

# **APPLICATION OF NUCLEAR METHODS**

## **THE EFFECT OF GAMMA RADIATION ON STRUCTURE OF STRUVITE-K**

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The effect of gamma radiation upon functional characteristics of nanostructural struvite-K is analyzed. Spectra of absorption struvite-K have been measured in infra-red area. Results of a microstructure of samples after of a gamma irradiation to a dose  $1.35 \cdot 10^5$  Gy are described. It has shown that after gamma irradiation the phase composition of the sample essentially does not change, and there is a crystallization of amorphous phosphate and the structural ordering of struvite-K and magnesite occurs.

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### **INTRODUCTION**

Struvite-K [ $\text{KMgPO}_4 \cdot 6\text{H}_2\text{O}$ ], is the natural potassium equivalent to struvite [ $\text{NH}_4\text{MgPO}_4 \cdot 6\text{H}_2\text{O}$ ], in which monovalent cation  $\text{K}^+$  replaces the  $\text{NH}_4^+$  ammonium cations [1]. These two compounds are isostructural, with the existence of a complete isomorphous series from 100%  $\text{K}^+$  to 100%  $\text{NH}_4^+$  struvite. This ion replacement is possible, as the ionic radii of  $\text{K}^+$  and  $\text{NH}_4^+$  are almost identical (1.52 vs 1.51 Å) [2].

Production of struvite-K is based on a chemical reaction between phosphate anions and metal cations to form a strong, dense, durable, low porosity matrix that immobilizes hazardous and radioactive contaminants as insoluble phosphates and microencapsulates insoluble radioactive components and other constituents. Struvite-K [ $\text{KMgPO}_4 \cdot 6\text{H}_2\text{O}$ ] is formed through an acid-base reaction between calcined magnesium oxide ( $\text{MgO}$ ; a base) and potassium hydrogen phosphate ( $\text{KH}_2\text{PO}_4$ ; an acid) in aqueous solution. The reaction product sets at room temperature to form a highly crystalline material.

New opportunities in the formation of such structures are opened by radiation methods of influence, which demonstrate their effectiveness in the synthesis and modification of the properties of nanostructured compounds. High-energy radiation of nanocrystalline objects of various nature can cause changes in such structures that have not been observed in other types of effect [3]. The processes that accompany the passage of radiation through such structures are multiform and unequal inherently of complexity.

The processes that accompany the passage of radiation through such structures are manifold and unequal in complexity. Several variants of the behavior of defects in nano objects are analyzed: the presence of a significant number of boundary surfaces; the annihilation of the nanostructure and its transformation into an amorphous state; recrystallization, etc.

According to [4, 5], the dissipation of the energy of fast particles in multi-component compositions is mainly realized on the sublattice of light atoms, such as hydrogen and oxygen, by ionization of atoms due to the emission of Auger electrons. Moreover, the higher mobility of these atoms in the lattice of the crystal is realized. In the process of relaxation, the positive ion charge interacts with

the macroscopic field of the crystal. In covalent crystals, the process due to the Auger electron relaxation, explains the rupture of bonds between atoms accompanied by atomic displacements. In this case, the establishment of equilibrium will be different in directions and intensity. The perturbed region usually extends to 1 nm with a binding energy of several electronvolt and a macroscopic electric field of about  $10^6$  V/cm. One of the consequences of such a process is the enrichment of the surface of metal atoms in halide crystals. Another consequence of this mechanism of action is the improvement of the crystallinity of the substance [7]. It should also be noted the formation of highly reactive oxygen species, which in turn, as a result of Coulomb interactions, increase the degree of radiation damage in  $\text{KMgPO}_4 \cdot 6\text{H}_2\text{O}$  [6]. The presence of highly reactive oxygen leads to the dissolution of the amorphous phase and, accordingly, improves the crystallinity of  $\text{KMgPO}_4 \cdot 6\text{H}_2\text{O}$  [7].

In recent years, various versions of the radiation effect on the functional characteristics of nanostructural compounds have been intensively studied. In our previous article [8], it was also shown that the diffusion rate depends not only on the energy state and not only from the chemical nature of cations and anions which are the nearest neighbors of a molecule of water. There is another parameter, for example, physical, or enterprise which is connected with the disorder in a locating of atoms. Character of atomic packaging of K, Mg and  $\text{PO}_4$  in magnesium potassium phosphate hexahydrate possesses specificity which is bound to the extreme dimensions of these ions. From the laws of dense atomic packing, it is known that atoms with large various sizes can be packaged in an unambiguous way with great difficulties. Ambiguity in the arrangement of atoms creates internodes that can participate in the formation of migration paths penetrating the whole crystal in a solid. In other words, we can say that enhanced diffusion in crystalline hydrates can be determined by not only by a suitable energy but also with a suitable space. Such space is in  $\text{KMgPO}_4 \cdot 6\text{H}_2\text{O}$  [8]. Magnesium potassium phosphate hexahydrate has a low specific gravity of  $1.7 \text{ g/cm}^3$ .

