OPTICAL AND THERMAL CHARACTERISTICS OF Ln-DOPED $LiZr_2(PO_4)_3$

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Abstract
Phosphate pigments on basis of $LiZr_2(PO_4)_3$ with a different content of lanthanides (Y, La, Ho, Er, Nd, Sm, Eu, Gd, Dy, Tm, Yb, Lu, Pr, Tb, Ce) were prepared by solid state reaction. The samples were calcinated at 1000-1200 °C and their colour properties were studied by measurement of VIS reflectance (400-700 nm). On basis of this experiment, the compounds with the most nice colouration - $Li_{1.5}Zr_{1.5}Ln_{0.5}(PO_4)_3$ (Ln(III) - Ho, Er, Nd, Sm) and $LiZr_{1.5}Ln_{0.5}(PO_4)_3$ (Ln(IV) - Pr, Tb, Ce) - have been chosen for the detailed characterisation (thermal stability and particle size) and tested for application in ceramic glaze. As a result it is shown that the doping with lanthanides induces interesting colouration however decreases thermal stability of $LiZr_2(PO_4)_3$.

1. Introduction

Phosphate compounds constitute an important part of coloured inorganic pigments and are considered as high performance thermally stable pigments [1-3]. 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. In this view, among the outstanding characteristics of phosphate compounds can be mentioned thermal stability, unique thermal behaviour (near zero expansion), structural flexibility, ionic conductivity and high leaching resistance.
Our attention has been focused on $NaZr_2(PO_4)_3$-related zirconium double phosphates – NASICON family (NAtrium Super Ionic CONductor, $Na_{1+x}Zr_2Si_xP_{3-x}O_{12}$), in particular $LiZr_2(PO_4)_3$. Considering the lattice symmetry, $LiZr_2(PO_4)_3$ belongs to NZP subtype and is characterised by rhombohedral crystal system: R-3c, a = 8.847 Å, c = 22.24 Å, V = 1507.5 $Å^3$, Z = 6 [4]. The structure of $LiZr_2(PO_4)_3$ consists of $[Zr_4(PO_4)_6]$ structural fragments arranged in 3-dimentional framework.
This phosphate has outstanding thermal stability (above 1500 °C), however its colour is white. A common approach to induce colour in inorganic compounds is doping by 3d or 4f metals. Thus, this paper deals with preparation of phosphate pigments on basis of $LiZr_2(PO_4)_3$ doped with lanthanides and investigation of their optical properties and thermal stability.
At the first stage of our study, Ln-doped $LiZr_2(PO_4)_3$ has been prepared for the full range of lanthanides (besides radioactive Pm) in molar concentration of 0.1 and 0.5. On basis of this experiment, the compounds with the most nice colouration - $Li_{1.5}Zr_{1.5}Ln_{0.5}(PO_4)_3$ (Ln(III) - Ho, Er, Nd, Sm) and $LiZr_{1.5}Ln_{0.5}(PO_4)_3$ (Ln(IV) - Pr, Tb, Ce) - have been chosen for the detailed characterisation.

2. Experimental part

2.1. Materials and methodology

Phosphate pigments on basis of $LiZr_2(PO_4)_3$ with molar content of lanthanides 0.1 and 0.5 were prepared by solid state reaction using Li_2CO_3, $ZrOCl_2.8H_2O$, $(NH_4)_2HPO_4$ and Ln_2O_3 (Ln – Y, La, Ho, Er, Nd, Sm, Eu, Gd, Dy, Tm, Yb, Lu) or Pr_6O_{11}, Tb_4O_7, CeO_2. Stoichiometric powders of initial reagents were thoroughly ground in an agate mortar with a pestle and transferred into corundum crucibles. Resultant powders were calcinated in an electric furnace at 400 °C during 6 h. Pigments were reground in a laboratory planetary mill after calcination and high-density pellets were prepared using a stainless laboratory press form and a pressure of 200 Bar. Pellets were calcinated in an electric furnace at 1000 – 1200 °C.
The general reactions of the formation of $Li_{1.5}Zr_{1.5}Ln_{0.5}(PO_4)_3$ and $LiZr_{1.5}Ln_{0.5}(PO_4)_3$ solid solutions can described with following schema:

$$3/4Li_2CO_3 + 1.5ZrOCl_2.8H_2O + 1/4Ln_2O_3 + 3(NH_4)_2HPO_4 \rightarrow Li_{1.5}Zr_{1.5}Ln_{0.5}(PO_4)_3, \text{ (Ln = Y, La, Ho, Er, Nd, Sm, Eu, Gd, Dy, Tm, Yb, Lu)}$$

