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**Synthesis and investigation of phosphate pigments**

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## References

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## Abstract

The dissertation thesis is focused on the study of phosphate compounds with NASICON structure, which were firstly investigated as ceramic pigments. The attention was paid to pigments of  $\text{CoZr}_4(\text{PO}_4)_6$  and  $\text{Co}_{1-x}\text{Mg}_x\text{Zr}_4(\text{PO}_4)_6$  type, where  $x = 0.25; 0.5$ . The pigments were prepared by classical ceramic route and sol-gel method. Cobalt carbonate, zirconium dioxide, magnesium carbonate, cobalt chloride hexahydrate, zirconium chloride octahydrate and ammonium hydrogen phosphate or phosphoric acid were used as raw materials. The prepared pigments were calcinated at  $600 - 1300\text{ }^\circ\text{C}$ . Final pigments were characterized by X-ray diffraction analysis, VIS spectrophotometry and thermal analysis. The influence of phase composition and calcination temperature on color properties, particle size and phase purity of pigments were studied.

The influence of mineralizers on the properties of the prepared pigments of the composition  $\text{CoZr}_4(\text{PO}_4)_6$  and  $\text{Co}_{1-x}\text{Mg}_x\text{Zr}_4(\text{PO}_4)_6$ , where  $x = 0.25; 0.5$ , which were also prepared by the classical ceramic route and the sol-gel method, was tested. Lithium carbonate, lithium borate and boric acid were used as mineralizers.

## Abstrakt

Disertační práce je zaměřena na studium fosforečnanových sloučenin s NASICON strukturou, které byly prvně zkoumány jako keramické pigmenty. Pozornost byla věnována pigmentům typu  $\text{CoZr}_4(\text{PO}_4)_6$  a  $\text{Co}_{1-x}\text{Mg}_x\text{Zr}_4(\text{PO}_4)_6$ , kde  $x = 0,25; 0,5$ . Pigmenty byly připraveny klasickou keramickou metodou a metodou sol-gel. Jako výchozí suroviny byly použity uhličitan kobaltnatý, oxid zirkoničitý, uhličitan hořečnatý, hexahydrát chloridu kobaltnatého, oktahydrát chloridu – oxidu zirkoničitého a hydrogenfosforečnan amonný nebo kyselina trihydrogenfosforečná. Připravené pigmenty byly kalcinovány při  $600 - 1300\text{ }^\circ\text{C}$ . Finální pigmenty byly charakterizovány pomocí rentgenové difrakční analýzy, VIS – spektrofotometrie a termické analýzy. Byl sledován vliv složení a teploty kalcinace na barevnost, velikost částic a fázovou čistotu připravených pigmentů.

Dále byl ověřen vliv mineralizátorů na vlastnosti připravených pigmentů o složení  $\text{CoZr}_4(\text{PO}_4)_6$  a  $\text{Co}_{1-x}\text{Mg}_x\text{Zr}_4(\text{PO}_4)_6$ , kde  $x = 0,25; 0,5$ , které byly připraveny také klasickou keramickou metodou a metodou sol-gel. Jako mineralizátory byly použity uhličitan lithný, boritan lithný a kyselina boritá.

## Keywords

Anorganické pigmenty, NZP fosfáty, keramická glazura, mineralizátor

## Klíčová slova

Inorganic pigments, NZP phosphates, ceramic glaze, mineralizer

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## **Introduction**

Inorganic and anorganic pigments are used for colouring of plastic, paints, glazes and for another application. Inorganic pigments give less clear shades than organic pigments but provide more thermally stable and chemical resistant shades. For this reason, inorganic pigments are used in particular for coloring building materials and ceramic materials.

Most inorganic pigments are not ecofriendly due to the content of toxic elements such as lead, mercury, cadmium, arsenic, selenium, chrome and others. At the present time, attention is paid to the environment and human health. There is an effort to reduce the content of toxic elements in the pigment composition. One possibility is to replace the toxic element by ecofriendly elements (for example Mg, Ni, Ti, Fe,...).

Phosphate pigments are very interesting material for investigation as ceramic pigment for colouring ceramic glazes. Phosphate pigments exhibit unique thermal properties and were therefore first time investigated as ceramic pigments.

## Aims of the thesis

The aim of this work was prepared phosphate pigments with the composition of  $\text{CoZr}_4(\text{PO}_4)_6$  for the coloration of ceramic glazes. Cobalt is used in the pigment industry as a source of blue in ceramic colorants. The cobalt accumulates in plants and animals and too high concentrations of it may damage the human health. The cobalt is classified as a carcinogen of category 2B.

Phosphate pigments with composition of  $\text{Co}_{1-x}\text{Mg}_x\text{Zr}_4(\text{PO}_4)_6$  ( $x = 0.25; 0.5$ ) were prepared to reduce the cobalt content. The pigments were prepared by classical ceramic route and sol-gel method. Prepared pigments were investigated through RTG diffraction, thermal analysis, particle size distribution and colour properties.

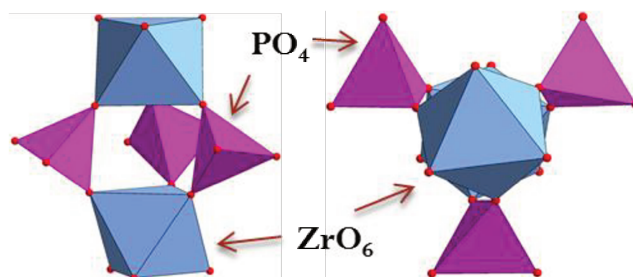
As the next aims, the influence of mineralizers (lithium carbonate, lithium borate and boric acid) on the properties of the prepared pigments of the composition  $\text{CoZr}_4(\text{PO}_4)_6$  and  $\text{Co}_{1-x}\text{Mg}_x\text{Zr}_4(\text{PO}_4)_6$ , where  $x = 0.25; 0.5$ , which were also prepared.

