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SYNTHESIS AND THERMAL TRANSFORMATIONS OF Ca, Mg-CARBONATEAPATITE

Abstract. Ca, Mg-carbonateapatite synthesized by precipitation method was characterized by low crystallinity and the existence of the amorphous phase. On heating crystallization of apatite occurred and it became possible to determine the lattice parameters. In spite of the different molar ratio Mg:Ca in the initial mixtures, this ratio was 0.5:9.5 in the products. The structure of the products is labile and under thermal influence it is subject to great changes in all anion groups identified by IR-spectroscopy.

The apatite series contains numerous different minerals. The mineral base of phosphate rock and bones of vertebrates also belongs here. Because of the expanding use of apatites in engineering, science, and medicine, research into the synthesis and properties of apatites has been gaining momentum recently.

In natural apatites isomorphism occurs both in the cation and anion parts of the crystal lattice. Phosphorites represent fluoro(hydroxy)carbonateapatite, in which substitution of magnesium for calcium often takes place to a small extent. However, the presence of magnesium in phosphate rock complicates its processing into fertilizers and other products. Data on the synthesis of apatites with substitutions of different cations, including magnesium, for calcium are available [1-5]. Cation substitutions in apatites, even in a small amount, can influence considerably their physical and chemical properties. We have made an attempt to synthesize Ca, Mg-fluoro(hydroxy)carbonateapatite and to study some of its properties.

Methods and Experimental Data

The synthesis was carried out by the method of precipitation. 200 ml of a solution, containing 110 g $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$, 16 g NaOH, and 5.8 g KF was added to the mixture of 10 g CaCO_3 and 0.5 g (sample 1) or 2.5 g (sample 2) $\text{MgCO}_3 \cdot \text{Mg}(\text{OH})_2$. After dilution with water, the volume obtained was 1 l. The mixture was held at 18—20°C for one month, with shaking it every day for 10 min. Then the precipitate was filtered and, to dissolve the excess of the carbonates, it was treated three times within 4 hours with 0.5 M solution of triammonium citrate at 65°C, dividing the phases in-between [6, 7]. The solid product was filtered, washed, and dried at 110°C. All the reagents were of analytical grade.

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The samples obtained were studied by methods of chemical and thermal analyses, X-ray diffraction, and infrared spectroscopy. The X-ray analysis was carried out by means of diffractometer DRON-3 using tubes with a copper anode. To increase the precision of the X-ray analysis, monochromatic radiation, automatic data collection, and machining were used. For IR-analysis the powdered samples were mixed with KBr in a mass ratio 1:300 (strong bands) or 10:140 (weak bands) and pelletized. The pellets were analysed on spectrophotometer Specord-75 IR. The thermal analysis was carried out on derivatograph MOM in a stream of air.

The products synthesized were characterized by low crystallinity, the existence of the amorphous phase, and molecular water. Their chemical composition is given in the Table. The curves of the thermal analysis of sample 2 are presented in Fig. 1, the IR spectra of the initial and heated samples in Figs. 2—6. The results of analyses of sample 1 were close to those of sample 2.

Chemical composition of samples, % mass

Sample	CaO	MgO	P ₂ O ₅	CO ₂	F	Loss on heating to 600 °C
1	48.91	2.05	35.88	2.19	4.05	8.57
2	47.24	1.77	35.21	1.64	3.99	11.11

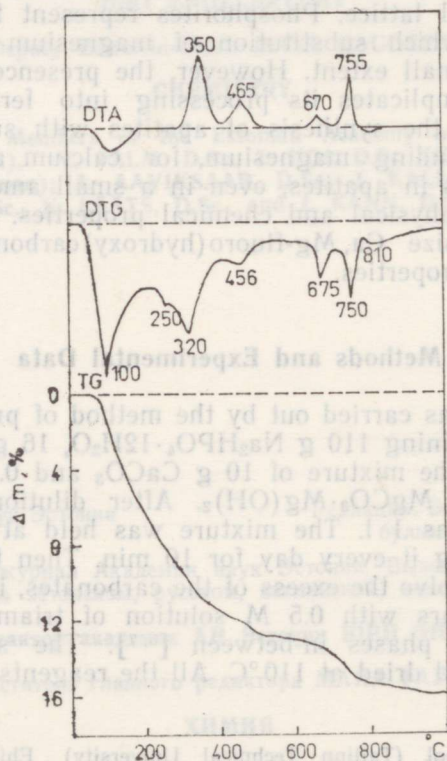


Fig. 1. Thermogram of Ca, Mg-carbonateapatite in an air stream.