The purpose of the present article is to study the effect of bremsstrahlung on the structure of  $\text{KMgPO}_4 \cdot 6\text{H}_2\text{O}$ .

## RESULTS AND DISCUSSION

The sample of struvite-K [ $\text{KMgPO}_4 \cdot 6\text{H}_2\text{O}$ ] (by size 1...10  $\mu\text{m}$ ) was irradiated by bremsstrahlung with a maximum energy of 13.5 MeV.

After activation of  $\text{KMgPO}_4 \cdot 6\text{H}_2\text{O}$  the  $\gamma$ -spectrum of the sample has been measured by Ge(Li)-detector (volume 50  $\text{cm}^3$ , energy resolution 3.2 keV in the area of 1332 keV). Isomorphous impurities of arsenic, strontium, rare-earth elements and also impurities of a titan, iron, uranium are contained in phosphates. Therefore, in the radiation spectra, we can see these elements (Fig. 1). Sodium is an isomorphous impurity of potassium. Therefore sodium detected in spectra of struvite-K samples also.

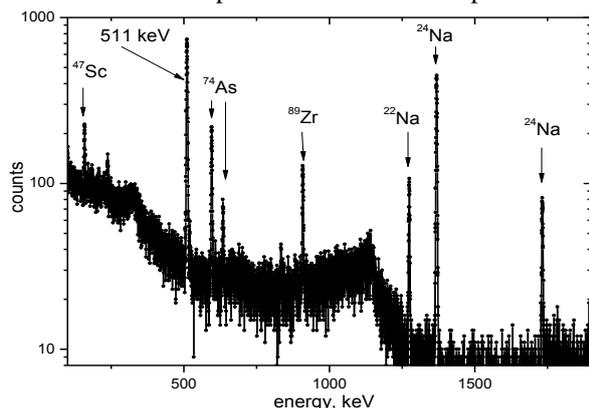


Fig. 1. Energy spectrum of the sample of struvite-K after an irradiation on the electronic accelerator

The phase analysis shows that initial and irradiated samples of struvite-K contain the phase of  $\text{KMgPO}_4 \cdot 6\text{H}_2\text{O}$ . Thus the initial sample has the widened lines that are probably connected with a considerable quantity of an isotropic amorphous phase [9, 10]. In the irradiated sample, the intensity increase of diffraction lines and reduction of their semi-width in connection with an ordering of the crystal structure and quantity reduction of the cryptocrystalline constituent is observed.

For measuring of the absorption spectra in the infrared range, the IR spectrophotometer IKS-29 (LOMO), acting in the NSC "KIPT" of the NAS of Ukraine, was used. The spectra were recorded in the spectral range 4000...400  $\text{cm}^{-1}$  (mean infrared region).

Powdered samples were examined after grinding them in agate mortars to particle size ~1...10  $\mu\text{m}$ . Samples were prepared in the form of transparently compressed tablets from the mixture KBr-matrix, and the test sample (in an amount of 1%, a sample of 100 mg). Tablets had a squared shape and dimensions of 25x5 mm. The pressing pressure was 9200  $\text{kg}/\text{cm}^2$ . A tablet of pure potassium bromide, pre-dried at 180°C for 10 hours, was placed in the instrument comparison channel to eliminate the absorption bands of the matrix. Powders were pounded and placed in a special closed box. Pressing was carried out immediately before recording the spectra. The grading was carried out from the spectrum of polystyrene with known frequencies of absorption maxima. The error was about  $10^{-5} \text{ cm}^{-1}$ .

The microscopic sample was a cryptocrystalline aggregate mass, which contained numerous inclusions of several phases (crystalline and amorphous) (Fig. 2). The anisotropic grains of the carbonate phase of magnesite

( $\text{MgCO}_3$ ), which had a yellowish brown color and possessed strong pleochroism, can be identified. The size of grains of magnesite from ~5 to 30  $\mu\text{m}$ . The content of magnesite carbonate phase was ~20 vol.%. Very small transparent grains of the crystalline phase (possibly magnesium oxide MgO) were also visible. The main aggregate mass mainly is composed of  $\text{KMgPO}_4 \cdot 6\text{H}_2\text{O}$  and partially from the products of incomplete synthesis, which are amorphous or cryptocrystalline phosphate compounds.

