**RESEARCH ON INFLUENCE OF TEMPERATURE
(20°-1000°C) ON BINARY MIXTURES OF SOLID
SOLUTIONS OF $\text{Zn}_3(\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ – $\text{Mg}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$**

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Abstract: We analysed thermal (20°–1000°C) phase changes of the substrates of $\text{Zn}_3(\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ (1) and $\text{Mg}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$ (7) and their binary mixtures (percentage ratio 10%–90%). Thermal differential analysis (TG, DTG, DTA), IR and XR, showed that the above mentioned substances, heated for 1 hour up to 500° and 1000°C changed the structure. Samples contain: 90%, 70%, 50% $\text{Zn}_3(\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ (1) in the binary mixtures with $\text{Mg}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$ (7) change the structure at 500°C into $\text{Zn}_3(\text{PO}_4)_2$ and at 1000°C in $(\text{ZnMg})_3(\text{PO}_4)_2$, other binary mixture (30%, 10%) have structure $\text{Mg}_3(\text{PO}_4)_2$ (at 1000°C).

INTRODUCTION

Inorganic phosphoric binary compounds are tested by reason of interesting physical and chemical properties [1–4] as well as their complicated structures [5–8]. In one of previous works [9] we have presented that heating from 20° to 1000°C of binary mixtures made of aluminum sulfate and magnesium phosphate leads to obtaining of differentiated reaction products, depending on molar composition of mixture.

In this work the aim was to analyze the behavior of binary mixtures (prepared in molar percentages from 90 to 10%) containing $\text{Zn}_3(\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ always combined with magnesium phosphate heated from 20° to 1000°C.

Substrates and products analysis obtained during thermal reactions has been performed by means of thermal differential analysis (TG, DTG DTA), IR and XR.

METHODOLOGY

1. Chemicals – substrates:

$\text{Zn}_3(\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ (1); $\text{Mg}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$ (7)

2. Substrates and their binary mixtures preparation:

Substrates (1,7) were used as given above (Tab. 1). Each compound was grounded in a mortar for about 15 minutes, sieved through 400 µm sieve and binary mixtures were prepared with percentage molar ratio 90%–10%. Weighed substrates were combined into binary mixtures, grounded in a mortar (15–min.) and sieved as presented above. Mixtures obtained in such a way (2–6) were subject to further analysis.

Tab.1. Containing of subtracts and their participation binary mixtures (in %– molar)

Number of sample	1	2	3	4	5	6	7
$\text{Zn}_3(\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ (%)	100	90	70	50	30	10	0
$\text{Mg}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$ (%)	0	10	30	50	70	90	100

3. Sinters preparation in temperature of 500° and 1000°C

Substrates as well as binary mixtures were transferred into porcelain melting – pots which were subsequently put in electric furnace which was heated 1 h in programmed temperatures up to 500°C and second series up to 1000°C for 1 h. Then the furnace was switched off and the samples were left to cool over 24 hours.

4. Apparatus and analysis procedure

Thermal differential analysis was performed with Derivatograph Q–1500 D: sample weight –200 mg, TG – 1 mV, DTA – 1 mV, T– 20° – 1000°C delta T – 10°C/min, sensitivity – 200.

IR analysis was carried out with use of the tablet method in potassium bromide – Bruker– Vector 22 apparatus

XR analysis was performed by powder diffraction in the following conditions: lamp with copper anticathode ($\lambda = 1,540598$ Angström) with nickel filter, lamp voltage $U = 300$ kV, current $I = 25$ mA, applied rate of measurement 2 theta from 6° to 80° stepping with 2theta = 0,04°.

RESULTS AND DISCUSSION

By thermal analysis it was shown that, within the range of 20° – 1000°C, $\text{Zn}_3(\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ is subject of dehydration process with mass loss (TG curve) at temperatures respectively: 50 – 160°C (5% mass loss), 160– 190°C (4.7% mass loss) and 190 – 280°C (2.5% mass loss). A large transformation on the DTA with maximum at 195°C corresponds to mentioned above transformations. Thermal analysis of $\text{Mg}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$ (Fig. 1.7) shows a two stages process connected with dehydration (TG curve – the total mass loss 42.02%). The first stage is at temperatures 75° – 170°C and the second at 170° – 220°C, this one with appropriate recording on DTG curve (max at 210°C). The third stage of phase transformations of the phosphate tested occurs at higher temperatures (220° – 720°C). All the three transformations are accompanied with partial mass losses respectively: 5%, 26.31% and 10.71%. Above 720°C to 1000°C no phase transformations are observed.

Thermal analyses carried out on the binary mixtures (Fig. 1. 2 – 6) showed that quantity and quality of each transformation (TG, DTG and DTA curves) for each test is dependent on percentage shares of individual substrates in these mixtures.

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Fig. TG, DTG, DTA (20°–100°C) for $\text{Zn}_3(\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ (1) and $\text{Mg}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$ (7) and their binary mixtures (samples 2–6).

By means of IR testing it was ascertained that the spectra of not heated samples $\text{Zn}_3(\text{PO}_4)_2 \times 2\text{H}_2\text{O}$ and $\text{Mg}_3(\text{PO}_4)_2 \times 8\text{H}_2\text{O}$ (Fig. 2.1 spectra 1 and 7) differ in spectra range describing water presence in a molecule, namely:

- the spectrum of $\text{Zn}_3(\text{PO}_4)_2 \times 2\text{H}_2\text{O}$ shows two maximums: first at 3400 cm^{-1} within the range from 4000 to 2600 cm^{-1} and the second at 1630 cm^{-1} within the range from 1750 cm^{-1} to 1520 cm^{-1} ;

- the spectrum of $\text{Mg}_3(\text{PO}_4)_2 \times 8\text{H}_2\text{O}$ has two intense maximums assigned to hydroxyl groups within the range of $4000 - 2500\text{ cm}^{-1}$ at 3500 cm^{-1} ; the second band of the same character was recorded from $1830 - 1500\text{ cm}^{-1}$ with maximum at 1630 cm^{-1} .

