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STUDY OF CERAMIC PIGMENTS BASED ON $Dy_2Sn_{2-x}V_xO_7$

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New high-stability yellow ceramic pigments based on pyrochlore solid solutions $Dy_2Sn_{2-x}V_xO_7$ were developed employing conventional solid-state reaction synthesis. The synthesis of these colourants involved high-temperature calcination of starting oxides and optimum conditions for their synthesis were determined. The pigments were evaluated from the standpoint of their structure, colour and ability to colour ceramic glazes.

Introduction

There are a great number of publications about magnetic and electric properties of materials with pyrochlore structure. However, very little has been published about ceramic pigments based on this structure. The present study focuses on the pyrochlore compounds of $Ln_2Sn_2O_7$ type (Ln are lanthanides) with the introduction

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of vanadium (V) as a chromophore. This type is derived from the yellow pyrochlore $Pb_2Sb_2O_7$ but it does not contain problematic Pb and Sb. This industrial yellow pigment, which is used at present, is questionable from the hygienic point of view.

The pyrochlore structure has the general formula $A_2B_6O_6O'$ 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 [1,2]. The A positions can be occupied by di- or trivalent ions, such as lanthanides (Ln), Pb(II), Cd(II), Tl(II), Y(III), Bi(III), Sc(III), In(III), and in some cases by alkaline-earth ions, in dodecahedral (distorted cubic) coordination with oxygen. The B positions are occupied by tetra- or pentavalent ions in octahedral coordination, such as Ti(IV), Sn(IV), Zr (IV), Hf(IV), Mn(IV), Ru(IV), Nb(IV), Ir(IV), V(V) or Sb(V).

In the present study, the formula $Dy_2Sn_{2-x}V_xO_7$ of new pigments was studied. The goal was to develop conditions for the synthesis of this type of pigments and to determine the influence of vanadium content on the colouring effects of $Dy_2Sn_{2-x}V_xO_7$ pigments. This work is meaningful because these pigments give interesting hues into ceramic glazes, are heat-resistant and represent potential alternative inorganic pigments from an environmental point of view.

Experimental

As starting materials for the preparation of the $Dy_2Sn_{2-x}V_xO_7$ pigments were used: SnO_2 of 99 % purity (Glazura, s.r.o. Roudnice nad Labem, CZ), V_2O_5 (Lachema Pliva, a.s. Brno, CZ) and Dy_2O_3 of 99 % purity (Indian Rare Earths Ltd., India).

The starting mixtures containing basic oxides (SnO_2, V_2O_5 and Dy_2O_3) with the required content of V (x = 0.02, 0.05, 0.1, 0.2, 0.3, 0.4 and 0.5) were homogenised in an agate mortar. The mixtures were then calcinated in corundum crucibles in an electric resistance furnace, increasing the temperature at 10 °C min^{-1}. The calcination temperature in region from 1300 to 1500 °C was maintained for 2 h. The pigments (10 % w/w) were added to a middle-temperature borate-silicate (transparent leadless) glaze at 1000 °C and the temperature was held for 15 min. The final glazes were evaluated for colour change by measuring spectral reflectance in the visible region of light (400-700 nm) using a ColorQuest instrument (HunterLab, USA). The measurement conditions were following: an illuminant *D*65, 10° complementary observer and measuring geometry *d*/8° [3].

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 grey scale. In the $L^*a^*b^*$ system it is described by numbers from zero (black) to hundred (white). The value *C* (chroma) represents saturation of the colour and is calculated according to the formula: $C = (a^{*2} + b^{*2})^{1/2}$. The hue angle $H°$ is defined by an angular position in the cylindrical colour space (for the red is $H° = 0°$-$35°$, for the orange $H° = 35°$-$70°$, for the yellow $H° = 70°$-$105°$). The powder pigments were also studied by X-ray diffraction analysis. The X-ray diffractograms of the samples were obtained using by equipment Difractometer D8 (Bruker, GB), CuK_{α} radiation with scintillation detector.

The distribution of particle sizes of the calcinated powders was obtained by laser scattering using Mastersizer 2000/MU (Malvern Instruments, GB). This is the highly integrated laser measuring system (He-Ne laser, $\lambda = 633$ nm) for the analysis of particle size distribution [3].