## 1. Theoretical part

Phosphate compounds constitute an important part of coloured inorganic pigments and consider as high performance thermally stable pigments. Compounds consist of synthetic crystalline oxide compounds of two or more different metals. The wide range of colours for these pigments is typically provided by the content of transition metals (V, Cr, Mn, Fe, Co, Ni, Cu).

The primary demands to this class of pigments include outstanding colour and heat stability as well as resistance to dissolution and chemical agents and solvent attack. Among the outstanding characteristics of these phosphates can be mentioned thermal stability, unique thermal behaviour (near zero expansion), structural flexibility, ionic conductivity and high leaching resistance [1-3].

Our attention has been focused on  $\text{NaZr}_2(\text{PO}_4)_3$ -related zirconium double phosphates – NASICON family. (NATrium Super Ionic CONductor,  $\text{Na}_{1+x}\text{Zr}_2\text{Si}_x\text{P}_{3-x}\text{O}_{12}$ ). Considering lattice symmetry, common NASICONs embrace rhombohedral, orthorhombic and monoclinic crystal systems and on this basis the NASICONs are divided into several subtypes: NZP subtype ( $\text{NaZr}_2\text{P}_3\text{O}_{12}$ ), CZP subtype ( $\text{CaZr}_2\text{P}_3\text{O}_{12}$ ) and SW subtype  $\text{Sc}_2\text{W}_3\text{O}_{12}$ . All subtypes deriving from NASICON differ mainly in the packing and/or orientation of  $[\text{M}_4^{\text{IV}}(\text{PO}_4)_6]$  structural fragments. The basic skeleton of NZP structure is presented at Fig. 1 [2,3].



*Fig. 1: Basic skeleton of NZP structure*

The crystal structure of the family prototype,  $\text{NaZr}_2(\text{PO}_4)_3$ , was determined to be rhombohedral. Generally, the structure can be characterised as a continuous framework formed by corner shared  $\text{PO}_4$  and  $\text{ZrO}_6$  units with two types of cavities where additional cations, providing charge compensation, are located. The stability and flexibility of its three-dimensional skeleton allows the existence of several hundred of compositions, the possibility of chemical absorption, exchange reactions, redox reactions and intercalation processes.

In the case of  $\text{M}^{\text{II}}\text{Zr}_4(\text{PO}_4)_6$ , most double phosphates with large divalent cation (Ca, Sr, Ba, Cd, Pb) adopt the CZP structure, while for smaller divalent metals (Mg, Mn, Co, Ni, Cu, Zn,) the SW-structure type is generally observed [4,5].

The sample of phosphate pigments provided an intensive bright colouration of glaze and showed very good thermal stability. However, in case of using classical ceramic route and the single phase of pigments was formed at the high temperature. This method of preparation is very long thermal process involving high economic costs. 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 [2,3].

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 [6,7]. 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 [8].

Mineraliser additives, which are usually low-melting compounds, favour interdiffusion processes of reactants through a product layer and facilitate the formation of more homogeneous products at lower temperatures [6-9]. 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.

During the last few years, several methods of synthesis were employed to obtain zirconium NZP phosphates. These are conventional solid-state reaction [10,11], coprecipitation [12], sol-gel reactions [13], hydrothermal [14], solvothermal [15] and even combustion reaction methods [16]. In our present work we have examined two synthesis approaches - conventional ceramic route and sol-gel reaction. Typically, the advantage of synthesising a ceramic via a sol-gel route becomes apparent as the crystallization temperature is greatly lowered. In addition this technique allows mixing of initial compounds on an atomic scale which is achieved by combining aqueous solutions of soluble salts. This procedure is also dependable for the formation of a pure single phase material where other methods may fail. We have employed this complicated synthesis route with the purpose to compare two different approaches and to evaluate the advantages of these methods for synthesis of phosphates as ceramic pigments, in particular with respect to colour performance, particle size distribution, thermal stability and phase composition [2,3].



## 2. Experimental part

### 2.1. Materials and methodology

Two different approaches were used for the synthesis of phosphate pigments. Firstly, the synthesis of  $\text{CoZr}_4(\text{PO}_4)_6$  and  $\text{Co}_{1-x}\text{Mg}_x\text{Zr}_4(\text{PO}_4)_6$  solid solutions was performed by classical ceramic route, i.e. solid-state reaction (SSR) with different combinations of initial components. As initial reagents in this case were employed  $\text{CoCO}_3$  (P., Shepherd, USA),  $\text{MgCO}_3$  (B., Lachema, CZ),  $\text{ZrO}_2$  (P.A., Sepr, FR),  $(\text{NH}_4)_2\text{HPO}_4$  (P.A., Lachema, CZ) or  $\text{H}_3\text{PO}_4$  (85 %, P.A., Lachema, CZ). Stoichiometric powder mixtures were thoroughly grinded in an agate mortar with a pestle and transferred into corundum crucibles.

Resultant powders were calcinated in an electric furnace at 300 °C for 4 h, reground and exposed to further calcination at a temperature range of 600-1300 °C with a heating rate of 5 °C/min for 12-48 h. In the case of employment of  $\text{H}_3\text{PO}_4$  as a phosphate source, obtained suspensions were dried in a temperature range of 80-150 °C overnight and reground before the calcination process.

With respect to the potential application of the powders as ceramic pigments, the colour parameters were measured at each calcination step (starting from 600 °C) and the maximal temperature and calcination time were chosen individually for each sample depending on the colour saturation and lightness of the obtained powders [2].