Two broad bands in zinc phosphate may be attributed to the phosphate group (Fig. 2.1 spectrum 1). One is from $1350 - 810\text{ cm}^{-1}$ with three maximums: at 1100 cm^{-1} , 1000 cm^{-1} and 940 cm^{-1} ; the second is from $810 - 350\text{ cm}^{-1}$ with the big maximum at 630 cm^{-1} and the small one at 355 cm^{-1} .

The band of $1350 - 750\text{ cm}^{-1}$ with the maximums at: 1040 , 990 , 950 and 860 cm^{-1} and the broad band of $750 - 350\text{ cm}^{-1}$ with the maximums at: 700 , 570 and 390 cm^{-1} correspond to the phosphate group of $\text{Mg}_3(\text{PO}_4)_2 \times 8\text{H}_2\text{O}$ (fig. 2.1 spectrum 7).

Spectral differences visible in the spectra of not heated binary mixtures caused by changes in spectrum of $\text{Zn}_3(\text{PO}_4)_2 \times 2\text{H}_2\text{O}$ as amount of magnesium phosphate increases in samples are seen within the band of $4000 - 2250\text{ cm}^{-1}$. Characteristic of $\text{Mg}_3(\text{PO}_4)_2 \times 8\text{H}_2\text{O}$ the absorption maximum appears at 3500 cm^{-1} . moreover, the wave range of phosphate band widens and the additional small maximum appears at 1040 cm^{-1} . The spectra within the ranges of $810 - 350\text{ cm}^{-1}$ also change visibly where more absorption maximums appear then it was observed for $\text{Zn}_3(\text{PO}_4)_2 \times 2\text{H}_2\text{O}$.

Fig.2. IR spectra of the samples in 20°C (1), 500°C (2), 1000°C (3) for $\text{Zn}_3(\text{PO}_4)_2 \times 2\text{H}_2\text{O}$ (1) and $\text{Mg}_3(\text{PO}_4)_2 \times 8\text{H}_2\text{O}$ (7) and their binary mixture (samples 2 – 6).

Analysis of spectra of heated substances at 500°C (Fig. 2.2 spectra 1 and 7) revealed disappearance of the maximum at 3400 cm⁻¹ (originated from magnesium phosphate) and standardization of spectral structure within the wave range of 4000 – 2500 cm⁻¹. The most large changes in spectral structure for all the samples (spectra 1 – 7) are observed within the range of 1350 – 810 cm⁻¹ that represent structural changes of the phosphate group under the influence of temperature. It has its reflection in changes within the band responsible for bending–stretching vibrations, i.e. within the range of 810 – 350 cm⁻¹. The changes within the both ranges varied with the percentage content of individual components in samples (Fig. 2.2 spectra 2 – 6).

The big change in structure of components tested appears with heating them at 1000°C. Further dehydrations and phase transformations of them followed which were recorded spectrophotometrically on IR (Fig. 2.3 spectra 1 – 7).

The differences in spectra of those series of testing appeared evidently within the phase range of 1500 – 800 cm⁻¹ just like within the range of 800 – 350 cm⁻¹. It was stated that the spectra of the both substrates within those ranges are very similar and they differ only in bigger width of absorption maximum for the PO₄³⁻ group of magnesium phosphate in comparison with more narrow for that function group observed on the spectrum of Zn₃(PO₄)₂ (Fig. 2.3 spectra 1 and 7). The binary mixtures spectra (Fig. 2.3 spectra 2 – 6) are mostly diverse within the spectral range of 800 – 350 cm⁻¹. The spectra 2, 3 and 4 have particularly dissimilar appearance which are fixed for samples of 50% – 90% of Zn₃(PO₄)₂, in order to straighten out changes in samples in samples tested – both substrates and binary mixtures in thermal processes (20° – 1000°C) identification of them was carried out by means of powder X-ray diffractionmetry and following results were obtained:

Substrates:

	500°C		1000°C
Zn ₃ (PO ₄) ₂ ·2H ₂ O (1)	® Zn ₃ (PO ₄) ₂	®	Zn ₃ (PO ₄) ₂
Hopeite (ID 30 – 1491)	(ID 29 – 1390)		(ID 29 – 1390)
	500°C		1000°C
Mg ₃ (PO ₄) ₂ ·8H ₂ O (7)	® amorph	®	Mg ₃ (PO ₄) ₂
Bobierite (ID 16 – 330)			Farringtonite ID 33 – 876
			ID 22 – 1151, ID 25 – 1373

Binary mixtures at 1000°C

90% (1) – 10% (2)	Zn ₂ Mg (PO ₄) ₂ and (ZnMg) ₃ (PO ₄) ₂	ID 31 – 1469 and ID 12 – 680
70% (1) – 30% (2)	Zn ₂ Mg (PO ₄) ₂ and (ZnMg) ₃ (PO ₄) ₂	ID 31 – 1469 and ID 12 – 680
50% (1) – 50% (2)	Zn ₂ Mg (PO ₄) ₂ and (ZnMg) ₃ (PO ₄) ₂	ID 31 – 1469 and ID 12 – 680
30% (1) – 70% (2)	Mg ₃ (PO ₄) ₂	ID 33 – 876
10% (1) – 90% (2)	Mg ₃ (PO ₄) ₂	ID 33 – 876 and ID 22 – 1151

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