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A comparative study of the influence of mineralisers on the properties of $CoZr_4(PO_4)_6$-based pigments

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ABSTRACT

This paper is devoted to the investigation of the influence of the mineralisers Li_2CO_3, $LiBO_2$ and H_3BO_3 with respect to formation, thermal stability and pigmentary properties of $Co_{1-x}Mg_xZr_4(PO_4)_6$ colourants. Calculation of the total colour difference between the samples which were obtained with and without mineraliser helped to reveal the mineraliser effect at each calcination stage and to find out the optimal calcination temperature on basis of the most saturated and intensive colouration. At all calcination temperatures the colour of the samples appeared more saturated and darker. Mineraliser H_3BO_3 caused the most significant changes of the colour parameters at 1200 °C, while the effect of Li-containing mineralisers was the most prominent at lower temperatures. Mineraliser H_3BO_3 also provided an essential advantage with regards to phase composition and thermal stability. Thermal behaviour of the pigments was explained by means of particle porosity and, in particular, particle density.

1. Introduction

Phosphate compounds constitute an important part of coloured inorganic pigments [1–7]. An extensive range of colour shades of complex phosphates depends mostly on the content of transition metal, which acts as a chromophore on the crystalline structure of the matrix, and on the arising coordination environment of the chromophore. The astonishing variety of available structural types of known phosphates as well as variation of chemical compositions allows to achieve the desired colouration as well as the required physical properties (density, refractive index, thermal behaviour) of the pigment depending on specific application.

One of the most investigated family of phosphates is NASICON (structurally related to **NA**trium **S**uper Ionic **CON**ductor, $Na_{1+x}Zr_2Si_xP_{3-x}O_{12}$). Due to the unique physical characteristics of numerous compounds belonging to this group, it has attracted attention of researches all over the world. Thermal stability, resistance to leaching agents as well as extended possibilities for chemical modification allow application of the related phosphates as inorganic pigments, in particular, for colouration of ceramic glazes. Recently we reported an extended study on potential purple-blue colourants based on $CoZr_4(PO_4)_6$ [1]. The samples provided an intensive bright colouration of ceramic glazes and showed excellent lightfastness to solar irradiation. However, in order to achieve the most saturated colour, long thermal processing of the powders at high temperatures (~1300 °C) is required, which, in turn, inevitably leads to excessive energy consumption as well as to phase degradation of these pigments. On the other hand, at low temperatures, the conventional ceramic route does not provide a single phase product, while colouration of the single-phase samples obtained by sol–gel method is too low. These peculiarities may complicate the implementation of these compounds on the pigment market and, thus, further research is required in order to optimize the colour properties and synthesis conditions of these pigments.

The optimization of synthesis conditions by employment of mineralisers usually helps to enable an intensification of colouration and the formation of more homogeneous crystalline products at lower temperatures [8,9]. In order to understand the principles of mineraliser action, it is important to discuss firstly the main aspects of the formation of polycrystalline solids. Considering the reaction in solid state, formation of the product depends on the area of interfacial contact between the initial reagents and the ease of their diffusion through a newly formed product layer. The formation of the product layer, in turn, tends to reduce the area of contact between the reactants and also to reduce the rate of the reaction, which further depends mainly on diffusion of reactants [10]. Mineraliser additives, which are usually low-melting compounds, favour interdiffusion processes of reactants through a

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product layer and facilitate the formation of more homogeneous products at lower temperatures [8,9,11,12]. Accompanying reinforcement of colour depends mostly on improved crystallinity of the product or in some cases is caused by modification of the crystalline field of chromophore or by the creation of defects and a decrease of band-gap width in semi-conducting materials.

The aim of our research was to achieve the formation of $Co_{1-x}Mg_xZr_4(PO_4)_6$ pigments with enhanced characteristics at lower temperatures by application of mineralisers during thermal processing. We paid special attention to the effects of mineralisers on phase composition, colour performance and thermal stability of the pigments.