The second synthesis approach, sol-gel method (SG), was employed only for the preparation of  $\text{CoZr}_4(\text{PO}_4)_6$ . The synthesis procedure was performed as follows: stoichiometric amounts of  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  (P., Shepherd, USA) and  $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$  (P.A., Merck, DE) were separately dissolved in distilled water. Zirconium solution was added to cobalt solution dropwise while continuously stirring. An appropriate amount of 1M solution of  $(\text{NH}_4)_2\text{HPO}_4$  or  $\text{H}_3\text{PO}_4$  was added dropwise to this mixture while heating (70 °C) and stirring to maintain uniform mixing. A gelatinous precipitate immediately formed after addition of the phosphate solution. The precipitate was dried overnight at 60 °C and after thorough regrinding in an agate mortar with a pestle, was further exposed to calcination. At the first stage samples were maintained under 600 °C during 24 h in order to remove all volatile residues and after this they were calcinated in steps with a final temperature of 1300 °C for 12-48 h. The heating rate employed in the thermal procedures was 5 °C/min. As in the case of a solid state reaction the calcination schedule was chosen according to the best colour properties of the samples [2].

### 2.2. Characterisation techniques

#### 2.2.1. RTG diffraction

Crystallochemical characterisation of calcined powders was performed by X-ray diffraction analysis (monochromatic  $\text{CuK}_\alpha$  radiation, a scintillation detector, equipment Diffractometer D8 Advance, Bruker, GB). Data were collected by step scanning over  $2\theta$  range from 10° to 80° with a step size of 0.02° and 3s counting time at each step [17].

### 2.2.2. Thermal analysis

Thermal behaviour of the reaction mixtures, dried precursors and final products were investigated using simultaneous differential thermal and thermogravimetric analysis (DTA/TG, Jupiter STA 449/C/6/F, Netzsch, Germany) with temperature intervals between 20-1400 °C and a heating rate of 5 °C/min.  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> was used as a reference material and the weight of samples was ~150 mg.

Thermal stability was tested using a heating microscope with automatic image analysis (EM201-12, Hesse Instruments, Germany). The equipment has been calibrated using Sn, In, Al, Zn and standard measurement uncertainty typically is  $\leq$  5°C. For measurement of the samples, pellets of cylindrical form with a diameter of 2.8 mm, a height of 3 mm and a mass of ~50-70 mg were prepared [17].

### 2.2.3. Particle size distribution

Laser apparatus Mastersizer 2000/MU (Malvern Instruments, Ltd. Worcestershire, UK), which uses the laser diffraction on particles dispersed in some medium and which enables to assess measured signal by Mie scattering theory and Fraunhofer diffraction theory, was used for measuring of particle size distribution. Its wide size range is from 20 nm to 2 mm. A blue light (wavelength 466 nm, solid-state light source) for wide angle forward and back scattering is used in conjunction with red light (wavelength 633 nm, He-Ne laser) for forward, side and back scattering [18].

At the measuring, solution Na<sub>4</sub>P<sub>2</sub>O<sub>7</sub> (40 ml, 0.15 g·l<sup>-1</sup>) adds to sample (0.5 g) crushed in agate mortar. This suspension undergoes dispergation in ultrasonic bath for 2 minutes. During dispergation, solution Na<sub>4</sub>P<sub>2</sub>O<sub>7</sub> (4.8 ml, 3 g·l<sup>-1</sup>) adds to distilled water (800 ml) and background measures. Dispersed suspension gets into this solution immediately after dispergation up to maximum concentration 12.5±0.5 % and measuring turns on. The measurement of particle size distribution has three steps and instrument calculates average automatically like values d[10], d[50], d[90] [18].

### 2.2.4. Colour properties

The colour properties of obtained samples pressed into a cuvette and enamelled samples were then analysed by measurement of spectral reflectance in the visible region of light (400-700 nm) using a spectrophotometer (ColorQuest XE, HunterLab, USA). The measurement conditions were following: an illuminant D<sub>65</sub>, 10° standard observer and measuring geometry d/8°.

The colour properties are described in CIE L\*a\*b\* system. 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 and is calculated according to the formula [18].

$$C = \left( a^{*2} + b^{*2} \right)^{\frac{1}{2}} \quad (1)$$

And parametr  $H^\circ$  represents the hue angle and is calculated according to the formula (2). Hue  $H^\circ$ s has interval 0 to  $360^\circ$  and for red color has value  $350-35^\circ$ , for orange  $35-70^\circ$ , yellow  $70-105^\circ$ , green  $105-195^\circ$ , blue  $195-285^\circ$  and violet  $285-350^\circ$  [18]:

$$H^\circ = \arctg (b^*/a^*) \quad (2)$$

Total colour difference between sample and standard is calculated according to the formula [18]:

$$\Delta E_{CE}^* = \left[ (\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2 \right]^{1/2} \quad (3)$$

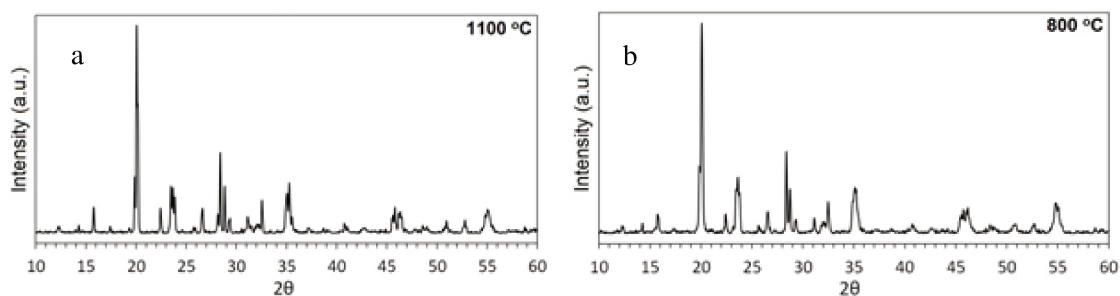
### 3. Results and discussion

#### 3.1. RTG diffraction of phosphate pigments

The RTG patterns of sample  $\text{CoZr}_4(\text{PO}_4)_6$  prepared by solid state reaction and sol-gel method obtained at different calcination temperatures are illustrated at Fig. 2. In the case solid state reaction, the single phase of  $\text{CoZr}_4(\text{PO}_4)_6$  was detected at 1100 °C (Fig. 2a). In the case of another synthesis, the single phase of  $\text{CoZr}_4(\text{PO}_4)_6$  was detected at 800 °C (Fig. 2b). Further temperature increase resulted in the formation of an additional zirconium oxide phosphate phase.

