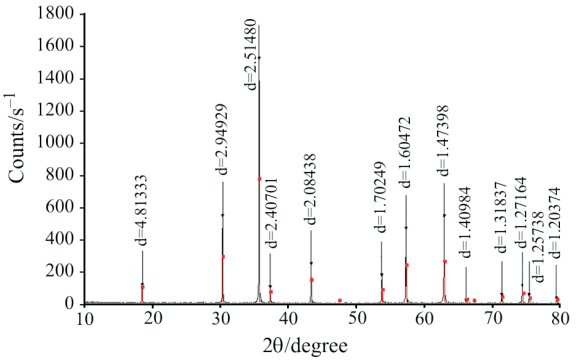

Fig. 4 X-ray diffraction pattern of $Co_{0.46}Zn_{0.55}(Ti_{0.064}Cr_{0.91})_2O_4$ obtained by calcination of the mixture No. 1 at 1100°C

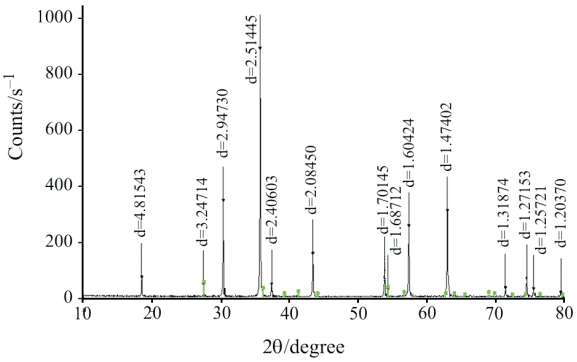

Fig. 5 X-ray diffraction pattern of $Co_{0.46}Zn_{0.55}(Ti_{0.064}Cr_{0.91})_2O_4$ obtained by calcination of the mixture No. 2 at 1200°C

On the other hand, the synthesis of the product using the titanium precursor $Na_2Ti_4O_9$ does not lead to the formation of a one-phase system (Fig. 5). Besides the spinel phase, the pigment prepared at 1200°C contains also a small amount of rutil phase TiO_2. The increase of temperature over 1200°C causes sintering of the product. The product prepared from the mixture No. 2 is also of cubic symmetry but the lattice parameter is higher; a=8.33764 Å.

The new compound $Co_{0.46}Zn_{0.55}(Ti_{0.064}Cr_{0.91})_2O_4$ provides a very interesting deep green colour. The pigments were applied into transparent ceramic glaze. From Table 4 it follows that the calcining temperature has a significant effect on the pigment colour. The most noticeable effect of temperature is on the yellow hue of pigment. The pigments prepared from mixture No. 1 have the similar values of brightness (L^*) in the whole range of temperatures as well as the values of green hue (b^*) and values of chroma (C). The different situation is in colour properties of the pigment prepared from mixture No. 2. The temperature higher than 1200°C markedly affects the value of brightness (L^*). The pigment prepared at the lowest temperature (1100°C) is the darkest one. However, amount of the green hue of pigment increases with increasing temperature, the highest value of b^* is not as high as value of product No. 1. The in-

Table 4 The colour properties of the pigment $Co_{0.46}Zn_{0.55}(Ti_{0.064}Cr_{0.91})_2O_4$

Reaction mixture	Calcining temperature/°C	L^*	a^*	b^*	C
No. 1	1100	39.92	–17.56	–3.38	17.88
No. 1	1150	39.87	–18.99	–1.86	19.08
No. 1	1200	39.83	–18.78	–1.01	18.81
No. 1	1250	39.85	–17.23	–2.98	17.49
No. 1	1300	38.36	–18.64	1.07	18.67
No. 2	1100	37.51	–15.18	–1.38	15.24
No. 2	1150	41.75	–17.37	–0.31	17.37
No. 2	1200	39.39	–17.86	–4.34	18.38
No. 2	1250		sintered		
No. 2	1300				

crease of chroma (C) has the same trend. The pigment No. 1 prepared by calcining at 1150°C provides the most interesting colour properties.

Conclusions

The main aim of the research was to prepare a new spinel compound which can be used as an inorganic pigment. The pigment prepared was of deep green colour. The temperature of the spinel structure formation and the thermal stability of the product were determined by thermoanalytical measurements. Two titanium precursors were used for preparation of the pigment $Co_{0.46}Zn_{0.55}(Ti_{0.064}Cr_{0.91})_2O_4$. The first used titanium compound TiO_2 gives a one-phase product at 1100°C but the product formed at 1150°C provides more interesting colour properties. Although the pigment $Co_{0.46}Zn_{0.55}(Ti_{0.064}Cr_{0.91})_2O_4$ can be integrated into the group of pigments with high thermal stability, the recommended temperature for its practical applications is lower than 1300°C. The temperature 1300°C causes the partial oxidation of Cr(III) to Cr(VI). The second titanium precursor $Na_2Ti_4O_9$ provides a two-phase pigment. The pigment prepared at temperature higher than 1200°C was sintered. The pigment No. 2 also provides interesting green colour but the colour quality of this pigment is worse than the colour quality of the pigment prepared from precursor TiO_2 (No. 1).

Acknowledgements

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