Results and Discussion

The aim of present work was to investigate the influence of growing vanadium content and calcination temperature on the colouring effect of the $Dy_2Sn_{2-x}V_xO_7$ compounds ($x = 0.02$, 0.05, 0.1, 0.2, 0.3, 0.4 and 0.5) after their application into ceramic glaze.

Table I Effect of V content on colour hue of $Dy_2Sn_{2-x}V_xO_7$ pigments prepared by calcination at 1300 °C

x	L^*	a^*	b^*	C	$H°$
0.02	87.18	0.79	18.22	18.24	87.52
0.05	83.07	2.03	20.53	20.63	84.35
0.1	83.04	2.83	27.87	28.01	84.20
0.2	82.85	3.05	30.05	30.20	84.20
0.3	81.50	3.63	35.63	35.81	84.18
0.4	77.60	6.79	33.92	34.59	78.68
0.5	71.31	9.30	25.60	27.24	70.03

The colour properties of the $Dy_2Sn_{2-x}V_xO_7$ samples prepared at the temperature of 1300 °C are given in Table I. From Table I it follows that the growing content of V decreases the value L^* (lightness). On the contrary, the value a^* (red hue) increases with the growing value x. The value b^* (yellow hue) also increases with the growing V content from $x = 0.02$ up to $x = 0.3$ then the value b^* decreases (Fig. 1). The chroma C demonstrates the same course as value b^*. The pigment with $x = 0.3$ has the highest value C (chroma). This sample is characterized by the yellow colour ($H° = 84.18$). The values of hue angle $H°$ for

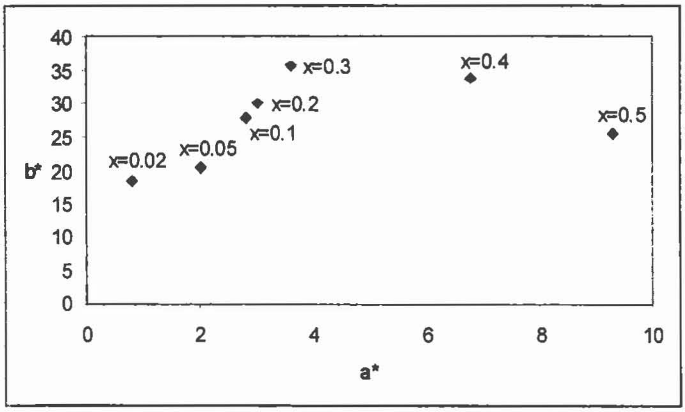

Fig. 1 Effect of V content on colour coordinates a^* and b^* of $Dy_2Sn_{2-x}V_xO_7$ pigments prepared at temperature of 1300 °C

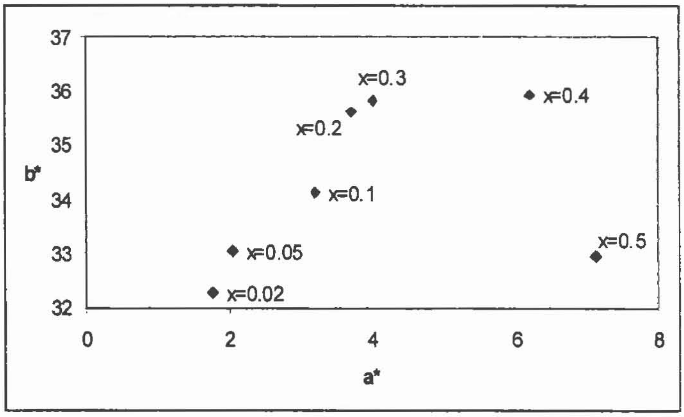

Fig. 2 Effect of V content on colour coordinates a^* and b^* of $Dy_2Sn_{2-x}V_xO_7$ pigments prepared at temperature of 1400 °C

samples x = 0.02 to 0.3 are characterized by their yellow colour but the higher value L^* makes the yellow colour too light. The samples with x = 0.4 and 0.5 give light yellow-orange colour. The growing temperature of calcination increases the value b^* and chroma. These values increase with growing V content from x = 0.02 to 0.4, then their values decrease (Fig. 2). All the pigments having x from 0.02 to 0.4 produce yellow hues because the value $H°$ of these pigments lies approx. from 83 to 87 (Table 2). The pigment with x = 0.4 gives the best intensive yellow hue owing to the highest value of chroma. The sample where x = 0.5 produces yellow-orange colour. The colour properties of samples prepared at the highest temperature of calcination, i.e. 1500 °C, are given in Table III. Based on values L^* it can be seen that increasing content of vanadium decreases this value and the