$$0.5Li_2CO_3 + 1.5ZrOCl_2.8H_2O + 1/12Pr_6O_{11} + 3(NH_4)_2HPO_4 \rightarrow LiZr_{1.5}Pr_{0.5}(PO_4)_3$$

$$0.5Li_2CO_3 + 1.5ZrOCl_2.8H_2O + 1/8Tb_4O_7 + 3(NH_4)_2HPO_4 \rightarrow LiZr_{1.5}Tb_{0.5}(PO_4)_3$$

$$0.5Li_2CO_3 + 1.5ZrOCl_2.8H_2O + 1/2CeO_2 + 3(NH_4)_2HPO_4 \rightarrow LiZr_{1.5}Ce_{0.5}(PO_4)_3$$

It was supposed, that the mixed valence lanthanides (Tb and Pr) will be oxidised to the state +4 in the final composition by atmospheric oxygen.
After the final calcination step, the obtained powders were ground in automatic mortar grinder during 20 min and subjected to the next investigation.

2.2. Particle size distribution

The particle size distribution of the samples was measured using a laser scattering system based on Fraunhofer bending (Mastersizer 2000/MU, Malvern Instruments, UK). Before the measurement, the powders were ultrasonically dispersed in water during 5 min.

2.3. Thermal stability

Thermal stability was tested using a heating microscope with automatic image analysis (EM201-12, Hesse Instruments, Germany) in a temperature interval 25-1500°C. The equipment has been calibrated using Sn, In, Al, Zn and standard measurement uncertainty typically is ≤ 5°C. For measurement of the samples, pellets of cylindrical form with a diameter and a height of 3mm and a mass of ~50-70mg were prepared.