The similar results of phase composition were obtained for the powder pigments with employment  $\text{H}_3\text{PO}_4$  as starting material.

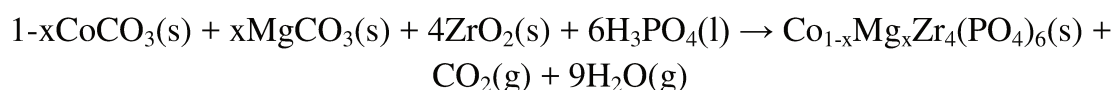
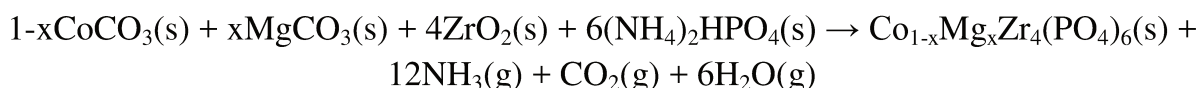
With respect to  $\text{Co}_{1-x}\text{Mg}_x\text{Zr}_4(\text{PO}_4)_6$  solid solution formation, RTG data confirmed the formation of double zirconium phosphates with the SW-structure type, related to the NZP-structure in the whole studied region ( $x = 0.25; 0.5$ ). With an increase of Mg content no significant change was observed in the obtained patterns. Due to the very close radii of these elements, the substitution of cobalt by magnesium does not cause any structural deformations. A contaminant phase of  $\text{Zr}_2\text{O}(\text{PO}_4)_2$  has also been detected in the composition of the sample calcinated above 1100 °C [2].



*Fig. 2. RTG patterns of sample  $\text{CoZr}_4(\text{PO}_4)_6$  ( $(\text{NH}_4)_2\text{HPO}_4$ ); a – SSR; b – SG*

#### 3.2. Thermal analysis of phosphate pigments

The general reaction of the formation of  $\text{CoZr}_4(\text{PO}_4)_6$  or  $\text{Co}_{1-x}\text{Mg}_x\text{Zr}_4(\text{PO}_4)_6$  solid solutions in the case of the solid state reaction can be described with following schemes [2]:

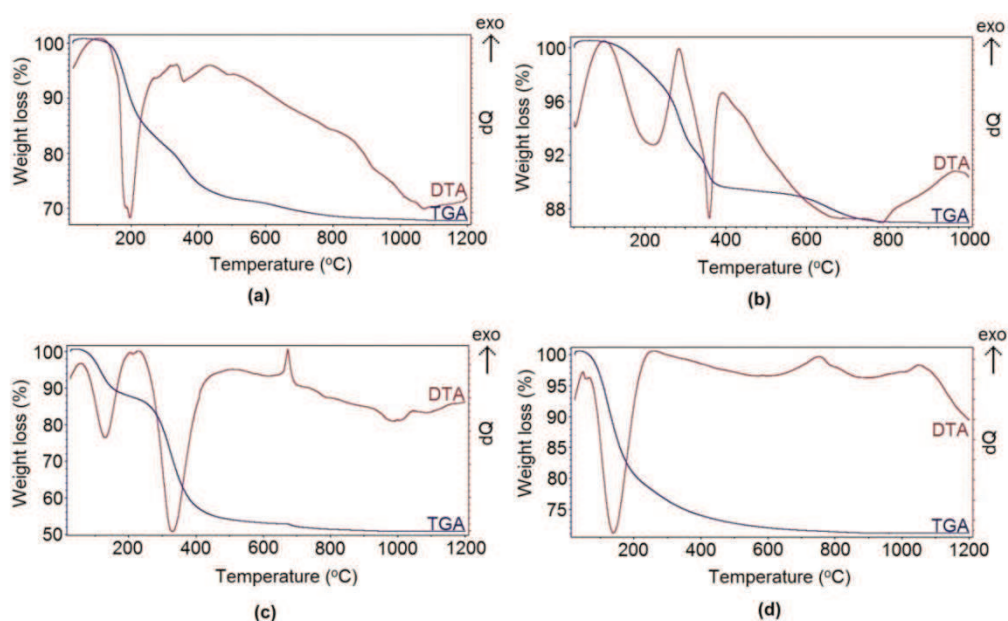


The samples with composition  $\text{CoZr}_4(\text{PO}_4)_6$  were selected as representatives and are shown at the Fig. 3.

Several endothermic effects at the DTA curve (Fig. 3, (a)) are observed with regards to the general endothermic character of the interaction in the starting mixture containing diammonium hydrogenphosphate. First effect with minimum about 200 °C and it is accompanied by substantial weight loss of ~16 %, which was attributed to dehydration, deamination and melting of diammonium hydrogenphosphate. Second effect (temperature 400 °C) corresponds to further dehydration and dimerization of the phosphate-component and decarbonation of initial carbonates. Total weight loss was approximately 32% of general weight [2].

Completely different curves were obtained for the dried precursor with a content of  $H_3PO_4$  (Fig. 3, (b)). Two strong endothermic effects with minima at 220 and 360 °C are observed at the thermoanalytical curve. First of these peaks can be associated with dehydration of trihydrogenphosphoric acid, and the second one – with decarbonation of initial carbonates [2].

