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The Effect of Lanthanides on Colour Properties of the $Ln_2Zr_{1.5}V_{0.5}O_7$ Pigments

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Abstract

New yellow and orange ceramic pigments based on the pyrochlore solid solution of $Ln_2Zr_{1.5}V_{0.5}O_7$ were synthesized as high-temperature environment friendly inorganic materials. This work is focused on mixed oxides based on ZrO_2 which are doped by rare earth elements. The optimum conditions for their synthesis were determined. Their colour properties were investigated depending on the content of various lanthanides and temperature of calcination. The richest hues were obtained by using holmium and thulium. All pigments give the yellow colour in ceramic glazes but Ho and Er provide orange hues. The pigments were evaluated from the standpoint of their structure, colour, ability to colour ceramic glaze, and particle size.

Keywords: Inorganic pigments, Pyrochlore compounds, Ceramic pigments, Colour properties

WPŁYW LANTANOWCÓW NA WŁAŚCIWOŚCI BARWNE PIGMENTÓW $Ln_2Zr_{1.5}V_{0.5}O_7$

Zsyntezowano nowe pigmenty, żółte i pomarańczowe, oparte na roztworze stałym $Ln_2Zr_{1.5}V_{0.5}O_7$ typy pirochloru jako nieorganiczne wysokotemperaturowe materiały przyjazne dla środowiska. W pracy skupiono się na tlenkach mieszanych ZrO_2 domieszkowanego pierwiastkami ziem rzadkich. Określono optymalne warunki syntezy tych związków. Ich właściwości barwne badano w zależności od zawartości lantanowców i temperatury kalcynacji. Najbogatsze odcienie uzyskano przy użyciu tlenków holmu i tulu. Wszystkie pigmenty dają kolor żółty w szkliwach ceramicznych, ale Ho i Er dostarczają odcieni pomarańczowych. Pigmenty oceniono z punktu widzenia ich struktury, barwy, zdolności do barwienia szkliwa ceramicznego oraz wielkości cząstek.

Słowa kluczowe: pigmenty nieorganiczne, związki typu pirochloru, pigmenty ceramiczne, właściwości barwne

1. Introduction

Inorganic natural and synthetic pigments are used for colouring plastics, paints, ceramics and enamels. In these applications, the pigments are dispersed in the media forming heterogenous mixtures. The powder materials used to colour ceramics must possess high thermal and chemical stability and must be inert to the action of molten glaze. The properties, such as colour tone and saturation, non-reactivity, insolubility, particle size, tinting strength, etc., are required for commercial uses of ceramic pigments [1].

However, most conventional inorganic pigments contain toxic metals such as Cd, Co, Cr, Hg, Pb and Sb that can adversely affect the environment and human health. Therefore, the development of safe inorganic pigments has been required in order to replace the toxic inorganic pigments with environment friendly or less toxic substances [2].

The present study focuses on the pyrochlore compound of $Ln_2Zr_2O_7$ with vanadium(V) incorporated as a chromophore. This type is derived from the yellow pyrochlore $Pb_2Sb_2O_7$, but it does not contain the problematical Pb and Sb. The pyrochlore structure has a general formula of $A_2B_6O_6O'$ where O and O´ are two crystallographically different types of oxygen. The symmetry is cubic, belonging to the Fd3m (No. 227) space group, and the unit cell comprises eight formula units [3]. The positions A can be occupied by di- or trivalent ions in the dodecahedral (disorder cubic) coordination with oxygen. The B positions are occupied by tetra- or pentavalent ions in the octahedral coordination [4].

Pyrochlore compounds have many good properties such as low thermal conductivity, high melting point, high thermal expansion coefficient, and high stability and ability to accommodate defects [5].

This study is directed to the preparation of pigments basing on ZrO_2 doped with selected lanthanides. The goal was to develop conditions for the synthesis of $Ln_2Zr_{1.5}V_{0.5}O_7$ pigments and to determine the influence of lanthanides and temperature of calcination on the colouring effects of this type of pigments. This research is very significant because the studied compounds give interesting hues in ceramic glazes. They are highly-resistant to chemicals and temperature, and represent the inorganic pigments alternative from the environmental point of view.