2. Experimental part

2.1. Materials and methodology

The synthesis of the pigments was performed by solid state reaction (SSR) and sol–gel method (SG), this procedure is fully described in our previous paper [1]. As initial reagents, the following chemicals were used: $CoCO_3$ (P., Shepherd, USA), $CoCl_2 \cdot 6H_2O$ (P., Shepherd, USA), $MgCO_3$ (B., Lachema, CZ), ZrO_2 (P.A., Sepr, FR) $ZrOCl_2 \cdot 8H_2O$ (P.A., Merck, DE) and $(NH_4)_2HPO_4$ (P.A., Lachema, CZ). Mineralisers (m.) Li_2CO_3 (P., Lachema, CZ), $LiBO_2$ (P.A., Acros Organics, BE) and H_3BO_3 (P.A., Lach-Ner, CZ) were added to the powders in an amount of 2 wt. % after thermal processing at 600 °C. Further calcination was performed at 800, 1000, 1200 and 1300 °C for 6 h. In order to remove any soluble impurities, the samples were thoroughly washed in boiling distillate water after calcination.

2.2. Characterisation techniques

Crystallochemical characterisation of the calcined powders was performed by X-ray diffraction analysis (monochromatic CuK_α radiation, a scintillation detector, equipment Diffractometer D8 Advance, Bruker, GB). Data were collected by step scanning over 2θ range from 10° to 80° with a step size of 0.02° and 3 s counting time at each step.

The colour properties of the powdered samples pressed into a cuvette were analysed by measurement of the spectral reflectance in the visible region of light (400–700 nm) using a spectrophotometer (ColorQuest XE, HunterLab, USA). The measurement conditions were the following: an illuminant D_{65}, 10° standard observer and measuring geometry d/8°. The colour properties are described in terms of CIE $L^*a^*b^*$ system recommended by CIE (Comission Internationale de l'Eclairage [13]). In this system, the values of a^* (the green (−) → red (+) axis) and b^* (the blue (−) → yellow (+) axis) indicate the colour hue, the value of L^* represents the lightness or darkness of colour as related to a neutral grey scale which is described by numbers from 0 (black) to 100 (white). The parameter C^* (chroma) represents saturation of the colour $((a^{*2} + b^{*2})^{0.5})$ and $h°$ represents the hue angle $(arctangent(b^*a^{*-1}360°(2 \cdot 3.14)^{-1}))$. For each colorimetric parameter of a sample, measurements were made in triplicate and an average value was chosen as its result. Generally, for a given sample, the standard deviation of the measured colorimetric parameters was <0.10 and the relative standard deviation was ≤1%, indicating that the measurement error can be ignored. The total colour difference between the samples which were obtained with and without the mineraliser was calculated according to the formula: $\Delta E^*_{CIE} = (\Delta L^{*2} + \Delta a^{*2} + \Delta b^{*2})^{0.5}$.

The particle size distribution of the samples was measured using a laser scattering system based on Fraunhofer bending (Mastersizer 2000/MU, Malvern Instruments, UK). Thermal stability was tested using a heating microscope with automatic image analysis (EM201-12, Hesse Instruments, DE). The equipment has been calibrated using Sn, In, Al, Zn and standard measurement uncertainty typically is ≤5 °C. For measurement, a pellet of cylindrical form with dimensions of 3 × 3 mm was prepared manually using ethanol as a binding agent. The test was performed with temperature intervals between 20 and 1500 °C at a heating rate of 10 °C min^{-1}. Density of the calcinated powders was measured by Archimedes' method using 25 ml pycnometer and deionised water as medium. The measurement of each sample was performed in triplicate and the difference in the estimated density between the independent measurements did not exceed 0.005 g cm^{-3}.

3. Results and discussion

3.1. X-ray diffraction characterisation (XRD)

Effects of mineralisers on phase composition of the pigment series were studied by powder XRD analysis. XRD patterns of the finely ground ceramic powders were recorded after calcination at 800, 1000, 1200 and 1300 °C before and after washing. The obtained patterns indicated that the washing procedure did not affect the phase composition of the samples and thus, it can be concluded, that no soluble phases formed in the systems. Results of the phase analysis are summarised in Table 1 and XRD patterns of the selected samples are presented in Fig. 1. Phase composition of $Co_{1-x}Mg_xZr_4(PO_4)_6$ powders which were synthesised without mineraliser are specified in the table as well. With employment of SSR, additives of Li-containing mineralisers resulted in the formation of an insignificant accompanying product, most probably NASICON-related double phosphate, $LiZr_2(PO_4)_3$ (ICDD #00-051-

Table 1
Evolution of phase composition of the samples with increase of calcination temperature.