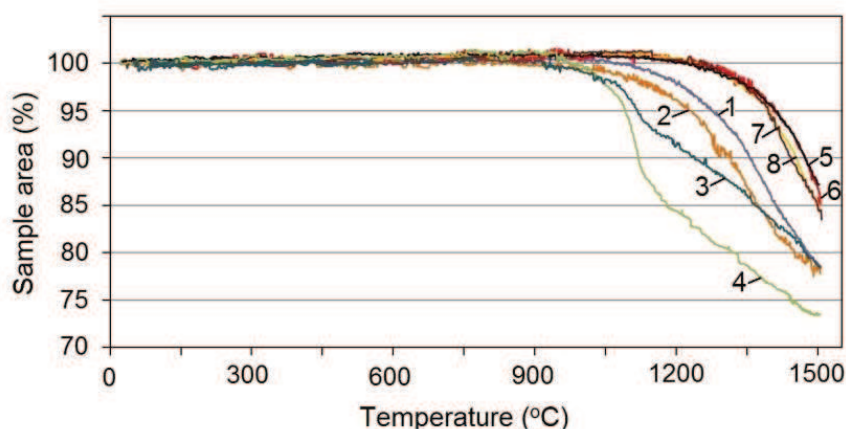
The behaviour of dried precursor during heating, which was obtained by sol-gel method, was also subjected to thermoanalytical analysis (Fig. 3(c,d)) The main observed difference between these two data is found in a strong endothermic effect around 330 °C, which arose in the case of employment of diammonium hydrogenphosphate. This effect is attributed to decomposition of ammonium chloride (338 °C). The first endothermic effect in both cases can be associated with dehydration of the phosphate component. An exothermic peak which reaches its maximum at 670 or 750 °C can be attributed to the crystallization of cobalt zirconium phosphate [2].



**Fig. 3.** DTA/TG curves of  $CoZr_4(PO_4)_6$  samples: (a) – SSR  $((NH_4)_2HPO_4)$ ; (b) – SSR  $(H_3PO_4)$ ; (c) – SG  $((NH_4)_2HPO_4)$ ; (d) – SG  $(H_3PO_4)$

In the case of the solid state reaction only small changes were observed as result of the replacement of Co by Mg in the DTA/TG curves, but significant distinctions were observed between DTA/TGA curves of the samples, which were prepared using a different phosphate source  $((NH_4)_2HPO_4$  or  $H_3PO_4$ ).

Calcinated powders were examined using a heating microscope on the subject of their thermal stability in a temperature range of 20-1500 °C. Obtained results are presented at Fig. 4. The curves represent the change of the sample area depending on the temperature [2].



**Fig. 4.** Heating microscopy results representing decrease of the sample areas with temperature increase: 1 –  $\text{CoZr}_4(\text{PO}_4)_6$  (SSR/ $(\text{NH}_4)_2\text{HPO}_4$ ); 2 –  $\text{CoZr}_4(\text{PO}_4)_6$  (SSR/ $\text{H}_3\text{PO}_4$ ); 3 –  $\text{CoZr}_4(\text{PO}_4)_6$  (SG/ $(\text{NH}_4)_2\text{HPO}_4$ ); 4 –  $\text{CoZr}_4(\text{PO}_4)_6$  (SG/ $\text{H}_3\text{PO}_4$ ); 5 –  $\text{Co}_{0.75}\text{Mg}_{0.25}\text{Zr}_4(\text{PO}_4)_6$  (SSR/ $(\text{NH}_4)_2\text{HPO}_4$ ); 6 –  $\text{Co}_{0.75}\text{Mg}_{0.25}\text{Zr}_4(\text{PO}_4)_6$  (SSR/ $\text{H}_3\text{PO}_4$ ); 7 –  $\text{Co}_{0.5}\text{Mg}_{0.5}\text{Zr}_4(\text{PO}_4)_6$  (SSR/ $(\text{NH}_4)_2\text{HPO}_4$ ); 8 –  $\text{Co}_{0.5}\text{Mg}_{0.5}\text{Zr}_4(\text{PO}_4)_6$  (SSR/ $\text{H}_3\text{PO}_4$ )

Considering the composition  $\text{CoZr}_4(\text{PO}_4)_6$  obtained by different approaches (SSR and SG), two different results were observed (Fig. 4, Curves 1-4). A sintering of these samples started at approximately the same temperature ( $\sim 950^\circ\text{C}$ ), but in the case of SG method (Fig. 4, Curves 3 and 4) the sintering progressed much faster. Concerning  $\text{Co}_{1-x}\text{Mg}_x\text{Zr}_4(\text{PO}_4)_6$  solid solutions, the obtained powders have improved the thermal stability in comparison with cobalt zirconium phosphate (Fig. 4, Curves 5-8). A sintering of these samples started only at  $\sim 1200^\circ\text{C}$ . An increase of the value “x”, the degree of the substitution, did not significantly affect the thermal stability of the samples and approximately the same curves were obtained for the solid solutions [2].