2. Experimental

ZrO_2 of 99 % purity (Glazura, s.r.o., Roudnice nad Labem, CZ), V_2O_5 (Lachema Pliva, a.s., Brno, CZ) and oxides of lanthanides (Dy_2O_3, Ho_2O_3, Er_2O_3, Tm_2O_3, Yb_2O_3 and Lu_2O_3; Bochemie Bohumín, CZ) were used as the starting compounds for the preparation of $Ln_2Zr_{1.5}V_{0.5}O_7$ pigments.

The starting mixtures, containing basic oxides (ZrO_2, V_2O_5 and Ln_2O_3), were homogenised in an agate mortar. The mixtures were then calcinated in corundum crucibles by using an electric resistance furnace and a heating rate of 10°C·min^{-1}. The calcination temperatures of 1300, 1400 and 1500°C were maintained for 2 h. The pigments (10 % w/w) were added to a middle-temperature borate-silicate (transparent leadless) glaze G 05091 (Glazura, s.r.o., Roudnice nad Labem, CZ) and the temperature was held for 15 min. The final glazes were evaluated for a colour change by measuring spectral reflectance in the visible region of light (400-700 nm) using a ColorQuest XE (HunterLab, USA). The measurement conditions were as follows: D65 illuminant, 10° complementary observer, and d/8°measuring geometry. The colour properties are described in terms of the CIE $L^*a^*b^*$ system (1976). The value a^* (the red-green axis) and b^* (the yellow-blue axis) indicate the colour hue. The value L^* represents the lightness or darkness of a colour in relation to scale extending from white (L^* = 100) to black (L^* = 0). The value C (chroma) represents the saturation of a colour and is calculated according to the formula: $C = (a^{*2} + b^{*2})^{1/2}$. The colour of pigment is also expressed by the hue angle $H°$ defined by an angular position in the cylindrical colour space (for the red $H°$ = 0-35°, for the orange $H°$ = 35-70 °, for the yellow $H°$ = 70-105°). The equation for calculation of the hue angle is $H° = \text{arc tg}\ (b^*/a^*)$.

The distribution of particle sizes of the calcinated powders was obtained by laser scattering using a Mastersizer 2000 MU (Malvern Instruments, Ltd. GB). It is the highly integrated laser measuring system (He-Ne laser, λ = 633 nm) for analysis of particle size distributions.

The structure of pigments was also investigated. The synthesized pigments were studied by X-ray diffractometry. The X-ray diffractograms of the samples were obtained using the Diffractometer D8 Advance equipment (Bruker, GB), CuK_α radiation, with a scintillation detector [6].

3. Results and discussion

The aim of the present work was to investigate the influence of several lanthanides on the colouring effect of $Ln_2Zr_{1.5}V_{0.5}O_7$. The colour hue of pigments applied into ceramic glaze is practically dependent on the lanthanide content. Based on the a^* and b^* values measured for the pigments calcinated at 1300°C (Table 1), it can be seen that Dy, Ho and Er have the positive values of the colour coordinate a^* (red hue), and all lanthanides have the colour value of b^* (yellow hue) of about 30, but Ho increases this value up to 40. The same tendency is also apparent for the chroma C. The values of the hue angle $H°$ are characteristic for the yellow colour but Er produces the yellow-orange colour. The pigment containing Ho has smaller value of L^* and this application is the darkness.

Table 1. The effect of Ln content on colour properties of the $Ln_2Zr_{1.5}V_{0.5}O_7$ samples calcinated at 1300°C and applied into ceramic.

