INFLUENCE OF TEMPERATURE (20°-1000°C) ON THE PHASE CHANGES IN $\text{Li}_2\text{CO}_3 - \text{MgHPO}_4 \cdot 3\text{H}_2\text{O}$ SYSTEM

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Abstract: We analyzed thermal phase changes of substrates (20°-1000°C) of binary mixtures $\text{Li}_2\text{CO}_3 - \text{MgHPO}_4 \cdot 3\text{H}_2\text{O}$ prepared with a percentage molar ratio of 90%-10%. The research was done using differential thermal analysis (TG, DTG, DTA), IR-spectrophotometry and WAXS. The above-mentioned substances changed the structure when heated for 1 h up to 500°C and 1000°C. $\text{MgHPO}_4 \cdot 3\text{H}_2\text{O}$ (Newberyite) changes its structure at 500°C into not completely formed $\text{Mg}_2\text{P}_2\text{O}_7$ and at 1000°C into $\text{Mg}_2\text{P}_2\text{O}_7$. Lithium carbonate (20°- 1000°C) does not change its structure. Binary mixtures change the structure depending on the molar ratio and at 1000°C they form Li_3PO_4 , LiMgPO_4 , MgO and $\text{Mg}_2\text{P}_2\text{O}_7$. At the molar ratio of 90% $\text{Li}_2\text{CO}_3 - 10\%$ $\text{MgHPO}_4 \cdot 3\text{H}_2\text{O}$ they form a sinter with the porcelain of the melting pot.

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INTRODUCTION

In previous papers, results of investigation into the influence of temperature on substrates and binary mixtures containing Li_3PO_4 and $\text{Mg}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$ were presented¹. Plenty of phase transformations and chemical reactions were observed, which encouraged us to carry out similar investigation using Li_2CO_3 instead of Li_3PO_4 . Apart from citrate, bromide and acetate, lithium carbonate has diverse applications in pharmacology.^{2, 3} In Tobon⁴ research was carried out on thermal properties of lithium salts. The results made it possible to determine the thermal stability of lithium salts. In atmospheres containing oxygen each of the lithium organic salts is transformed into lithium carbonate. Together with other carbonates (Na^+ , K^+), lithium carbonate was used for testing sintering and mechanical properties of β -tricalcium phosphates (Yoshida⁵). The authors of those papers also used Li_2CO_3 with silver ions to synthesize and test tricalcium phosphate as an antimicrobial agent⁶. The thermal reaction of Li_2CO_3 with $\text{MgHPO}_4 \cdot 3\text{H}_2\text{O}$ in binary mixtures with percentage molar ratios from 90% to 10% is the subject of the present paper. Substrates and binary mixtures were tested at a temperature of 20°, 500° and 1000°C. Thermal Differential Analysis, IR spectrophotometry and WAXS were methods of choice for carrying out the research.

METHODOLOGY

Chemicals-substrates: Li_2CO_3 (1), Aldrich cat.: 554-13-2; $\text{MgHPO}_4 \cdot 3\text{H}_2\text{O}$ (11), Aldrich cat.: 7782-75-4.

Preparation of the substrates and their binary mixtures: Substrates (1,11) were used as supplied (TABLE 1). Each compound was grounded, sieved, and binary mixtures were prepared with percentage molar ratios of 90% to 10% as described by Umbreit⁷.

TABLE 1 Percentage molar ratios of substrates in binary mixtures.

Sample number	1	2	3	4	5	6	7	8	9	10	11
Li_2CO_3	100	90	80	70	60	50	40	30	20	10	0
$\text{MgHPO}_4 \cdot 3\text{H}_2\text{O}$	0	10	20	30	40	50	60	70	80	90	100

Preparation of sinters at 500°C and 1000°C: Substrates and binary mixtures were heated in melting pots at 500°C and 1000°C for 1 h as described by Umbreit⁷.

Apparatus and analytical procedure: Differential Thermal Analysis was performed using Derivatograph Q-1500D as reported by Umbreit⁷. IR analysis was carried out using tablets of potassium bromide and Carl Zeiss Jena spectrophotometer. WAXS radiography analysis was performed as described by Umbreit⁷.