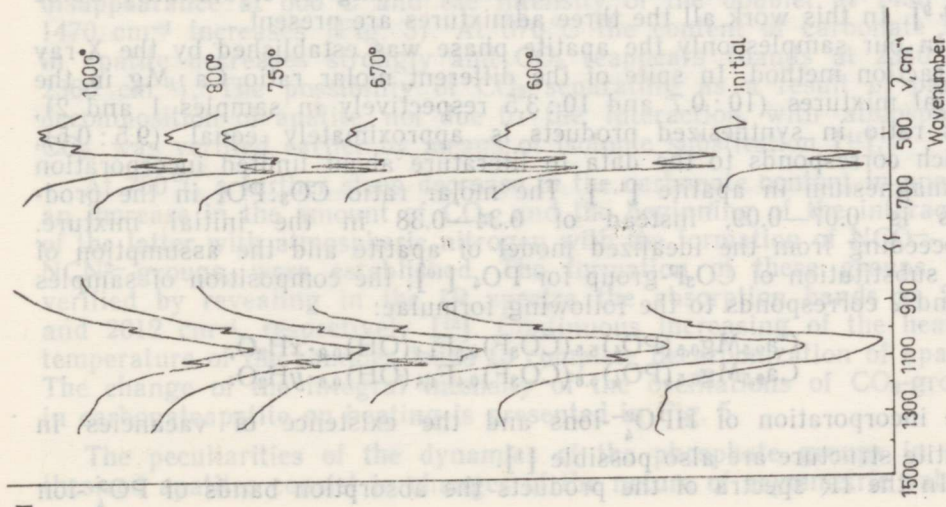


Fig. 2. IR spectra of Ca, Mg-carbonate-apatite in the PO_4^{3-} oscillations domain.

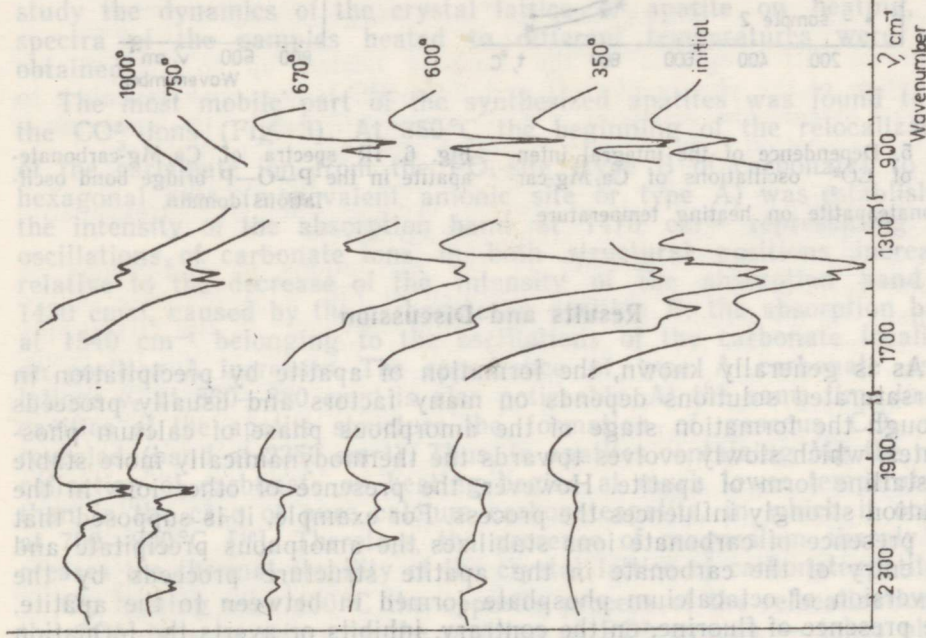


Fig. 3. IR spectra of Ca, Mg-carbonateapatite in the CO_3^{2-} oscillations domain.

