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STUDY OF CERAMIC PIGMENTS BASED ON $Y_2Sn_{2-x}V_xO_7$

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New high-stability yellow ceramic pigments based on pyrochlore solid solutions $Y_2Sn_{2-x}V_xO_7$ were developed employing conventional solid-state reaction synthesis. The synthesis of these colourants involved high-temperature calcination of starting oxides. The 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

The search for new ceramic pigments is now a high-priority field in the applied research in the field of the ceramics industry, where there is need for developing pigments with better colours and thermal stability. In this sense, the obtaining of new yellow-shade ceramic pigments is a necessity, because of the scarce variety of existing ones and the limitation imposed on their use by the current

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technological and environmental requirements. Thus, the list of such pigments produced on industrial scale contains only the following systems: V-doped ZrO_2, V-doped SnO_2, Pr-doped $ZrSiO_4$, rutile yellow Ti-Sb-Cr or $Pb_2Sb_2O_7$ [1].

There are a great number of publications about magnetic and electric properties of materials with pyrochlore structure. However, very little is 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 of vanadium (V) as a chromophore. This type is derived from the yellow pyrochlore $Pb_2Sb_2O_7$ but it does not contain problematical Pb and Sb. This industrial yellow pigment used just now 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 [2,3]. 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 $Y_2Sn_{2-x}V_xO_7$ 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 on the colouring effects of $Y_2Sn_{2-x}V_xO_7$ pigments. This work is meaningful because these pigments give interesting hues in 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 $Y_2Sn_{2-x}V_xO_7$ pigments were used: SnO_2 of 99 % purity (Glazura, s.r.o. Roudnice nad Labem, the Czech Republic), V_2O_5 (Lachema Pliva, a.s. Brno, the Czech Republic) and Y_2O_3 of 99 % purity (Indian Rare Earths Ltd., India).

The starting mixtures containing basic oxides (SnO_2, V_2O_5 and Y_2O_3) with the required content of V ($x = 0.02$ and 0.2) were homogenised in an agate mortar. The mixtures were then calcinated in corundum crucibles in an electric resistance furnace, increasing the temperature at a rate of 10 °C min^{-1}. The calcination temperature in the 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 nm-700 nm) using a ColorQuest instrument (HunterLab, USA). The measurement conditions were as follows: an illuminant *D*65, 10° complementary observer and measuring geometry *d*/8°.

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 the 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). It is the highly integrated laser measuring system (He-Ne laser, λ = 633 nm) for the analysis of particle size distribution [4].

Results and Discussion

The aim of present work was to investigate an influence of growing vanadium content on the colouring effect of the $Y_2Sn_{2-x}V_xO_7$ where $x = 0.02$ and 0.2.

Based on values a^* and b^* of pigments with $x = 0.02$ applied into organic matrix (Table I) it can be seen that increasing calcination temperature makes the shift of the colour co-ordinate a^* from the centre of colour cross to negative values, i.e. the green shade appears in final colour of these pigments. The increasing temperature produces also growth of the colour value b^* (yellow hue) and the highest value is for the temperature of 1400 °C (Fig. 1). The same tendency is seen for values of chroma *C*. The values of hue angle $H°$ are characterized for yellow colour but the higher value L^* makes the yellow colour too light.

Table I The effect of calcination temperature on the colour properties of $Y_2Sn_{1.98}V_{0.02}O_7$ pigment applied into organic matrix and ceramic glaze

x=0.02	Pigments applied into organic matrix					Pigments applied into ceramic glaze				
T, °C	L^*	a^*	b^*	*C*	$H°$	L^*	a^*	b^*	*C*	$H°$
1300	88.81	−0.08	26.74	26.71	90.17	86.07	−0.15	26.42	26.42	90.33
1400	88.70	−1.31	34.37	34.39	92.18	83.97	1.92	27.59	27.66	86.02
1500	90.40	−2.05	25.89	25.97	94.53	83.46	2.22	22.49	22.60	84.36

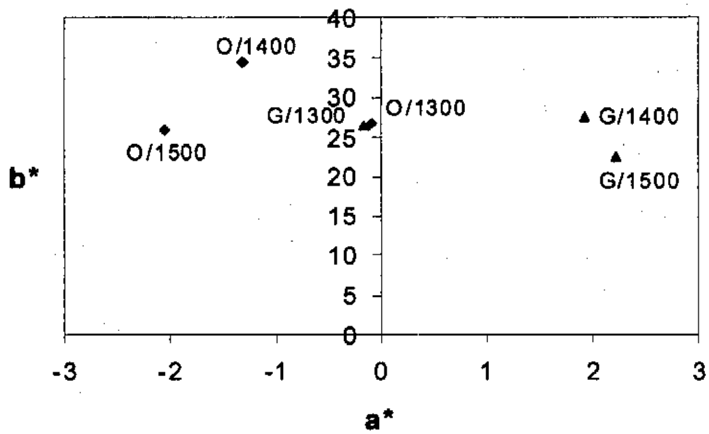

Fig. 1 The effect of calcination temperature on the colour co-ordinates a^* and b^* of $Y_2Sn_{1.98}V_{0.02}O_7$ pigment applied into organic matrix (O) and ceramic glaze (G)

After application into the glaze the $Y_2Sn_{1.98}V_{0.02}O_7$ pigments obtain an intense light yellow colour. The increase in calcination temperature produces a decrease in value L^* and the colour becomes darker. The co-ordinate a^* shifts from negative value to positive. At the same time, the value b^* increases and the highest value is attained at the temperature of 1400 °C, i.e. as well as for application into organic matrix. Considering that the value $H°$ of these pigments lies from approx. 84 to 90, the pigments are also characterized by yellow colour. The intensive hue is produced at temperature 1400 °C because this pigment has the highest values of chroma.