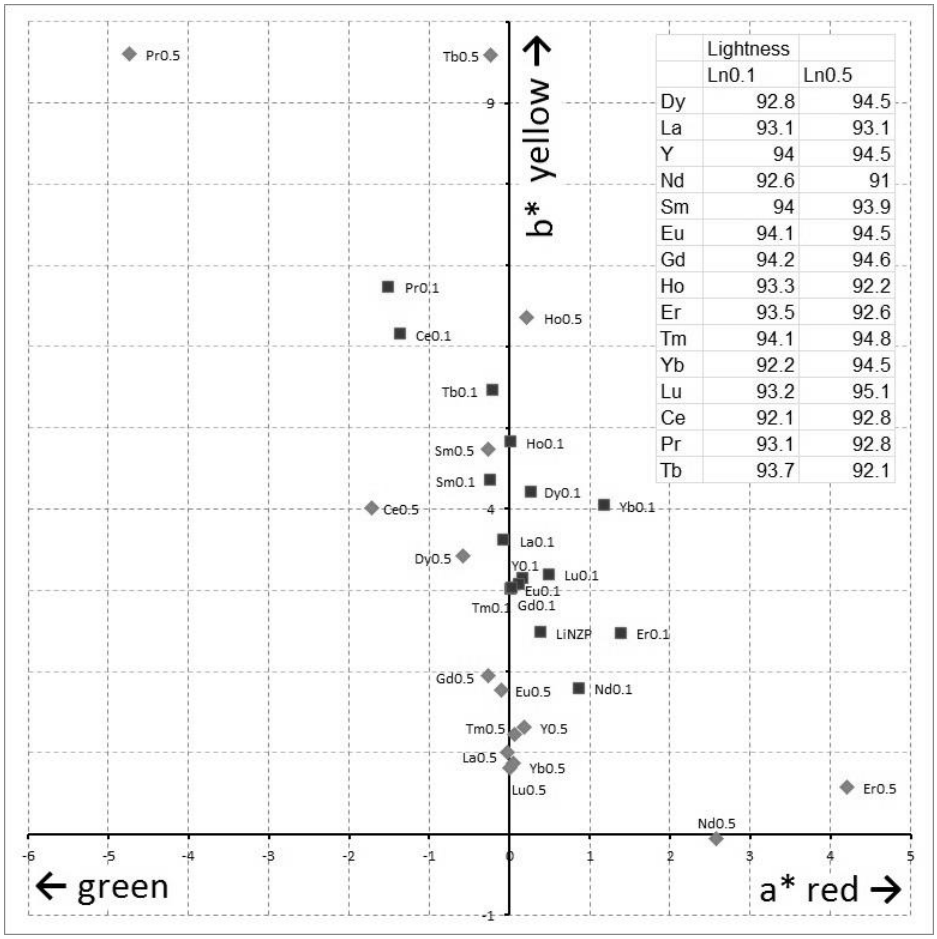
2.4. Colour properties

The colour properties of the powdered samples were analysed by measurement of spectral reflectance in the visible region of light (400-700 nm) using a spectrophotometer (ColorQuest XE, HunterLab, USA). The measurement was performed for the samples pressed into a quartz cuvette. The measurement conditions were as follows: an illuminant D_{65}, 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)).
Prepared pigments were also applied into conventional ceramic glaze in the amount of 10% and ceramic biscuits and fired with a temperature of 950 °C during 15 min with a heating rate of 10 °C/min. The colour of the samples was tested by the measurement of spectral reflectance as it is described above.

3. Results and discussion

3.1. Study of Ln-doped $LiZr_2(PO_4)_3$

At the first step the whole series of Ln-containing $LiZr_2(PO_4)_3$ was prepared and the colour of the powders was analysed. To this purpose, the samples with two various content of lanthanides (Ln = 0.1: compositions $Li_{1.1}Zr_{1.5}Ln_{0.1}(PO_4)_3$, where Ln is Y, La, Ho, Er, Nd, Sm, Eu, Gd, Dy, Tm, Yb, Lu, and $LiZr_{1.5}Ln_{0.1}(PO_4)_3$, where Ln is Pr, Tb, Ce; Ln = 0.5: compositions $Li_{1.5}Zr_{1.5}Ln_{0.5}(PO_4)_3$, where Ln is Y, La, Ho, Er, Nd, Sm, Eu, Gd, Dy, Tm, Yb, Lu, and $LiZr_{1.5}Ln_{0.5}(PO_4)_3$, where Ln is Pr, Tb, Ce) were prepared by solid state reaction and the colour of the powders was analysed.
According to the colour analysis of the powders, the values of L* (correspond to lightness of the colour) are in interval 94,2 (Gd) – 92,1 (Ce) for content of Ln = 0.1 and in interval 95,1 (Lu) – 92,1 (Tb) for content Ln = 0.5. The lightness values as weel as a*b* parameters representing the saturation and colour shade are shown in Figure 1. Samples $Li_{1.5}Zr_{1.5}Er_{0.5}(PO_4)_3$ and $Li_{1.5}Zr_{1.5}Nd_{0.5}(PO_4)_3$ provide the most red shade, $LiZr_{1.5}Pr_{0.5}(PO_4)_3$ provide the most green shade, $LiZr_{1.5}Tb_{0.5}(PO_4)_3$ provide the most yellow shade. Colour of $Li_{1.5}Zr_{1.5}Ho_{0.5}(PO_4)_3$ depends on the nature of the incident light: under the day light it is light yellow while under fluorescent light it is pink.
Based on the colour properties of the prepared samples, the compounds with the most nice colouration - $Li_{1.5}Zr_{1.5}Ln_{0.5}(PO_4)_3$ (Ln(III) - Ho, Er, Nd, Sm) and $LiZr_{1.5}Ln_{0.5}(PO_4)_3$ (Ln(IV) - Pr, Tb, Ce) have been chosen for next study.



	Lightness	
	Ln0.1	Ln0.5
Dy	92.8	94.5
La	93.1	93.1
Y	94	94.5
Nd	92.6	91
Sm	94	93.9
Eu	94.1	94.5
Gd	94.2	94.6
Ho	93.3	92.2
Er	93.5	92.6
Tm	94.1	94.8
Yb	92.2	94.5
Lu	93.2	95.1
Ce	92.1	92.8
Pr	93.1	92.8
Tb	93.7	92.1

Figure 1: Colour properties of Ln-doped $LiZr_2(PO_4)_3$ powders

3.2. Particle size distribution

Before the application in ceramic glaze, the particle size distribution of samples was measured. The obtained values of d[50] are in interval 2,28 – 5,47. Lanthanide Ce provides the smallest particle size and conversely lanthanide Tb provides the bigger particle size. The obtained values of d[50] are optimal for the glaze application, because the optimum particle sizes of inorganic pigments for pigmentary applications are in range of 0.01–10 µm. Particle size distribution of samples is shown in Figure 1 and values of d[50] are in Table I.