Table II Effect of V content on colour hue of $Dy_2Sn_{2-x}V_xO_7$ pigments prepared by calcination at 1400 °C

x	L^*	a^*	b^*	C	H^o
0.02	84.26	1.77	32.27	32.32	86.86
0.05	83.57	22.04	33.05	33.11	86.47
0.1	82.01	3.21	34.12	34.27	84.63
0.2	81.23	3.72	35.61	35.80	84.04
0.3	80.77	4.03	35.82	36.05	83.58
0.4	79.67	6.21	35.94	36.47	80.20
0.5	79.43	7.13	32.95	33.42	77.79

Table III Effect of V content on colour hue of $Dy_2Sn_{2-x}V_xO_7$ pigments prepared by calcination at 1500 °C

x	L^*	a^*	b^*	C	H^o
0.02	83.57	3.05	38.15	38.27	85.43
0.05	82.39	3.62	38.40	38.57	84.61
0.1	80.63	3.85	39.33	39.52	84.41
0.2	80.51	4.21	40.14	40.36	84.01
0.3	80.49	4.38	41.14	41.37	83.92
0.4	77.41	5.09	42.10	42.41	83.11
0.5	75.76	5.96	40.62	41.05	81.65

colour becomes darker. The value a^* (red hue) increases with the growing value x and the value b^* (yellow hue) also increases with the growing V content up to $x = 0.4$; then the value b^* a little decreases (Fig. 3). The same tendency is seen for values of chroma C. Considering that the value $H^{o\circ}$ of these pigments lies from approx. 81 and 85, all the pigments are also characterized by yellow colour. The colour difference between these yellow pigments is produced by values of chroma C. The best intensive hue is produced for pigment with $x = 0.4$ because this pigment has the highest values of chroma.

The particle sizes and particle size distribution can markedly affect the colour properties of inorganic pigments, so the pigment grain sizes (particle sizes) of the prepared compounds were also tested. The mean particle sizes (d_{50}) of pigment used for colouring of ceramic glazes or bodies lie in region from 5 to 15 μm.

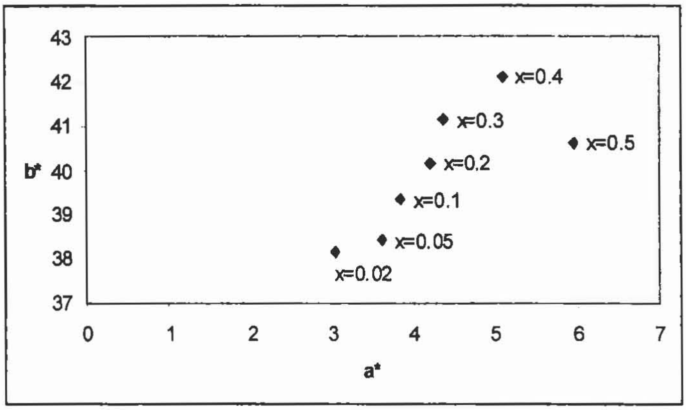

Fig. 3 Effect of V content on colour coordinates a^* and b^* of $Dy_2Sn_{2-x}V_xO_7$ pigments prepared at the temperature of 1500 °C

Table IV Particle sizes of $Dy_2Sn_{2-x}V_xO_7$ pigments

T, °C	x = 0.05			x = 0.5		
	d_{10}, μm	d_{50}, μm	d_{90}, μm	d_{10}, μm	d_{50}, μm	d_{90}, μm
1300	3.42	9.34	29.28	2.98	9.28	40.86
1400	3.92	13.16	38.50	3.01	10.07	47.50
1500	4.29	13.96	40.78	3.02	12.37	49.58

The measurement of particle size distribution was performed with the unmilled pigments. The sizes of pigment particles are in range approx. from 3 μm to 41 μm for pigments with x = 0.05 and from 3 μm to 50 μm for x = 0.5. The growing calcination temperature increases the particle size of both pigments. The average particle size of the $Dy_2Sn_{1.95}V_{0.05}O_7$ pigment after calcination obtained at 50 % cumulative mass is from 9.34 μm to 13.96 μm (Table IV), for pigment with formula $Dy_2Sn_{1.5}V_{0.5}O_7$ it is from 9.28 μm to 12.37 μm. All these values are suitable for colouring ceramic glazes.