From Table II it follows that increasing calcination temperature increases L^* values of pigment with formula $Y_2Sn_{1.8}V_{0.2}O_7$ after its application into organic matrix. The growing temperature of calcination decreases a^* co-ordinate down to negative value for 1500 °C (Fig. 2). The same decrease is also seen in the values of co-ordinate b^* (yellow hue) and chroma C. The $Y_2Sn_{1.8}V_{0.2}O_7$ pigments applied into ceramic glaze have lower values of L^* than the pigments applied into organic matrix and, therefore, become the darkest. The values of co-ordinate a^* decrease with increasing calcination temperature. The values of co-ordinate b^* and chroma C decrease with the growing temperature, at the temperature of 1500 °C the both values increase a little. The values of hue angle $H°$ do not differ for temperatures 1300 and 1400 °C, at 1500 °C the value $H°$ a little increases. But the values $H°$ of all pigments indicate the yellow colour.

From Tables I and II it follows that pigments with $x = 0.02$ and 0.2 have yellow colour in ceramic glaze. The values $H°$ lie from approx. 84 to 90 for $x = 0.02$, and for pigment with $x = 0.2$ the interval is smaller, i.e. from approx. 86 to 88. A colour difference between these yellow pigments is produced by lower values of chroma C for $x = 0.02$. The better yellow colour is produced with higher

Table II The effect of calcination temperature on the colour properties of $Y_2Sn_{1.8}V_{0.2}O_7$ pigment applied into organic matrix and ceramic glaze

x=0.2	Pigments applied into organic matrix					Pigments applied into ceramic glaze				
T, °C	L^*	a^*	b^*	C	$H°$	L^*	a^*	b^*	C	$H°$
1300	85.56	3.21	44.20	44.32	85.85	82.36	2.65	39.23	39.32	86.14
1400	87.63	0.28	39.46	39.46	89.59	83.03	1.88	29.88	29.94	86.40
1500	88.39	−1.98	37.52	37.57	93.02	83.47	0.91	31.35	31.36	88.34

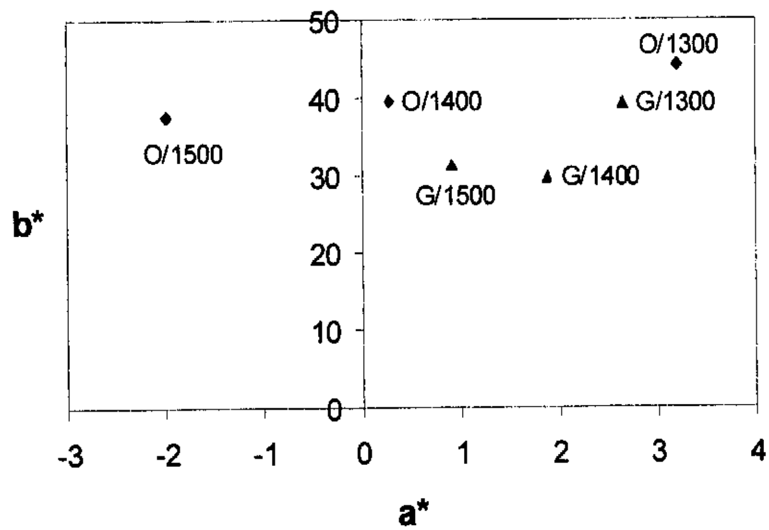

Fig. 2 The effect of calcination temperature on the colour co-ordinates a^* and b^* of $Y_2Sn_{1.8}V_{0.2}O_7$ pigment applied into organic matrix (O) and ceramic glaze (G)

content of vanadium, i.e. $x = 0.2$.

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

The measurement of particle size distribution was determined for unmilled pigments. The values of pigment particles are in the range from 2 μm to 36 μm for pigments with $x = 0.02$ and from 2 μm to 45 μm for $x = 0.2$. The growing calcination temperature increases the particles size of both pigments. The average particle size of the $Y_2Sn_{1.98}V_{0.02}O_7$ pigment after calcination obtained at 50% cumulative mass is from 5.61μm to 10.94 μm (Table III), for pigment with formula $Y_2Sn_{1.8}V_{0.2}O_7$ it is from 9.40 μm to 12.35 μm. All these values are applicable to colouring ceramic glazes.

