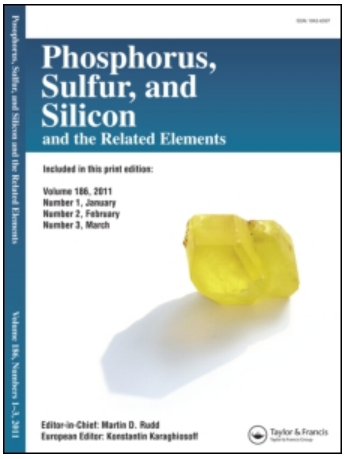

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Comparative Research of Influence of Temperature (20-1000°C) on Binary Mixtures of Solid Solutions Mg 3 (PO 4) 2 ·8H 2 O with Sulphate of Differentiated Cation Compound (Na + , Ca 2+ , Al 3+)

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COMPARATIVE RESEARCH OF INFLUENCE OF TEMPERATURE (20–1000°C) ON BINARY MIXTURES OF SOLID SOLUTIONS $Mg_3(PO_4)_2 \cdot 8H_2O$ WITH SULPHATE OF DIFFERENTIATED CATION COMPOUND (Na^+, Ca^{2+}, Al^{3+})

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We analyzed thermal (20–1000°C) phase changes of the substrates of $Mg_3(PO_4)_2 \cdot 8H_2O$ (I), $Al_2(SO_4)_3 \cdot 16H_2O$ (II), $CaSO_4 \cdot 2H_2O$ (III), Na_2SO_4 (IV) and their binary mixtures (percentage ratio 10–90%) in the presence of magnesium phosphate (I). Thermal differential analysis, IR and XR, showed that these substances, heated for 1 hour up to 500 and 1000°C, changed the structure.

Keywords: $Al_2(SO_4)_3 \cdot 16H_2O$; binary system; $CaSO_4 \cdot 2H_2O$; IR spectra; $Mg_3(PO_4)_2 \cdot 8H_2O$; Na_2SO_4; phosphate; sulphate; thermal analysis; XR spectra

INTRODUCTION

In a previous work,[1] we discovered that heating binary mixtures made of aluminium sulphate and magnesium phosphate at 20 to 1000°C leads to obtaining differentiated reaction products, depending on the molar composition of the mixture.

In this work, the aim was to analyze the behavior of three binary mixtures (prepared in molar percentages from 90 to 10%) containing aluminium sulphate, calcium sulphate, and sodium sulphate, always combined with magnesium phosphate heated from 20 to 1000°C.

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Substrates and products analysis obtained during thermal reactions has been performed by means of thermal differential analysis, IR and XR.

METHODOLOGY

Chemicals–Substrates

$Mg_3(PO_4)_2 \cdot 8\ H_2O$ (I), $Al_2(SO_4)_3 \cdot 16H_2O$ (II), $CaSO_4 \cdot 2H_2O$ (III), Na_2SO_4 (IV).

Substrates and Their Binary Mixtures Preparation

Substrates were used as given above. Each compound was grounded in mortar for about 15 minutes and sieved through a 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 were subjected to further analysis.

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 an electric furnace that was heated up to 500°C during 1 hour and in a second series of research up to 1000°C after 1.5 h of heating. Samples in each case remained in programmed temperatures (500 and 1000°C) for an hour. Then the furnace was switched off and the samples were left to cool over 24 hours.

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, ΔT: 10°C/min^{-1}, sensitivity: 200).
- IR analysis was carried out with use of the tablet method in potassium bromide—Specord M 80 apparatus.
- XR analysis was performed by powder diffraction in the following conditions: lamp with copper anticathode ($\lambda = 1.540598$ Å) with nickel filter, lamp voltage U = 300 kV, current I = 25 mV, applied rate of measurement 2Θ from 6° to 80° stepping with (2Θ) s = 0.04°.

RESULTS AND DISCUSSION

Substrates and binary mixtures were subjected to the following conversions influenced by temperature:

The Set: $Al_2(SO_4)_3 \cdot 16H_2O$ (II)—$Mg_3(PO_4)_2 \cdot 8H_2O$ (I)

On the basis of DTA analysis (Figure 1) for $Al_2(SO_4)_3 \cdot 16H_2O$, it has been proved that this compound undergoes dehydration (two endothermal peaks with maxima at 149.6 and 337.5°C) and subsequently undergoes two-step thermal dissociation with a preparatory phase from 416 to 850°C and a dissociation phase from 850 to 1000°C, with a maximum at 920.2°C. In this process, SO_3 is emitted and converted into SO_2.

The second substrate—$Mg_3(PO_4)_2 \cdot 8H_2O$—only undergoes a thermal dehydration from 20 to 220°C with a maximum at 185°C, and then a gradual mass decrease can be observed, ending at 666°C without any changes in DTA.