The powder pigment samples $Dy_2Sn_{2-x}V_xO_7$ with x = 0.05 and 0.5 were studied by X-ray diffraction analysis. The diffractograms of the samples with x = 0.05 were homogenous for the pigments calcinated at higher temperature, i.e. 1400 and 1500 °C (Fig. 4). The pigment calcinated at 1300 °C was heterogeneous because free oxides (SnO_2 and Dy_2O_3) were also identified beside the pyrochlore compound. The samples with higher vanadium content (x = 0.5) were heterogeneous for the pigments calcinated at 1300 and 1400 °C. Only the sample calcinated at the highest temperature (1500 °C) was homogenous and exhibited diffraction lines that could be assigned only to pyrochlore compound.

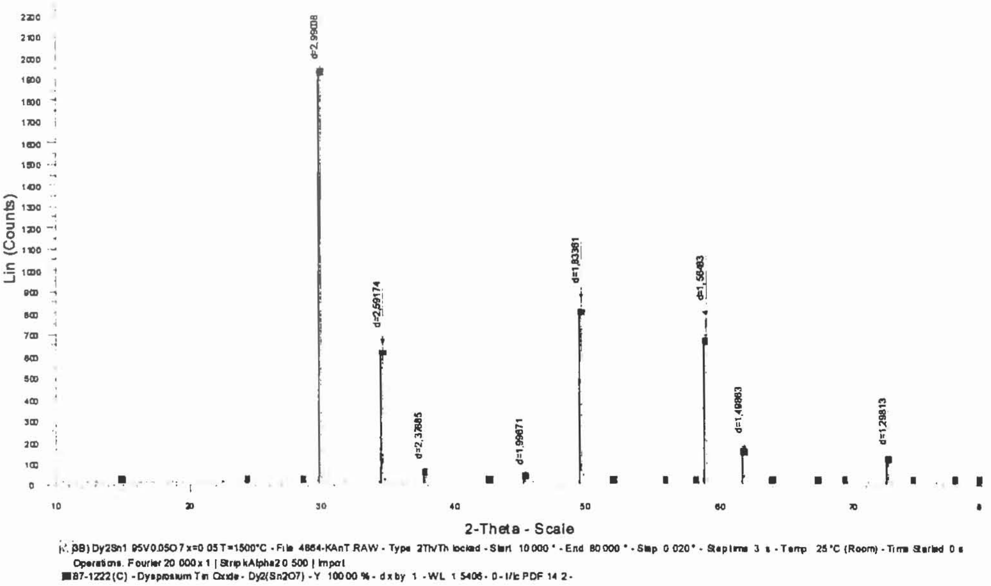

Fig. 4 Powder X-ray diffreaction pattern of $Dy_2Sn_{1.95}V_{0.05}O_7$ pigment calcinated at 1500 °C

Conclusion

The compounds $Dy_2Sn_{2-x}V_xO_7$ with $x = 0.02$, 0.05, 0.1, 0.2, 0.3, 0.4 and 0.5 were studied. All the pigments give yellow colour into ceramic glazes but a higher content of vanadium ($x = 0.4$ and 0.5) produces the intensive and deep yellow hue as compared with the pigments containing lower content of vanadium ($x = 0.02$ and 0.05). The studies of X-ray diffraction showed that single-phased sample with formula $Dy_2Sn_{1.5}V_{0.5}O_7$ was formed at the highest temperature, i.e. 1500 °C. This results together with colour properties proves that the best yellow sample is the pigment $Dy_2Sn_{1.6}V_{0.4}O_7$ calcinated at 1500 °C which is also single-phased and, at the same time, is characterized by the highest value of chroma C.

This study confirms the preparation of solid solution $Dy_2Sn_{2-x}V_xO_7$ with pyrochlore structure that was obtained by conventional solid-state reaction at temperature about 1500 °C. The research regarding $Dy_2Sn_{2-x}V_xO_7$ demonstrates heat and chemical resistance of these compounds for ceramic glazes.

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