Ln	L^*	a^*	b^*	C	$H°$
Dy	82.70	0.34	29.17	29.17	89.33
Ho	75.86	0.81	40.32	40.33	88.85
Er	79.16	8.61	25.10	26.54	71.07
Tm	79.31	-1.62	29.66	29.70	93.12
Lu	79.05	-1.85	27.18	27.24	93.89
Yb	79.50	-1.53	27.54	27.58	93.18

The increase of calcination temperature up to 1400°C produces in some cases lower values of L^* and chroma C, and it means that the colour becomes lighter (Table 2). Considering that the value $H°$ of these pigments ranges from ~89 to 95, the pigments are also characterized by yellow colour except for the Er doped pigment, where the hue angle $H°$ is only 71, and the colour is shifted to orange.

The highest temperature of calcination (1500°C) causes the increase of chroma values for the pigments with the formula of $Ln_2Zr_{1.5}V_{0.5}O_7$. On the other hand, L^* changes alternately, and the pigment containing Lu produces the darkest hue. But the most saturated application for this temperature is the compound with Tm, providing the yellow hue with the highest value of $H°$, being equal to 92.72 (Table 3).

From Tables 1, 2 and 3, it follows that the powder pigments have a very close interval of a^* values (without Er) which is shifted from -2.56 to 1.14. On the other hand, the b^* coordinate has the wide interval of values ranging from 25.10 to 40.82. These values correspond to the yellow tinge. The richest hue was obtained for the pigment with the content of Tm (1500°C), and Ho (1300°C), and from these information it follows, that increasing the temperature of calcination for this type of pigments produces increasing the chroma.

Table 2. The effect of Ln content on colour properties of the $Ln_2Zr_{1.5}V_{0.5}O_7$ samples calcinated at 1400°C and applied into ceramic glaze.

Ln	L^*	a^*	b^*	C	$H°$
Dy	83.13	0.23	27.31	27.31	89.52
Ho	82.56	0.67	33.19	33.19	88.84
Er	79.81	8.64	25.25	26.69	71.11
Tm	79.03	-2.56	32.64	32.74	94.48
Lu	80.32	-1.52	27.81	27.85	93.13
Yb	79.13	-1.21	28.35	28.38	92.44

Table 3. The effect of Ln content on colour properties of the $Ln_2Zr_{1.5}V_{0.5}O_7$ samples calcinated at 1500°C and applied into ceramic glaze.

Ln	L^*	a^*	b^*	C	$H°$
Dy	80.09	-0.77	30.38	30.38	91.45
Ho	76.74	1.14	38.73	38.73	88.31
Er	75.55	9.31	27.44	27.44	71.26
Tm	80.83	-1.94	40.82	40.82	92.72
Lu	71.02	-0.44	29.38	29.38	90.69
Yb	73.70	-0.29	29.44	29.44	90.56

The particle sizes and particle size distributions can markedly affect the colour properties of inorganic pigments. Therefore, the synthesized samples were measured from this point of view. The mean particle sizes (d_{50}) of the pigments used for colouring ceramic glazes lie in the region from 5 to 15 μm. The test was performed with reference to the unmilled pigments. The values of pigment particle sizes are in the range from 5.35 μm (Lu) to 13.84 μm (Er) for the samples calcined at 1300 °C. At higher temperature (1400°C), the range is a little bit wider, i.e., from 5 μm (Lu) to 17.47 μm (Er). The highest temperature of calcination (1500°C) increases the mean particle size from 7.92 μm (Lu) to 31.55 μm (Er). Based on this information, it follows that the pigments with the content of Lu provide the lowest values of particle size (about 6 μm). On the other hand, the highest values have the pigments with the presence of Er (d_{50} is about 21 μm). So, the pigments, which were calcinated at 1300°C and 1400°C (except for Er doped from 1400°C), are applicable to colouring ceramic glazes. Only the pigments containing Tm, Lu, and Yb calcinated at 1500°C (Table 4) are suitable for this application.

Table 4. Mean particle sizes of the $Ln_2Zr_{1.5}V_{0.5}O_7$ pigments.