### 3.3. Particle size of distribution phosphate pigments

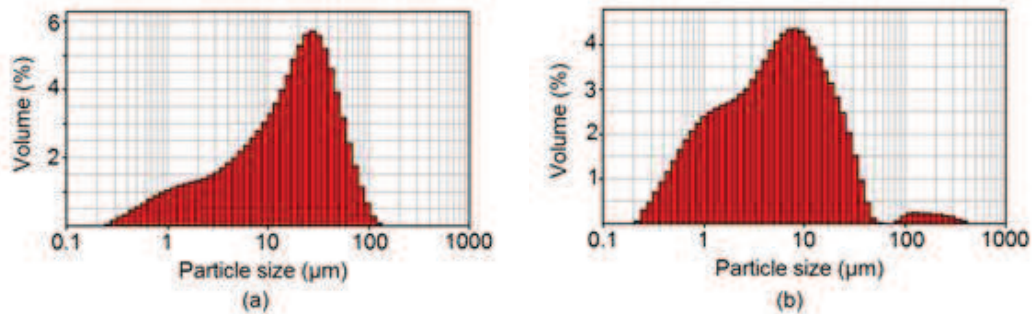
For the samples with the composition of  $\text{CoZr}_4(\text{PO}_4)_6$ , which were obtained by SSR and SG method, the values of  $d[50]$  are in an interval from 10.5 to 14.48  $\mu\text{m}$ . In case of solid state reaction the smaller particles were obtained than in the case of sol-gel method. When  $\text{H}_3\text{PO}_4$  is used as initial reagent, provides bigger particles.

The substitution of cobalt by magnesium in the sample composition led to a decrease of mean size value, the values of  $d[50]$  are in an interval from 5.12 to 10.81  $\mu\text{m}$ . Values of  $d[50]$  are shown in Tab.1 [2].

**Table 1:** Mean particle size distribution (d[50]  $\mu\text{m}$ ) of the obtained samples

Sample	Method/ Initial reagents	d[50] [ $\mu\text{m}$ ]
$\text{CoZr}_4(\text{PO}_4)_6$	SSR/ $(\text{NH}_4)_2\text{HPO}_4$	10,5
$\text{CoZr}_4(\text{PO}_4)_6$	SSR/ $\text{H}_3\text{PO}_4$	13,34
$\text{CoZr}_4(\text{PO}_4)_6$	SG/ $(\text{NH}_4)_2\text{HPO}_4$	12,32
$\text{CoZr}_4(\text{PO}_4)_6$	SG/ $\text{H}_3\text{PO}_4$	14,48
$\text{Co}_{0.75}\text{Mg}_{0.25}\text{Zr}_4(\text{PO}_4)_6$	SSR/ $(\text{NH}_4)_2\text{HPO}_4$	6,49
$\text{Co}_{0.75}\text{Mg}_{0.25}\text{Zr}_4(\text{PO}_4)_6$	SSR/ $\text{H}_3\text{PO}_4$	10,81
$\text{Co}_{0.5}\text{Mg}_{0.5}\text{Zr}_4(\text{PO}_4)_6$	SSR/ $(\text{NH}_4)_2\text{HPO}_4$	5,12
$\text{Co}_{0.5}\text{Mg}_{0.5}\text{Zr}_4(\text{PO}_4)_6$	SSR/ $\text{H}_3\text{PO}_4$	5,33

As it is shown at Fig. 5, representing the particle size in the form of size bars on logarithmic scale, the particle size of  $\text{Co}_{0.5}\text{Mg}_{0.5}\text{Zr}_4(\text{PO}_4)_6$  sample is distributed in two different size ranges. Most of the particles have a size in an interval from 0.2 to 50  $\mu\text{m}$ , but a certain amount is also distributed in a higher size interval from 80 to 400  $\mu\text{m}$  (Fig. 5, (b)). This effect was observed only for  $\text{Co}_{0.5}\text{Mg}_{0.5}\text{Zr}_4(\text{PO}_4)_6$  composition, while in a lower Mg content the particle size distribution is similar to other samples (as a representative sample  $\text{CoZr}_4(\text{PO}_4)_6$  (SSR/ $(\text{NH}_4)_2\text{HPO}_4$ /1300  $^\circ\text{C}$ /6 h) is shown at Fig. 5, (a)) [2].



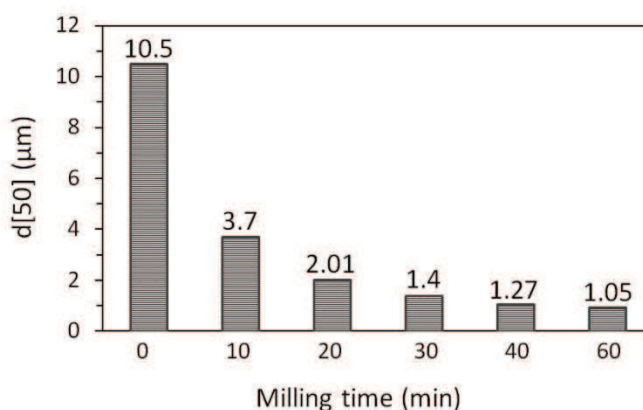
**Fig. 5.** Particle size distribution of the selected samples (on logarithmic scale):  
*a* –  $\text{CoZr}_4(\text{PO}_4)_6$  (SSR/ $(\text{NH}_4)_2\text{HPO}_4$ /1300  $^\circ\text{C}$ /6 h) and *b* –  $\text{Co}_{0.5}\text{Mg}_{0.5}\text{Zr}_4(\text{PO}_4)_6$   
 (SSR/ $(\text{NH}_4)_2\text{HPO}_4$ /1300  $^\circ\text{C}$ /6 h)

The recommended particle size for pigment applications should be within the interval 0.01–10  $\mu\text{m}$ . Thus most of the obtained results are not satisfactory for further pigmentary application of these powders and the samples need additional milling. The milling procedure was performed in a laboratory planetary mill (200 rpm) in an agate milling form in time range 10 – 60 minutes. After 60 minutes of milling the particle size about 1  $\mu\text{m}$  was provided, which was optimal for further application of a pigment. Mean particle size distribution of phosphate pigments is shown in Tab. 2. Mean particle size distribution depending on the milling time is shown at Fig. 6 [2].