Table III Particle sizes of the $Y_2Sn_{2-x}V_xO_7$ pigments

T °C	$x = 0.02$			$x = 0.20$		
	d_{10}, µm	d_{50}, µm	d_{90}, µm	d_{10}, µm	d_{50}, µm	d_{90}, µm
1300	2.01	5.61	19.85	1.98	9.40	35.74
1400	2.51	8.70	25.30	2.27	10.56	33.80
1500	3.67	10.94	35.60	2.77	12.35	45.07

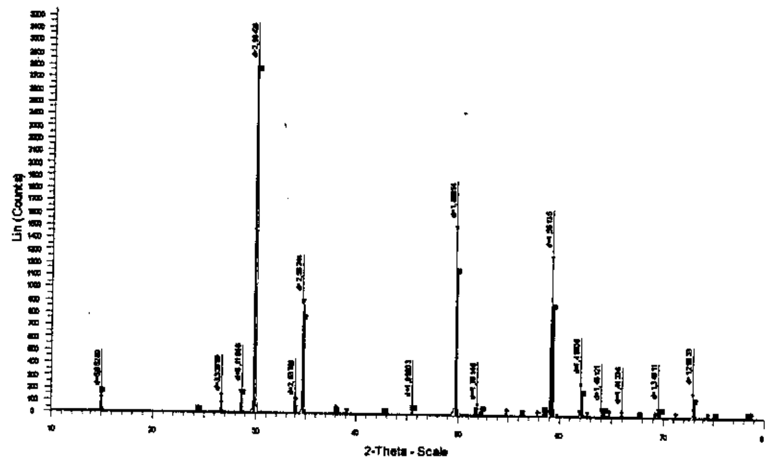

Fig. 3 Powder X-ray diffraction pattern of $Y_2Sn_{1.98}V_{0.02}O_7$ pigment calcinated at 1400 °C

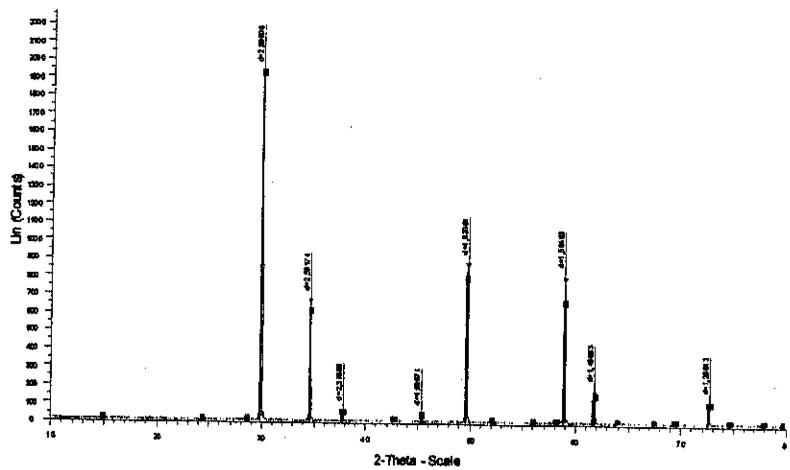

Fig. 4 Powder X-ray diffraction pattern of $Y_2Sn_{1.8}V_{0.2}O_7$ pigment calcinated at 1500 °C

Powder pigment samples $Y_2Sn_{2-x}V_xO_7$ with $x = 0.02$ and 0.2 were studied by X-ray diffraction analysis. Diffractograms of the system samples with $x = 0.02$

were homogenous at higher temperature, i.e. 1400 and 1500 °C. The pigment calcinated at 1300 °C was heterogeneous because free SnO_2 was identified beside pyrochlore compound. Samples with higher vanadium content (x = 0.2) were heterogeneous at 1300 and 1400 °C (Fig. 3). Only the sample calcinated at the highest temperature (1500 °C) was homogenous and exhibited diffraction lines that could be assigned to pyrochlore compound (Fig. 4).

Conclusion

The compounds $Y_2Sn_{2-x}V_xO_7$ with $x = 0.02$ and 0.2 were studied. All the pigments give yellow colour in ceramic glazes but a higher content of vanadium ($x = 0.2$) gives a more intensive and deeper yellow hue than the pigment with $x = 0.02$. The studies of X-ray diffraction showed that single-phased sample with formula $Y_2Sn_{1.8}V_{0.2}O_7$ was prepared at the highest temperature, i.e. 1500 °C. The connection of this result with colour properties proves that the best yellow sample is pigment $Y_2Sn_{1.8}V_{0.2}O_7$ calcinated at 1500 °C, which is single-phased and, at the same time, is characterized by the second highest value of chroma C. The pigment calcinated at 1300 °C has the highest C value this sample is heterogeneous.

This study confirms the formation of solid solution $Y_2Sn_{1.8}V_{0.2}O_7$ with pyrochlore structure that was obtained by conventional solid-state reaction at temperature about 1500 °C. The research regarding $Y_2Sn_{2-x}V_xO_7$ with $x = 0.02$ and 0.2 showed that the heat resistance and chemical resistance of these compounds are sufficient for ceramic glazes.

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