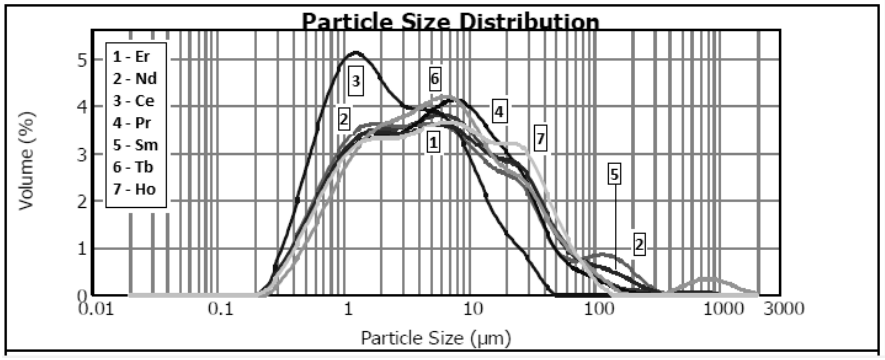


Figure 2: Particle size distribution of phosphate pigments $Li_{1.5}Zr_{1.5}Ln_{0.5}(PO_4)_3$ and $LiZr_{1.5}Ln_{0.5}(PO_4)_3$

Table I
Values of d[50] of samples

Sample	d[50] (μm)
$Li_{1.5}Zr_{1.5}Er_{0.5}(PO_4)_3$	4,93
$Li_{1.5}Zr_{1.5}Nd_{0.5}(PO_4)_3$	4,55
$LiZr_{1.5}Ce_{0.5}(PO_4)_3$	2,28
$LiZr_{1.5}Pr_{0.5}(PO_4)_3$	5,04
$Li_{1.5}Zr_{1.5}Sm_{0.5}(PO_4)_3$	4,99
$LiZr_{1.5}Tb_{0.5}(PO_4)_3$	5,47
$Li_{1.5}Zr_{1.5}Ho_{0.5}(PO_4)_3$	5,46

3.3. Thermal stability

Calcinated powders were examined using a heating microscope on the subject of their thermal stability in a temperature range of 25-1500 °C. Obtained results are presented at Figure 2. The curves represent the change of the sample area depending on the temperature. Accordingly, when sintering of the sample starts, a decrease of the sample area should appear.

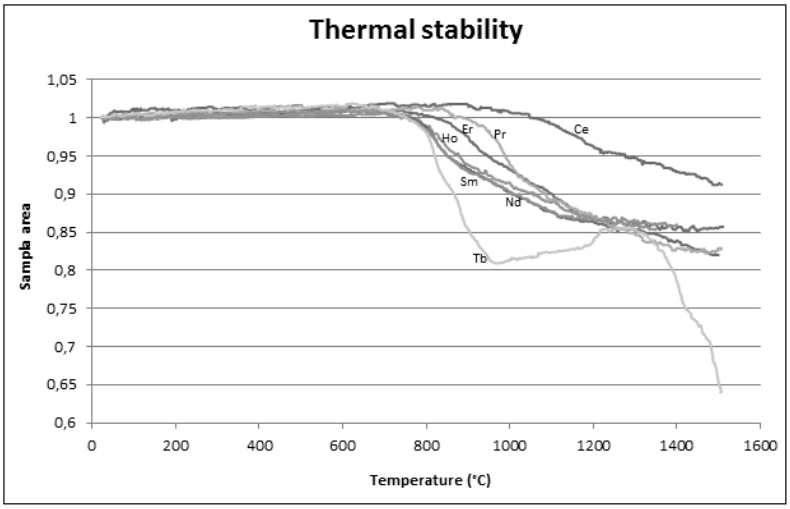


Figure 2: Heating microscopy results representing decrease of the sample areas with temperature increase

A sintering of these samples started in the temperature interval between 720 and 1000 °C; the maximal shrinkage at 1500°C reached 9-35%. The most significant value was observed for sample $LiZr_{1.5}Tb_{0.5}(PO_4)_3$. Complete heating microscopy results are shown in Table II.

Table II
Heating microscopy results

Sample	Sintering Start (°C)	Shrinkage (%)
$Li_{1.5}Zr_{1.5}Er_{0.5}(PO_4)_3$	800	15
$Li_{1.5}Zr_{1.5}Nd_{0.5}(PO_4)_3$	800	18
$LiZr_{1.5}Ce_{0.5}(PO_4)_3$	1000	9
$LiZr_{1.5}Pr_{0.5}(PO_4)_3$	850	18
$Li_{1.5}Zr_{1.5}Sm_{0.5}(PO_4)_3$	720	15
$LiZr_{1.5}Tb_{0.5}(PO_4)_3$	730	35
$Li_{1.5}Zr_{1.5}Ho_{0.5}(PO_4)_3$	800	14