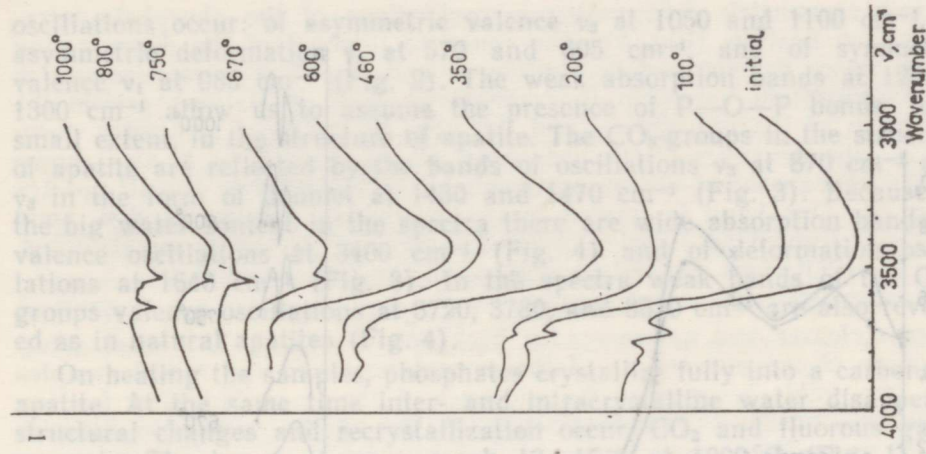


Fig. 4. IR spectra of Ca, Mg-carbonate-apatite in the oscillations domain of the group containing OH^- .

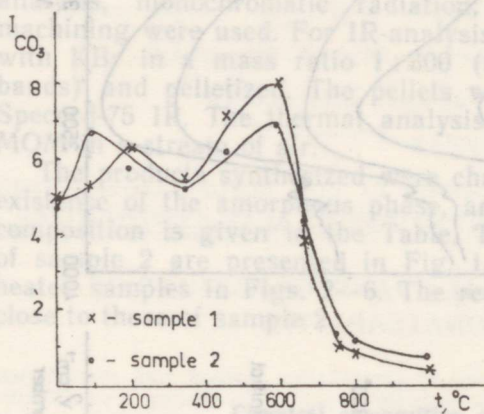


Fig. 5. Dependence of the integral intensity of CO_3^- oscillations of Ca, Mg-carbonateapatite on heating temperature.

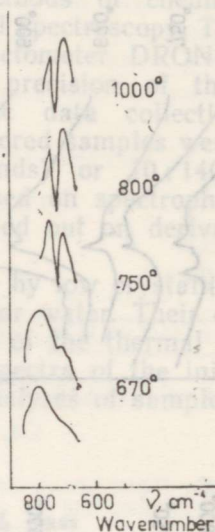
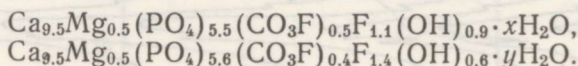


Fig. 6. IR spectra of Ca, Mg-carbonateapatite in the P—O—P bridge bond oscillations domain.

Results and Discussion

As is generally known, the formation of apatite by precipitation in oversaturated solutions depends on many factors and usually proceeds through the formation stage of the amorphous phase of calcium phosphates, which slowly evolves towards the thermodynamically more stable crystalline form of apatite. However, the presence of other ions in the solution strongly influences the process. For example, it is supposed that the presence of carbonate ions stabilizes the amorphous precipitate and the entry of the carbonate in the apatite structure proceeds by the conversion of octacalcium phosphate formed in between to the apatite. The presence of fluorine, on the contrary, inhibits or averts the formation of octacalcium phosphate. The introduction of magnesium into the mixture inhibits the formation of apatite, making its crystallinity worse [2, 8, 9]. In this work all the three admixtures are present.

In our samples only the apatite phase was established by the X-ray diffraction method. In spite of the different molar ratio Ca : Mg in the initial mixtures (10 : 0.7 and 10 : 3.5 respectively in samples 1 and 2), this ratio in synthesized products is approximately equal (9.5 : 0.5), which corresponds to the data in literature about limited incorporation of magnesium in apatite [1, 2]. The molar ratio $\text{CO}_3:\text{PO}_4$ in the products is 0.07—0.09, instead of 0.34—0.38 in the initial mixture. Proceeding from the idealized model of apatite and the assumption of the substitution of CO_3F -group for PO_4 [10], the composition of samples 1 and 2 corresponds to the following formulae:



The incorporation of HPO_4^{2-} -ions and the existence of vacancies in apatite structure are also possible [1].