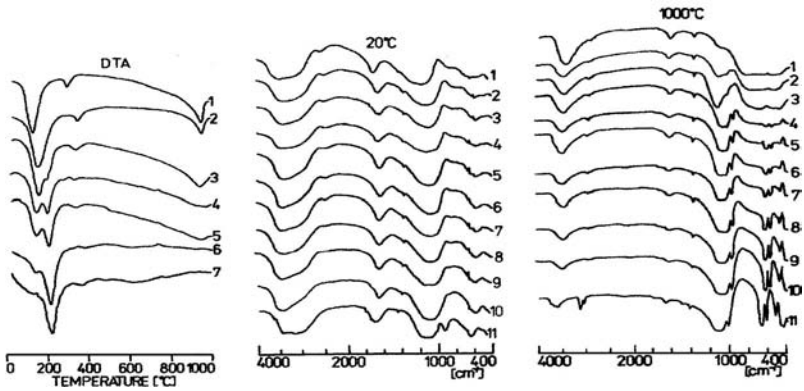

FIGURE 1 DTA (20–1000°C) and IR spectra (20°C and 1000°C) for $Al_2(SO_4)_3 \cdot 16H_2O$ (I) and $Mg_3(PO_4)_2 \cdot 8H_2O$ (II) and their binary mixtures (samples 2–10) containing:

Number of sample	DTA	1	2		3		4		5		6	7
	IR	1	2	3	4	5	6	7	8	9	10	11
$Al_2(SO_4)_3 \cdot 16H_2O$%		100	90	80	70	60	50	40	30	20	10	0
$Mg_3(PO_4)_2 \cdot 8H_2O$%		0	10	20	30	40	50	60	70	80	90	100

Binary mixtures prepared from substrates and analyzed by thermal differential analysis (Figure 1, 2–10), depending on substrate quantitative ratio in samples, differ in the number of endothermal conversions and the shape of the line illustrating particular thermal dissociation processes.

Substrates IR spectra analysis (Figure 1, 20°C, 1, 11) showed that the studied compounds are characterized by different spectra, but IR spectra of their non-heated binary mixtures (Figure 1, 20°C, 2–10) do not differ in a significant way because magnesium phosphate greatly influence their shape.

Heating substrates and their binary mixtures over 1 hour in 500°C caused alterations in IR spectra in 1500-400 cm^{-1}, and the same heating in 1000°C (Figure 1, 1000°C, 1–11) resulted in the creation of the following structures: γAl_2O_3 from $Al_2(SO_4)_3 \cdot 16H_2O$ and anhydrous $Mg_3(PO_4)$ from $Mg_3(PO_4)_2 \cdot 8H_2O$.

10 and 20% of anhydrous magnesium phosphate in binary samples (Figure 1, 1000°C; 2–3) had no influence on spectrum change registered for Al_2O_3, but starting with 30% content in the mixture, its influence becomes more visible on the shape of IR spectra (Figure 1, 1000°C, 3–10).

Studies carried out by means of X-ray diffraction allowed to determine a spectrum for $Al_2(SO_4)_3 \cdot 16H_2O$ and $Mg_3(PO_4)_2 \cdot 8H_2O$ and also to identify compounds that could not have been determined by previously mentioned methods.

Diffractogram of binary mixture composed in 70% of aluminium sulphate and in 30% of magnesium phosphate after being heated in 1000°C over 1 hour contains Farringtonite (Identification Card-33-0876), $AlPO_4$ (ID-20-0044), and MgAl=O (ID-10-0238).

Alterations in proportion of compounds in binary mixture (50% of each substrate) after heating in 1000°C creates Spinel - $MgAl_2O_4$ (ID-3-0901) and magnesium aluminium oxide—Mg–Al=O (ID—10–0238 Q). If in a binary mixture of 30% sulphate and 70% phosphate, it was only possible to identify by X-ray analysis anhydrous magnesium phosphate—Farringtonite (ID—33–0876).

The Set: $CaSO_4 \cdot 2H_2O$ (III) and $Mg_3(PO_4)_2 \cdot 8H_2O$ (I)

On the basis of accomplished studies by thermal differential analysis, IR and XR, it has been proved that under the influence of temperature (20–1000°C), substrates as well as binary mixtures undergo dehydration processes do not interact chemically (Figure 2).

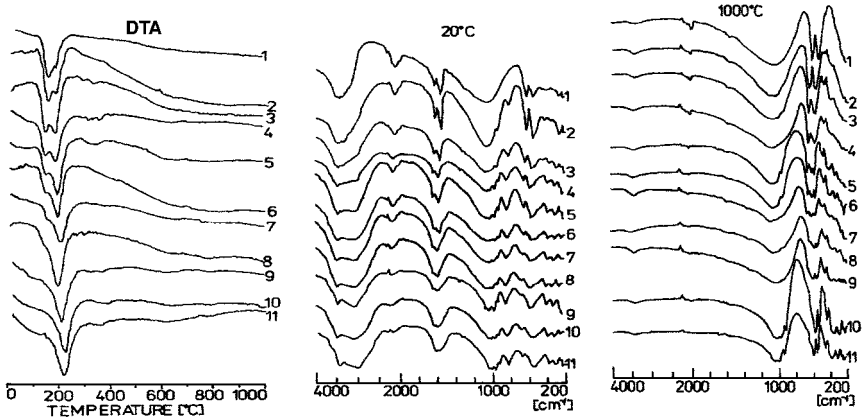

FIGURE 2 DTA (20–1000°C) and IR spectra (20°C and 1000°C) for $CaSO_4 \cdot 2H_2O$ (I) and $Mg_3(PO_4)_2 \cdot 8H_2O$ (II) and their binary mixtures (samples 2–10) containing:

Number of samples DTA and IR	1	2	3	4	5	6	7	8	9	10	11
$CaSO_4 \cdot 2H_2O$%	100	90	80	70	60	50	40	30	20	10	0
$Mg_3(PO_4) \cdot 8H_2O$%	0	10	20	30	40	50	60	70	80	90	100

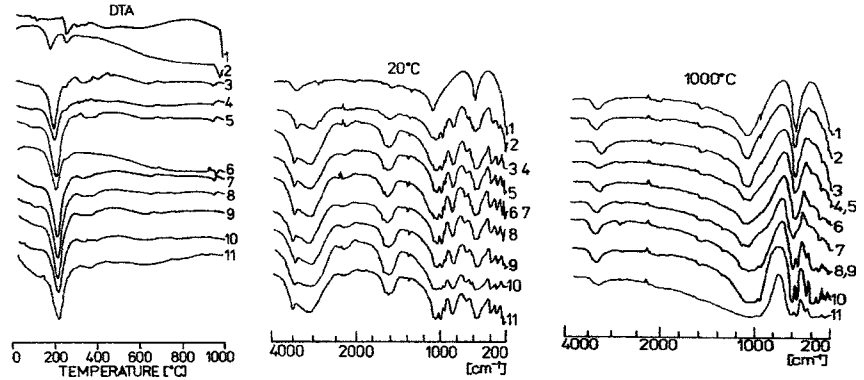

FIGURE 3 DTA (20–1000°C) and IR spectra (20°C and 1000°C) for Na_2SO_4 (I) and $Mg_3(PO_4)_2 \cdot 8H_2O$ (II) and their binary mixtures (samples 2–10) containing:

Number of samples DTA and IR	1	2	3	4	5	6	7	8	9	10	11
Na_2SO_4%	100	90	80	70	60	50	40	30	20	10	0
$Mg_3(PO_4)_2 \cdot 8H_2O$%	0	10	20	30	40	50	60	70	80	90	100

The Set: Na_2SO_4 (IV) and $Mg_3(PO_4)_2 \cdot 8H_2O$ (I)

On the basis of obtained results, it can be pointed out that:

- Thermal differential analysis allowed to register only endothermal conversions connected with dehydration of all samples, substrates as well as their binary mixtures (Figure 3).
- IR spectra performed for particular series of samples (non-heated and heated in 500°C or 1000°C) change their shape depending on conversions caused by thermal process and in IR spectra heated in 1000°C, we can observe changes in spectra shape resulting from creation of new compounds. This can be seen particularly well if we compare the spectrum of Na_2SO_4 substrate (1), the spectrum obtained for the mixture of 30% of Na_2SO_4–70% $Mg_3(PO_4)_2 \cdot 8H_2O$ (8), and the spectrum of magnesium phosphate substrate (11) (Figure 3).
- XR analysis proves that in 20°C, substrates have structure Na_2SO_4 Thenardite (ID: 37–1465) and $Mg_3(PO_4)_2 \cdot 8H_2O$ is identified as Bobierite (ID: 16–330). After heating in 1000°C, Na_2SO_4 still keeps the structure of Thenardite, but magnesium phosphate, upon dehydration, changes into Farringtonite (ID: 33–876). In binary samples, depending on their percentage ratio, the product content changes as it is presented in Table I.

TABLE I Products of Thermal Reaction in 1000°C (1 hour) of Substrates and Their Binary Mixtures with Different Percentage of Na_2SO_4 and $Mg_3(PO_4)_2 \cdot 8H_2O$

Percentage (%)		Chemical formula (mineral name)	Card
Na_2SO_4	$Mg_3(PO_4)_2 \cdot 8H_2O$		
100	0	Na_2SO_4	37-1465; 5-631; 36-397
90	10	Na_2SO_4 (Thenardite)	24-1132
70	30	Na_2SO_4	24-1132
		$NaMg_4(PO_4)_3$	34-671
		$Na_2S_5O_{16}$	21-1370
		$Mg_2P_2O_7$	32-626
50	50	$NaPO_4$	11-648
		Na_2SO_4 (Thenardite)	5-631
30	70	$Mg_3(PO_4)_2$ (Farringtonite)	33-876
		$Na_6Mg(SO_4)_4$ (Vanthoffite)	21-1138
		Na_2SO_4 (Thenardite)	36-397
10	90	$Mg_3(PO_4)_2$ (Farringtonite)	33-876
		$Mg_2P_2O_7$	32-626
0	100	$Mg_3(PO_4)_2$ (Farringtonite)	33-0876

On the basis of these results, we can state that not all binary solid solution systems in 500 and 1000°C have chemical reactions resulting in the creation of new chemical compounds, and even if they appear, this cannot be predicted in a way of theoretical assumptions.

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[1] M. H. Umbreit, *Phosphorus, Sulfur, and Silicon*, **147,** 411 (1999).