3.4. Colour properties

The colour properties of the samples were analysed by measurement of VIS reflectance (400-700 nm). The colour shades of the pigments can be characterised as follows: Er- light pink, Nd-light purple, Pr-light green, Tb-yellow, Ce, Ho and Sm - light yellow; after application in the ceramic glaze, the colour of all samples became very light. An interesting property of the Ho sample is its colour change which depends on the nature of the incident light: under the day light it is light yellow while under fluorescent light it is pink. This phenomenon can be explained with the luminescent properties of this compound. Lanthanide Sm provides the most light colour and lanthanide Nd provides the most dark colour. The colour parameters (CIE L*a*b*) and colour of the samples are shown in Table III. The Fig. 3 shows a*b* parameters of the samples.

Table III
The colour parameters (CIE(L*a*b*) and colour of the samples

Sample	L*	a*	b*	Colour
$Li_{1.5}Zr_{1.5}Sm_{0.5}(PO_4)_3$	94,03	-0,26	4,74	Light yellow
$Li_{1.5}Zr_{1.5}Ho_{0.5}(PO_4)_3$	92,31	0,22	6,36	Light yellow/pink
$Li_{1.5}Zr_{1.5}Er_{0.5}(PO_4)_3$	92,63	4,21	0,58	Light pink
$Li_{1.5}Zr_{1.5}Nd_{0.5}(PO_4)_3$	90,75	2,58	-0,05	Light purple
$LiZr_{1.5}Ce_{0.5}(PO_4)_3$	93,60	-1,72	4,01	Light yellow
$LiZr_{1.5}Pr_{0.5}(PO_4)_3$	92,79	-4,74	9,60	Light green
$LiZr_{1.5}Tb_{0.5}(PO_4)_3$	92,61	-0,23	9,59	Yellow

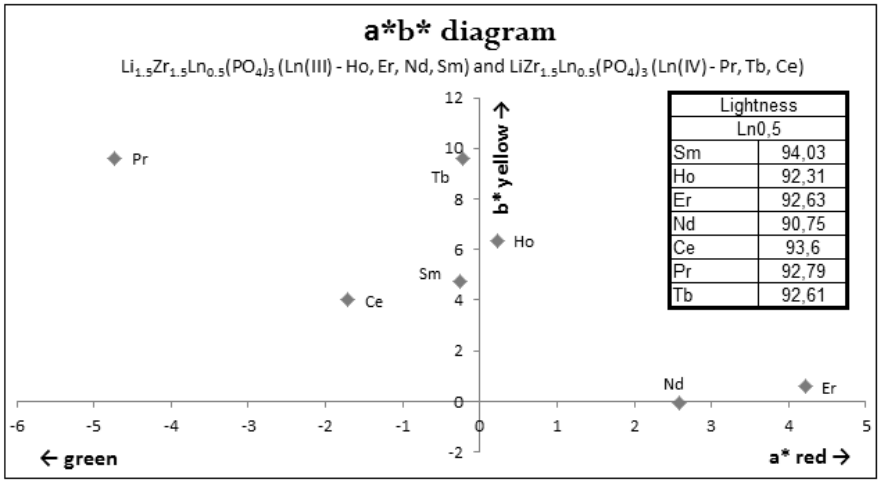


Figure 3: a*b* diagram of $Li_{1.5}Zr_{1.5}Ln_{0.5}(PO_4)_3$ (Ln(III) - Ho, Er, Nd, Sm) and $LiZr_{1.5}Ln_{0.5}(PO_4)_3$ (Ln(IV) - Pr, Tb, Ce)

4. Conclusions

Samples of pigments were prepared by classical ceramic route – solid state reaction and tested for application in ceramic glaze. The colour shades of the pigments can be characterised as follows: Er- light pink, Nd-light purple, Pr-light green, Tb- yellow, Ce, Ho and Sm - light yellow; after application in the ceramic glaze, the colour of all samples became very light. An interesting property of the Ho sample is its colour change which depends on the nature of the incident light: under the day light it is light yellow while under fluorescent light it is pink.
The particle size distribution of the samples was measured. The obtained values of d[50] are in an interval 2,28-5,46 μm, which is optimal for the glaze application.
Thermal stability of the samples was tested. A sintering of these samples started in the temperature interval between 720 and 1000 °C; the maximal shrinkage at 1500°C reached 9-35%.
In general, Ln-doping induces interesting colouration however decreases thermal stability of $LiZr_2(PO_4)_3$.

5. Acknowledgment

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6. References

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4. ICDD # 00-084-0998.