**Table 2:** Mean particle size distribution ( $d[50]$   $\mu\text{m}$ ) of the obtained samples after milling 60 minutes

Sample	Method/ Initial reagents	$d[50]$ after milling [ $\mu\text{m}$ ]
$\text{CoZr}_4(\text{PO}_4)_6$	SSR/ $(\text{NH}_4)_2\text{HPO}_4$	1,05
$\text{CoZr}_4(\text{PO}_4)_6$	SSR/ $\text{H}_3\text{PO}_4$	1,00
$\text{CoZr}_4(\text{PO}_4)_6$	SG/ $(\text{NH}_4)_2\text{HPO}_4$	1,02
$\text{CoZr}_4(\text{PO}_4)_6$	SG/ $\text{H}_3\text{PO}_4$	1,05
$\text{Co}_{0.75}\text{Mg}_{0.25}\text{Zr}_4(\text{PO}_4)_6$	SSR/ $(\text{NH}_4)_2\text{HPO}_4$	1,03
$\text{Co}_{0.75}\text{Mg}_{0.25}\text{Zr}_4(\text{PO}_4)_6$	SSR/ $\text{H}_3\text{PO}_4$	1,02
$\text{Co}_{0.5}\text{Mg}_{0.5}\text{Zr}_4(\text{PO}_4)_6$	SSR/ $(\text{NH}_4)_2\text{HPO}_4$	1,07
$\text{Co}_{0.5}\text{Mg}_{0.5}\text{Zr}_4(\text{PO}_4)_6$	SSR/ $\text{H}_3\text{PO}_4$	1,03



**Fig. 6.** Mean particle size distribution ( $d[50]$ ,  $\mu\text{m}$ ) of sample  $\text{CoZr}_4(\text{PO}_4)_6$  (SSR/ $(\text{NH}_4)_2\text{HPO}_4$ /1300 °C/6 h) depending on the milling time

### 3.4. Colour properties phosphate pigments

The colour parameters of the powders were measured after each calcination temperature. Particular attention was paid to C (colour saturation) and L\* (lightness) parameters. Final colour hue of the samples belongs to the purple region of the colour spectra (hue angle between blue 240° and red 360°) and is shifted to blue hue, and thus can be described as purple-blue. SG method is relatively high colour saturation and lower lightness of the samples after the calcination at low temperatures in comparison with SSR, but resultant saturation and lightness of the sample colours were worse.

$\text{H}_3\text{PO}_4$  as initial reagent provides better results with respect to colour properties, because the final products are more saturated colours and lightness. Pigment with Mg-containing ( $\text{Co}_{0.75}\text{Mg}_{0.25}\text{Zr}_4(\text{PO}_4)_6$ ) prepared by solid state reaction and with employment of  $\text{H}_3\text{PO}_4$  provides the best result with respect to colour properties. The sample of pigment is the most saturated. Colour properties of phosphate pigments are shown in Tab. 3 [2].



**Table 3:** Colour properties of powder phosphates

Sample	Method/Initial reagents	L*	C	H°
CoZr <sub>4</sub> (PO <sub>4</sub> ) <sub>6</sub>	SSR/(NH <sub>4</sub> ) <sub>2</sub> HPO <sub>4</sub>	53,0	42,1	297,7
CoZr <sub>4</sub> (PO <sub>4</sub> ) <sub>6</sub>	SSR/ H <sub>3</sub> PO <sub>4</sub>	50,2	44,2	298,7
CoZr <sub>4</sub> (PO <sub>4</sub> ) <sub>6</sub>	SG/(NH <sub>4</sub> ) <sub>2</sub> HPO <sub>4</sub>	55,1	35,7	296,4
CoZr <sub>4</sub> (PO <sub>4</sub> ) <sub>6</sub>	SG/ H <sub>3</sub> PO <sub>4</sub>	55,9	38,2	295,5
Co <sub>0.75</sub> Mg <sub>0.25</sub> Zr <sub>4</sub> (PO <sub>4</sub> ) <sub>6</sub>	SSR/(NH <sub>4</sub> ) <sub>2</sub> HPO <sub>4</sub>	53,6	41,3	299,1
Co <sub>0.75</sub> Mg <sub>0.25</sub> Zr <sub>4</sub> (PO <sub>4</sub> ) <sub>6</sub>	SSR/ H <sub>3</sub> PO <sub>4</sub>	53,2	45,2	298,8
Co <sub>0.5</sub> Mg <sub>0.5</sub> Zr <sub>4</sub> (PO <sub>4</sub> ) <sub>6</sub>	SSR/(NH <sub>4</sub> ) <sub>2</sub> HPO <sub>4</sub>	57,3	38,3	297,1
Co <sub>0.5</sub> Mg <sub>0.5</sub> Zr <sub>4</sub> (PO <sub>4</sub> ) <sub>6</sub>	SSR/ H <sub>3</sub> PO <sub>4</sub>	55,3	39,9	298,4

The milling procedure and reduction of the particle size distribution affected the colour parameters of the samples. The information of the changes in the colour parameters are shown in Tab. 4 in comparison with the parameters before milling. The total colour difference  $\Delta E_{CIE}^*$  was also calculated between the colour parameters of the samples before and after milling. The milling procedure affected the colour parameters dramatically and the total colour difference constituted 28,4-36,6. The colour of the samples became lighter and less saturated, and the values of colour hue shifted to the blue region [2].