RESULTS AND DISCUSSION

Thermal analysis of Li_2CO_3 was carried out ranging from 20° to 1000°C (FIGURE 1.1). This compound is characterized by the lack of mass change of the sample within the range from 20° to 780°C (TG curve). There are no thermal transformations seen on the other curves (DTG and DTA). Above the temperature of 780°C phase transformation of lithium carbonate (DTA curve) with a maximum at 800°C and with a slight mass loss of the sample (TG curve) occurs. Thermal transformation of the other substrate, $\text{MgHPO}_4 \cdot 3\text{H}_2\text{O}$, was presented in Umbreit⁸ and on FIGURE 1.2. The analysis of DTG and DTA curves of the binary mixtures shows that the addition of even 10% of $\text{MgHPO}_4 \cdot 3\text{H}_2\text{O}$ to the binary system causes dehydration of the sample. In the second phase of the transformation a distinct transformation of Li_2CO_3 is

evident as it takes place in the substrate itself (FIGURE 1.1). It was stated that, within the concentration of $\text{MgHPO}_4 \cdot 3\text{H}_2\text{O}$ from 10% to 40% in the binary samples, the mass loss caused by the increase in temperature occurs due to the thermal transformation of Li_2CO_3 (TG curves) and proportional decrease of the endothermic maximum at 800°C on the DTA curve. After exceeding the ratio of 40% Li_2CO_3 and 60% $\text{MgHPO}_4 \cdot 3\text{H}_2\text{O}$ (FIGURE 1.3), increasingly smaller mass loss of binary mixtures at 800°C on the TG curve and a gradually disappearing maximum on the DTA curve are observed. It follows from the above mentioned research that both substrates are involved in the phase transformation. The transformation which takes place at 800°C may be interesting from the point of view of physical chemistry; it has been proved in further studies carried out in this research.

FIGURE 1 TG, DTG, DTA for Li_2CO_3 (1) and $\text{MgHPO}_4 \cdot 3\text{H}_2\text{O}$ (2) and their binary mixture: Li_2CO_3 (50%) - $\text{MgHPO}_4 \cdot 3\text{H}_2\text{O}$ (50%) (3).

To this end, a series of tests were performed in which the substrates and their binary mixtures were heated for 1 h at 500°C and 1000°C. Three series of tests were carried out in this way: non-heated; heated at 500°C and at 1000°C for 1 h. They were subject to IR (FIGURE 2) and WAXS (FIGURE 3) analysis. Spectrophotometric IR analyses of non-heated Li_2CO_3 (FIGURE 2.1.1) show the characteristic bands of carbonates: - a wide band within the range of 1900 to 1100 cm^{-1} with a maximum at 1440 cm^{-1} which corresponds to the vibrations of ν_3 (CO_3^{2-}),

- a narrow band within the range of 1100 to 1030 cm^{-1} with a maximum at 1081 cm^{-1} which corresponds to the ν_1 vibrations of the carbonate group.
- a band within the range of 1030 to 809 cm^{-1} with a prominent maximum at 868 cm^{-1} which corresponds to the ν_2 vibrations (CO_3^{2-}),
- a small maximum at 728 cm^{-1} (FIGURE 2.1.1) was also observed.

The spectrum of $\text{MgHPO}_4 \cdot 3\text{H}_2\text{O}$ (Figure 2.1.11) was discussed by Umbreit⁸. The analysis of spectra of binary mixtures reveals changes in absorbance frequencies in the range of 1900-810 cm^{-1} .

The addition of 10% of $\text{MgHPO}_4 \cdot 3\text{H}_2\text{O}$ (FIGURE 2.1.2) slightly changes the spectrum of Li_2CO_3 . Starting from 20% molar ratio of lithium carbonate a change occurs in absorbance frequencies in the 1900-1100 cm^{-1} range; in this case, however, instead of one maximum two maxima were observed: they were increasingly more visible with the increase of the amount of $\text{MgHPO}_4 \cdot 3\text{H}_2\text{O}$. Sample No. 4 has a small maximum at 1654 but sample No. 9 has an intense band with two maxima at 1640 cm^{-1} and 1700 cm^{-1} .

The second change occurred in the range of 1603-1280 cm^{-1} of absorbance frequencies. Sample No. 4 has two small maxima and sample No. 9 has two distinct ones at 1470 cm^{-1} and 1426 cm^{-1} . These changes disappear in the case of sample containing 10% Li_2CO_3 and 90% $\text{MgHPO}_4 \cdot 3\text{H}_2\text{O}$ (Fig 2.1.10). The other maxima, in the frequency range from 1250 to 400 cm^{-1} , are retained. They correspond to the bending – stretching vibrations due to the interactions between positive ions forming the individual compounds and their negative ions.