Ln	Mean particle size d_{50} [μm]		
	1300°C	1400°C	1500°C
Dy	9.11	14.65	17.89
Ho	9.99	10.52	29.31
Er	13.83	17.47	31.55
Tm	6.38	8.59	9.96
Lu	5.35	5.00	7.92
Yb	7.83	8.45	10.43

The powder pigments of $Ln_2Zr_{1.5}V_{0.5}O_7$ were subjected to X-ray diffraction analysis (Fig. 1). Diffractograms of the samples were homogenous only for the pigments calcinated at the highest temperature of 1500°C. The pigments prepared at 1300°C and 1400°C were heterogeneous, because ZrO_2 and Ln_2O_3 were detected beside the pyrochlore compound. The best results were obtained for the pigment containing Tm calcined at 1500°C which exhibited cubic symmetry and diffraction lines that could be assigned to the pyrochlore compound. Ln_2O_3 was also detected from the XRD patterns for all three calcination temperatures and majority of lanthanides. Increasing the calcination temperature increases the peak intensity of the major phases and at the same time decreases the intensity of peaks belonging to Ln_2O_3. The pigment $Tm_2Zr_{1.5}V_{0.5}O_7$ was the most interesting from the point of view of both its phase composition and particle size distribution.

4. Conclusion

The $Ln_2Zr_{1.5}V_{0.5}O_7$ compounds, where Ln = Dy, Ho, Er, Tm, Yb and Lu, were studied as pigments. All pigments give the yellow colour in ceramic glazes, but those containing Ho and Er provide orange hues. From the particle size distribution point of view, the pigments prepared at 1300°C and 1400°C are applicable into ceramic glaze (d_{50} is from 5 μm to 17 μm). For the highest temperature of calcination (1500°C), only pigments with Lu, Tm and Yb are suitable for ceramic glazes. The X-ray diffraction results showed that the single-phase pigment with a formula of $Tm_2Zr_{1.5}V_{0.5}O_7$ was prepared at 1500°C. At the same time, this pigment is characterized by the highest value of chroma *C*.

This study confirms that the solid solution of $Ln_2Zr_{1.5}V_{0.5}O_7$ with the pyrochlore structure was obtained by conventional solid-state reaction at the temperature of about 1500°C. This type of pigments is environmentally friendly and could contribute to the basic assortment of yellow and orange inorganic pigments. So, the research showed that the heat and chemical resistance of these compounds are sufficient for ceramic glazes.

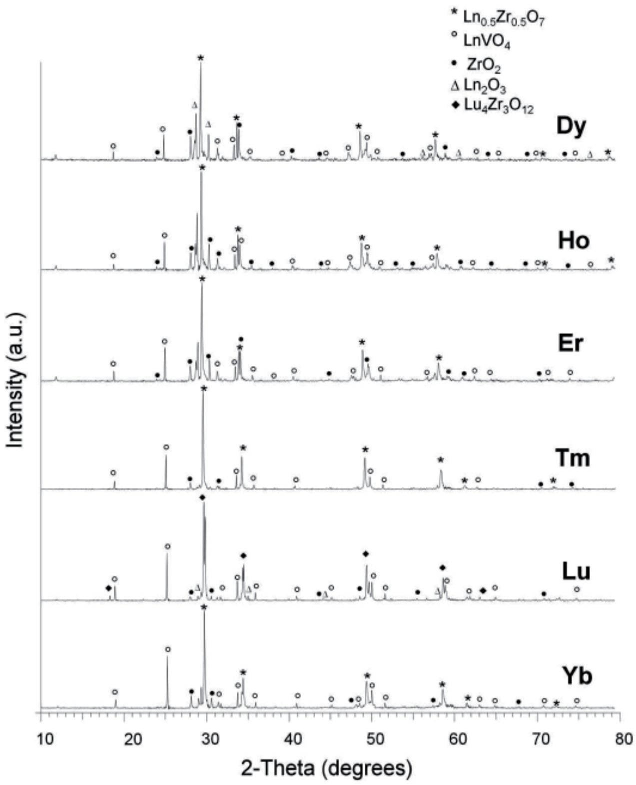

Fig. 1. X-ray diffraction patterns of the $Ln_2Zr_{1.5}V_{0.5}O_7$ pigments calcined at 1500°C.

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