In the IR spectra of the products the absorption bands of PO_4^{3-} -ion

oscillations occur: of asymmetric valence ν_3 at 1050 and 1100 cm^{-1} , of asymmetric deformation ν_4 at 570 and 605 cm^{-1} , and of symmetric valence ν_1 at 980 cm^{-1} (Fig. 2). The weak absorption bands at 1200—1300 cm^{-1} allow us to assume the presence of P—O—P bonds, to a small extent, in the structure of apatite. The CO_3 -groups in the structure of apatite are reflected by the bands of oscillations ν_2 at 870 cm^{-1} and ν_3 in the form of doublet at 1430 and 1470 cm^{-1} (Fig. 3). Because of the big water content in the spectra there are wide absorption bands of valence oscillations at 3400 cm^{-1} (Fig. 4) and of deformation oscillations at 1640 cm^{-1} (Fig. 3). In the spectra weak bands of the OH-groups valence oscillations at 3720, 3780, and 3820 cm^{-1} are also revealed as in natural apatites (Fig. 4).

On heating the samples, phosphates crystallize fully into a carbonate-apatite. At the same time inter- and intracrystalline water disappears, structural changes and recrystallization occur, CO_2 and fluorine gases separate. The losses of mass reach 13—15% at 1000°C (Fig. 1). To study the dynamics of the crystal lattice of apatite on heating, IR spectra of the samples heated to different temperatures were also obtained.

The most mobile part of the synthesized apatites was found to be the CO_3^{2-} -ions (Fig. 3). At 350°C the beginning of the relocalization of the carbonate ion from the PO_4 -site (type B of carbonate) to the hexagonal axes (monovalent anionic site or type A) was established; the intensity of the absorption band at 1470 cm^{-1} representing the oscillations of carbonate ions in both structural positions increases relative to the decrease of the intensity of the absorption band at 1430 cm^{-1} , caused by the carbonate on position B; the absorption band at 1540 cm^{-1} belonging to the oscillations of the carbonate localized on position A increases. The appearance of type A carbonate oscillations ν_2 at 860—880 cm^{-1} is also noticeable. At the same time in the cavities of the apatite structure the formation of gaseous CO_2 was revealed (band at 2350 cm^{-1}). Thus, in apatites containing Mg the relocalization of carbonate on heating begins at much lower temperatures than in the case of pure calcium carbonate-apatite, in which it occurs at 700—800°C [10]. Therefore, the presence of magnesium sharply decreases the thermal stability of the crystal lattice of carbonate-apatite.

On heating over 400°C the opposite process of the relocalization of the CO_3^{2-} -ions — return to the position of PO_4^{3-} -groups — takes place: the intensity of the oscillation at 1540 cm^{-1} decreases up to its complete disappearance at 600°C and the intensity of the doublet at 1430 and 1470 cm^{-1} increases (Fig. 3). At 670°C the content of carbonate ions in apatite decreases strongly and CO_2 reappears (bands at 2340 and 2360 cm^{-1}). The possibility of CO_2 separating as a result of partial decomposition of apatite, not due to the interaction with atmospheric CO_2 , was verified earlier by means of isotopic substitution [11].

At 750°C a further steep decrease in the carbonate content in apatite, an increase in the amount of CO_2 , and the beginning of the interaction of the latter with atmospheric nitrogen with the formation of NCO- and NCN^{2-} -groups, were established. The formation of these groups was verified by revealing in the IR spectra the absorption bands at 2200 and 2012 cm^{-1} , respectively [12]. Continuous increasing of the heating temperature of the samples leads to complete decarbonization of apatite. The change of the integral intensity of the oscillations of CO_3 -groups in carbonate-apatite on heating is presented in Fig. 5.