The analysis of the spectrum of Li_2CO_3 heated for 1 h at 500°C (FIGURE 2.2.1) shows the same absorption maxima as observed in the non-heated substrate. Slight differences occur only in slight changes in the maxima. For example: in the non-heated substrate, within the band of 1100-1080 cm^{-1} a maximum occurs at 1081 cm^{-1} and in the substrate heated for 1 h at 500°C it is observed at 1088 cm^{-1} . Next tests in that series of research of binary mixtures which have increasingly greater contents of $\text{MgHPO}_4 \cdot 3\text{H}_2\text{O}$ and heated for 1 h at 500°C reveal spectra characteristic of lithium carbonate within the wide band range of 1110 to 2250 cm^{-1} which has a maximum at 1530 cm^{-1} .

In sample No. 2 this maximum occurs at 1162 cm^{-1} and in sample No. 5 at 1250 cm^{-1} . With the increase of $\text{MgHPO}_4 \cdot 3\text{H}_2\text{O}$ content from sample No. 3, two small maxima emerge in this broad band: one at 1485 cm^{-1} and the other at 1426 cm^{-1} . These maxima are characteristic and they don't undergo any shift until the sample containing 80% $\text{MgHPO}_4 \cdot 3\text{H}_2\text{O}$ (FIGURE 2.2.9).

FIGURE 2 IR spectra of the samples non-heated (1), heated: 1 h at 500°C (2), 1 h at 1000°C (3) for Li_2CO_3 (sample 1), $\text{MgHPO}_4 \cdot 3\text{H}_2\text{O}$ (sample 11) and their binary mixtures (samples 2-10).

FIGURE 3 Diffractograms (WAXS) obtained for substrates Li_2CO_3 (a); $\text{MgHPO}_4 \cdot 3\text{H}_2\text{O}$ (b) and their binary mixtures (50% - 50%) (c), non-heated (1) and heated for 1h at 500°C (2) and for 1h at 1000°C (3).

TABLE 2 Identification of substrates, Li_2CO_3 and $\text{MgHPO}_4 \cdot 3\text{H}_2\text{O}$, and binary mixtures by powder X-ray diffractometry (WAXS).

Temp.	Sample number	Chemical formula	Compound name	Identity card number
20°C	1.1: 100% (1)	Li_2CO_3	Lithium carbonate	22-1141
	1.6: 50%(1) – 50%(2)	Li_2CO_3 $\text{MgHPO}_4 \cdot 3\text{H}_2\text{O}$	Lithium carbonate Newberyite	22-1141 35-780
	1.11: 100% (2)	$\text{MgHPO}_4 \cdot 3\text{H}_2\text{O}$	Newberyite	35-780 20-153 19-762
500°C	2.1: 100% (1)	Li_2CO_3	Lithium carbonate	22-1141
	2.6: 50%(1) – 50% (2)	Li_2CO_3 $\text{Mg}_2\text{P}_2\text{O}_7$	Lithium carbonate Magnesium pyrophosphate	22-1141 22-1152
	2.11: 100% (2)	$\text{Mg}_2\text{P}_2\text{O}_7$	Magnesium pyrophosphate	22-1152
1000°C	3.1: 100% (1)	Li_4SiO_4 Li_2CO_3	Lithium Silicate Lithium carbonate	20-637 22-1141
	3.2: 90% (1) – 10% (2)	$\text{Li}_4\text{SiO}_4^*$ $\text{Li}_{3,2}\text{Mg}_4\text{SiO}_4^*$	Lithium silicate Lithium Magnesium Silicate	20-637 24-637
	3.3: 80% (1) – 20% (2)	Li_3PO_4	Lithium phosphate	15-760
	3.4: 70% (1) – 30% (2)	Li_3PO_4 Li_2CO_3 MgO	Lithium phosphate Lithium carbonate Periclase, syn.	15-760 22-1141 4-829
	3.5: 50% (1) – 50% (2)	LiMgPO_4 MgO	Lithium magnesium phosphate Periclase, syn.	18-735 32-574 4-829
	3.8: 30% (1) – 70% (2)	LiMgPO_4	Lithium magnesium phosphate	32-574
	3.9: 20% (1) – 80% (2)	LiMgPO_4	Lithium magnesium phosphate	32-574
	3.10: 10% (1) – 90% (2)	LiMgPO_4 $\text{Mg}_2\text{P}_2\text{O}_7$	Lithium magnesium phosphate Magnesium pyrophosphate	32-574 8-38
	3.11: 100% (2)	$\text{Mg}_2\text{P}_2\text{O}_7$	Magnesium pyrophosphate	8-38 32-626