Synthesis method	Mineraliser	T [°C]	Phase composition
SSR	–	800	ZrP_2O_7, ZrO_2, MP_2O_6[a]
		1000	ZrP_2O_7, ZrO_2, $M_2P_2O_7$[a]
		1200	$Co_{1-x}Mg_xZr_4(PO_4)_6$, $Zr_2O(PO_4)_2$
		1300	$Co_{1-x}Mg_xZr_4(PO_4)_6$, $Zr_2O(PO_4)_2$
	Li_2CO_3	800	$Co_{1-x}Mg_xZr_4(PO_4)_6$, $LiZr_2(PO_4)_3$
		1000	$Co_{1-x}Mg_xZr_4(PO_4)_6$, $LiZr_2(PO_4)_3$[b]
		1200	$Co_{1-x}Mg_xZr_4(PO_4)_6$, $LiZr_2(PO_4)_3$, $Zr_2O(PO_4)_2$[b]
		1300	$Co_{1-x}Mg_xZr_4(PO_4)_6$, $LiZr_2(PO_4)_3$, $Zr_2O(PO_4)_2$
	$LiBO_2$	800	$Co_{1-x}Mg_xZr_4(PO_4)_6$, $LiZr_2(PO_4)_3$
		1000	$Co_{1-x}Mg_xZr_4(PO_4)_6$, $LiZr_2(PO_4)_3$
		1200	$Co_{1-x}Mg_xZr_4(PO_4)_6$, $LiZr_2(PO_4)_3$, $Zr_2O(PO_4)_2$
		1300	$Co_{1-x}Mg_xZr_4(PO_4)_6$, $LiZr_2(PO_4)_3$, $Zr_2O(PO_4)_2$
	H_3BO_3	800	$Co_{1-x}Mg_xZr_4(PO_4)_6$
		1000	$Co_{1-x}Mg_xZr_4(PO_4)_6$[b]
		1200	$Co_{1-x}Mg_xZr_4(PO_4)_6$, $Zr_2O(PO_4)_2$[b]
		1300	$Co_{1-x}Mg_xZr_4(PO_4)_6$, $Zr_2O(PO_4)_2$
SG	–	800	$CoZr_4(PO_4)_6$
		1000	$CoZr_4(PO_4)_6$
		1200	$CoZr_4(PO_4)_6$, $Zr_2O(PO_4)_2$
		1300	$CoZr_4(PO_4)_6$, $Zr_2O(PO_4)_2$
	Li_2CO_3	800	$CoZr_4(PO_4)_6$, unknown phase
		1000	$CoZr_4(PO_4)_6$, unknown phase
		1200	$CoZr_4(PO_4)_6$, unknown phase, $Zr_2O(PO_4)_2$
		1300	$CoZr_4(PO_4)_6$, unknown phase, $Zr_2O(PO_4)_2$
	$LiBO_2$	800	$CoZr_4(PO_4)_6$, unknown phase
		1000	$CoZr_4(PO_4)_6$, unknown phase[b]
		1200	$CoZr_4(PO_4)_6$, unknown phase, $Zr_2O(PO_4)$[b]
		1300	$CoZr_4(PO_4)_6$, unknown phase, $Zr_2O(PO_4)_2$
	H_3BO_3	800	$CoZr_4(PO_4)_6$
		1000	$CoZr_4(PO_4)_6$
		1200	$CoZr_4(PO_4)_6$, $Zr_2O(PO_4)_2$
		1300	$CoZr_4(PO_4)_6$, $Zr_2O(PO_4)_2$

[a] M = Co or Mg.

[b] XRD patterns of these samples are presented in Fig. 1.