The peculiarities of the dynamics of the phosphate groups in synthesized apatites consist in changes of the nature of asymmetric valence

ν_3 and asymmetric deformation ν_4 oscillations of the phosphate tetrahedron on heating (Fig. 2). The complete removal of the degeneration of the thrice degenerated oscillations ν_3 and ν_4 at 750°C (appearance of three absorption bands in the domain of each oscillation) proves the distortion of the PO_4 -groups and the drop of the local symmetry down to C_{2v} . The dynamics of the phosphate groups on heating is also shown by the appearance of the absorption band at 740 cm^{-1} in the IR spectra (Fig. 6). This band is related to the oscillation of the bridge bond $\text{P}-\text{O}-\text{P}$ formed as a result of condensation of phosphate tetrahedrons, also of HPO_4^{2-} -ions, possibly contained in the initial samples.

In diffractograms crystallization of apatite is revealed: the lines become clearer and narrower, the background weaker. The exact determination of the parameters of the crystal lattice in the initial samples was impossible because of the wideness of the lines, but after heating it became possible. The parameters of the apatite lattice in samples heated up to 750°C are:

$$a = 9.379 \pm 0.005 \text{ \AA}; \quad c = 6.887 \pm 0.003 \text{ \AA}.$$

In the diffractograms of the samples heated up to 1000°C the formation of the phases of CaO and $\beta\text{-Ca}_3(\text{PO}_4)_2$ was also revealed, to a small extent. The existence of CaO was confirmed by the appearance of the absorption band at 3630 cm^{-1} of the valence oscillations of the OH -groups in $\text{Ca}(\text{OH})_2$, formed as a result of the hydration of CaO . The formation of $\text{Ca}_3(\text{PO}_4)_2$ on thermal decomposition of hydroxyapatite containing Mg had been also established earlier [4].

The changes in the domain of the oscillations of OH -groups in apatite spectra on heating are presented in Fig. 4. A decrease in the intensity of the bands at 3720, 3790, and 3820 cm^{-1} of the OH -groups valence oscillations occurs already at 100°C. With increasing the temperature the intensity of these bands continues to decrease and finally they disappear. At 670°C bands at 3540 and 670 cm^{-1} related to the valence and librational oscillations of OH -groups forming hydrogen bonds $\text{OH} \dots \text{F}$ were revealed. In apatites which do not contain magnesium the formation of $\text{OH} \dots \text{F}$ bonds usually proceeds at higher temperatures. With rising temperature the intensity of the band at 3540 cm^{-1} increases testifying to an increase in the spread of hydrogen bonds and to the regulation of OH -groups on the hexagonal axis of the apatite structure. On heating at 1000°C an absorption band in the form of a shoulder, belonging to the oscillations of the hydrogen bond $\text{OH} \dots \text{O}$, was revealed at 3570 cm^{-1} .

Thus, the structure of carbonateapatite containing Mg is relatively labile and under thermal influence it is subject to changes in all its anion groups — phosphate, carbonate, and hydroxy. The presence of magnesium in carbonateapatite leads to a decrease in the thermal stability of the structure, especially in the part of carbonate ions.

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Ca, Mg-KARBONAATAPATIIDI SÜNTEES JA TERMILISED MUUTUSED

Sadestusmeetodil saadi madala kristalsusega amorfset faasi sisaldav Ca, Mg-karbonaatapatiit. Kuumutamisel toimus apatiidi kristallisatsioon, mis võimaldas määrata võre parameetrid. Sõltumata Mg : Ca moolsuhtest lähtesugus oli see saadustes 0,5 : 9,5. Produktide struktuur oli labiilne ja nende anioonne osa allus kuumutamisel olulistele muutustele, mis identifitseeriti IP-spektroskoopia meetodil.

Хейнрих ВИЛЬБОК, Рэна **КНУБОВЕЦ**, Михкель **ВЕЙДЕРМА**

СИНТЕЗ И ТЕРМИЧЕСКИЕ ПРЕВРАЩЕНИЯ Ca, Mg-КАРБОНАТАПАТИТА

Методом осаждения синтезирован низкокristаллический Ca, Mg-карбонатапатит, содержащий аморфную фазу. После нагревания апатита и его кристаллизации определены параметры решетки. В продуктах молярное соотношение Mg : Ca составляло 0,5:9,5 независимо от его соотношения в исходной смеси. Структура продуктов лабильна, в частности их анионная часть претерпевает под термическим воздействием существенные изменения, что идентифицировано методом ИК-спектроскопии.