* Li_4SiO_4 and $\text{Li}_{3,2}\text{Mg}_4\text{SiO}_4$ were obtained in a sintering reaction of the melting pot with Li_2CO_3 in the presence of $\text{MgHPO}_4 \cdot 3\text{H}_2\text{O}$

The shift takes place in the absorption minimum which limits the carbonate spectrum toward longer waves, namely 1110 cm^{-1} , 1162 cm^{-1} , 1250 cm^{-1} and 1353 cm^{-1} for samples No. 1, No. 2, No. 5 and No. 9, respectively. In all the binary mixtures magnesium pyrophosphate tetrabasic forms. This is proven by maxima in two ranges, namely one band within the range of $1162\text{--}912\text{ cm}^{-1}$ with two maxima at 1088 cm^{-1} and 1030 cm^{-1} and the other band within the range of $912\text{--}816\text{ cm}^{-1}$ with a maximum at 860 cm^{-1} . In this spectral range an increase or decrease of the characteristic maxima occurs only in the same ranges until the sample labeled as No. 10 (10% Li_2CO_3 and 90% $\text{MgHPO}_4 \cdot 3\text{H}_2\text{O}$). The spectrum of sample No. 11 shows a structure of magnesium pyrophosphate tetrabasic not completely formed when $\text{MgHPO}_4 \cdot 3\text{H}_2\text{O}$ is heated for 1 h at 500°C .

The heating of the samples of substrates and their binary mixtures for 1 h at 1000°C caused significant changes in their structures, which was reflected in their IR spectra (FIGURE 2.3, spectra 1-11). The spectrum of Li_2CO_3 shows two large absorption maxima, one within the range of $1780\text{--}1280\text{ cm}^{-1}$ with a maximum at 1470 cm^{-1} . These maxima occur also in the next samples (No. 2-4). With the decrease of Li_2CO_3 from 90% to 70% and increase of $\text{MgHPO}_4 \cdot 3\text{H}_2\text{O}$, this band divides into two small maxima at 1500 cm^{-1} and 1449 cm^{-1} . With a larger content of $\text{MgHPO}_4 \cdot 3\text{H}_2\text{O}$ (from sample No. 5) the band fades. The second band in IR for Li_2CO_3 extends from 1280 cm^{-1} to 750 cm^{-1} and divides into three absorption maxima at 963 cm^{-1} , 860 cm^{-1} and 809 cm^{-1} . The maximum at 963 cm^{-1} extends and slightly shifts toward shorter waves. The maximum at 860 cm^{-1} is retained and does not change its position in the samples containing 90, 80 and 70% of Li_2CO_3 . However, the maximum at 809 cm^{-1} fades with the decrease of Li_2CO_3 and does not exist in sample No 5. From sample No. 3 and 4 which contain 80% and 70% Li_2CO_3 one large band is observed within the range of $1500\text{--}810\text{ cm}^{-1}$ with a maximum at 1030 cm^{-1} . This maximum is very characteristic of PO_4^{3-} . The spectra of samples 5-8 containing 60%-30% Li_2CO_3 are very similar and characteristic of LiMgPO_4 . With the increase of $\text{MgHPO}_4 \cdot 3\text{H}_2\text{O}$ content, the spectra become increasingly more characteristic of the pyrophosphate spectrum. The structure of pyrophosphate is observed in sample No. 11.

To substantiate the structure of individual substrates prepared from the binary mixtures and also compounds formed during the heating of the samples at 500°C and 1000°C roentgenographic analyses were carried out using a powder WAXS diffractometer. The results obtained were characterized with bibliographical identification cards contained in the library of the XRAYAN system. The results are reported in FIGURE 3 and TABLE 2. The diagrams in FIGURE 3 "a" presents X-ray patterns for non-heated Li_2CO_3 (1a), heated for one hour at 500°C (2a) and heated for one hour at 1000°C (3a). The examination

of non-heated sample evidenced that pure Li_2CO_3 is present. The vertical lines came from the base of X-RAYAN programme confirm the presence of this compound (ID: 22-1141). The annealing in 500°C doesn't change the structure of the investigated samples. The X-ray pattern for the samples annealed for one hour at 1000°C demonstrated changes. Apart Li_2CO_3 there is present in majority Li_4SiO_4 (ID: 20-637). In similar way the identification analysis of another systems was performed (FIGURE 3 b,c). The results of all observed structural changes are presented in the TABLE 2.

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