**Table 4:** The effect of the milling process on the colour parameters of the powdered samples

Sample	Method/Initial reagents	Milling time [min]	L*	C	H°	$\Delta E_{CIE}^*$
CoZr <sub>4</sub> (PO <sub>4</sub> ) <sub>6</sub>	SSR/(NH <sub>4</sub> ) <sub>2</sub> HPO <sub>4</sub>	0	53,0	42,1	297,7	
		60	63,9	11,4	287,8	32,8
CoZr <sub>4</sub> (PO <sub>4</sub> ) <sub>6</sub>	SSR/ H <sub>3</sub> PO <sub>4</sub>	0	50,2	44,2	298,7	
		60	63,7	12,7	288,3	34,6
CoZr <sub>4</sub> (PO <sub>4</sub> ) <sub>6</sub>	SG/(NH <sub>4</sub> ) <sub>2</sub> HPO <sub>4</sub>	0	55,1	35,7	296,4	
		60	64,6	10,5	287,2	31,0
CoZr <sub>4</sub> (PO <sub>4</sub> ) <sub>6</sub>	SG/ H <sub>3</sub> PO <sub>4</sub>	0	55,9	38,2	295,5	
		60	67,7	11,4	286,3	28,4
Co <sub>0.75</sub> Mg <sub>0.25</sub> Zr <sub>4</sub> (PO <sub>4</sub> ) <sub>6</sub>	SSR/(NH <sub>4</sub> ) <sub>2</sub> HPO <sub>4</sub>	0	53,6	41,3	299,1	
		60	65,0	10,8	288,4	32,9
Co <sub>0.75</sub> Mg <sub>0.25</sub> Zr <sub>4</sub> (PO <sub>4</sub> ) <sub>6</sub>	SSR/ H <sub>3</sub> PO <sub>4</sub>	0	53,2	45,2	298,8	
		60	64,8	10,8	288,4	36,6
Co <sub>0.5</sub> Mg <sub>0.5</sub> Zr <sub>4</sub> (PO <sub>4</sub> ) <sub>6</sub>	SSR/(NH <sub>4</sub> ) <sub>2</sub> HPO <sub>4</sub>	0	57,3	38,3	297,1	
		60	65,6	9,2	286,4	30,5
Co <sub>0.5</sub> Mg <sub>0.5</sub> Zr <sub>4</sub> (PO <sub>4</sub> ) <sub>6</sub>	SSR/ H <sub>3</sub> PO <sub>4</sub>	0	55,3	39,9	298,4	
		60	66,8	9,0	287,4	33,2

The milled powders were applied into two types of conventional ceramic glazes. The summarised information of the measured colour parameters are given in Tab. 5. The enamelled samples had intense purple-blue colours and their colour shade highly depend on the type of ceramic glaze. Colour hue of the enamelled samples changes from purple-blue to the blue region depending on the composition of employed glaze. For G05091 ceramic glaze a rich purple-blue colour was observed and colour saturation reached a value of 24.7 and lightness – 56.4.

The other type of ceramic glaze provided less saturated colour which is shifted to the blue shade, but lightness of the samples decreased to a value of 43.6 and their colour can be characterised as dark blue. Mg content in an amount of 25 % from general  $M^{II}$  content slightly affected the colour and as a result of Co substitution lighter and less or more saturated colours were obtained.  $CoZr_4(PO_4)_6$  samples obtained by SG method being enamelled provided approximately the same saturation, but lighter colours in comparison with the enamelled samples of  $CoZr_4(PO_4)_6$  (SSR) [2].

**Table 5:** The colour parameters of the samples applied into ceramic glaze (G05091 and G07091)

Sample	Method/Initial reagents	Glaze	L*	C	H°
$CoZr_4(PO_4)_6$	(SSR/ $(NH_4)_2HPO_4$ )*	G05091	57,3	24,7	282,4
		G07091	43,6	18,5	280,5
$CoZr_4(PO_4)_6$	(SSR/ $H_3PO_4$ )*	G05091	56,4	24,6	283,1
		G07091	45,9	19,6	278,5
$CoZr_4(PO_4)_6$	(SG/ $(NH_4)_2HPO_4$ )**	G05091	58,3	23,9	281,6
		G07091	51,5	20,0	275,7
$CoZr_4(PO_4)_6$	SG/ $H_3PO_4$ )*	G05091	57,9	24,1	281,9
		G07091	51,1	20,1	276,2
$Co_{0.75}Mg_{0.25}Zr_4(PO_4)_6$	(SSR/ $(NH_4)_2HPO_4$ )*	G05091	58,9	23,8	281,4
		G07091	52,4	19,9	274,4
$Co_{0.75}Mg_{0.25}Zr_4(PO_4)_6$	(SSR/ $H_3PO_4$ )*	G05091	59,2	23,2	281,1
		G07091	52,1	20,5	275,6
$Co_{0.5}Mg_{0.5}Zr_4(PO_4)_6$	(SSR/ $(NH_4)_2HPO_4$ )*	G05091	63,7	21,0	278,9
		G07091	54,7	18,1	271,2
$Co_{0.5}Mg_{0.5}Zr_4(PO_4)_6$	(SSR/ $H_3PO_4$ )	G05091	63,2	20,8	279,1
		G07091	58,6	17,3	271,2

#### 4. Conclusion

Cobalt zirconium phosphate  $\text{CoZr}_4(\text{PO}_4)_6$  has been prepared by a solid state reaction and a sol-gel method and was characterised through thermal analysis, XRD, VIS-spectrophotometry.

In order to reduce the cobalt content in the samples the series of solid solution of  $\text{Co}_{1-x}\text{Mg}_x\text{Zr}_4(\text{PO}_4)_6$  ( $x = 0.25; 0.5$ ) have also been prepared using a solid state reaction and were investigated with the same techniques. Sol-gel method provides better result with respect to the phase composition. Single phase is formed at lower temperature (at  $800\text{ }^\circ\text{C}$ ). Considering the particle size distribution, for the samples with the composition of  $\text{CoZr}_4(\text{PO}_4)_6$  both synthesis methods provide  $d[50]$  values in an interval between  $10.5 - 14.48\text{ }\mu\text{m}$ . The substitution of cobalt by magnesium led to a decrease of mean size value.

The mixed phosphates exhibit saturated purple-blue colours. Samples showed excellent thermal stability and very interesting colour shades. Prepared phosphates pigments can be considered as high performance inorganic pigments for coloration of ceramic glazes [2].

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