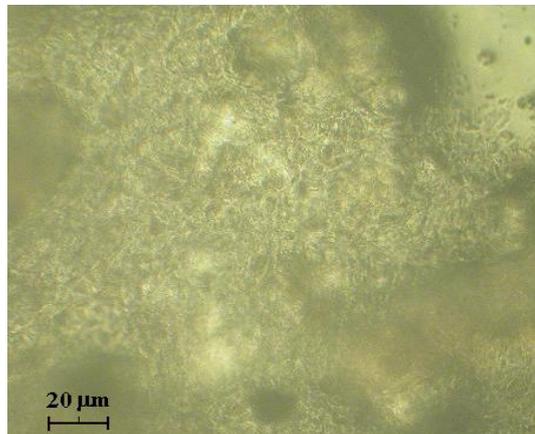


Fig. 2. A microphotograph of the immersion preparation of the initial K-Mg phosphate sample in transmitted light, without an analyzer

The infrared spectrum of the initial sample contains a large number of intense bands with narrow maxima and a number of fine peaks (Figs. 3 and 4, curve 1). Identification of the bands is given in Table. The most intense main bands in the spectrum refer to  $\text{KMgPO}_4 \cdot 6\text{H}_2\text{O}$ : 570, 630, 765, 1050, 2350, 2910 and 3210  $\text{cm}^{-1}$  [11]. The bands 475, 880, the doublet from the strong, sharp bands 1430 and 1470, 2350 and 3420 are associated with the presence of the carbonate phase-magnesite ( $\text{MgCO}_3$ ) [12]. The small peaks of 405 and 425  $\text{cm}^{-1}$  are most likely related to the MgO impurity.

A group of bands – 950, 980 and 1095  $\text{cm}^{-1}$ , which are associated with the vibrations of the  $\text{P}(\text{OH})_2$  and  $\text{PO}_4$  groups, are located around the 1050  $\text{cm}^{-1}$  main band that is attached to K-Mg phosphate ( $\text{KMgPO}_4 \cdot 6\text{H}_2\text{O}$ ) in the structure of amorphous or cryptocrystalline phosphate phases, which may be intermediate products of incomplete synthesis.

An additional confirmation of the fact that the sample consists of several phases is that the wide strong band, which is associated with stretching vibrations of H-O-H in the region of 3500...2800  $\text{cm}^{-1}$ , consists of four peaks (2790, 2910, 3210 and 3420  $\text{cm}^{-1}$ ). Each of these peaks belongs to a certain type of water, which is contained in various phases.

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KMgPO <sub>4</sub> ·6H <sub>2</sub> O	KMgPO <sub>4</sub> ·6H <sub>2</sub> O irradiated (D=1.35·10 <sup>5</sup> Gy)	Assignment of band [9-11]
405	405↑	MgO
425	425↑	
475 c	470→	MgCO <sub>3</sub>
560	560↓	
570*	570↑	Bending vibrations M-O (M-metal) in phosphate structure
630*	630↑	
765*	760↑→	
880 c	870↑→	MgCO <sub>3</sub> , out-of-plane bending vibrations of ion CO <sub>3</sub> <sup>2-</sup>
950	950	
980	980↓	Bending vibrations P (OH) <sub>2</sub> , stretching non-central vibrations PO <sub>4</sub>
1050*	1050↓	
1095	1095↑	
1430 c	1430↑	
1470 c	1470↑	Vibrations C-O in magnesite structure MgCO <sub>3</sub>
1645	1650←↑	
2350*	2340↓→	Stretching vibrations H-O-H in structure KMgPO <sub>4</sub> ·6H <sub>2</sub> O and semiamorphous phosphate phase
2790	2790↓	
2910	2910↓	Deformation modes H-O-H in semiamorphous phosphate phase
3210*	3210↑	
3420 c	3420	Stretching vibrations H-O-H in magnesite structure MgCO <sub>3</sub>

\* – KMgPO<sub>4</sub>·6H<sub>2</sub>O;

c – Carbonate phase (MgCO<sub>3</sub>).

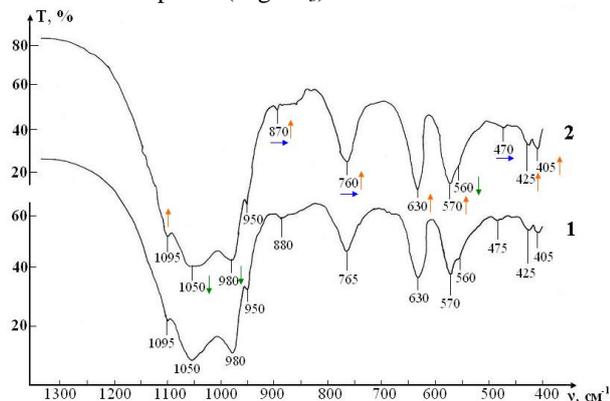


Fig. 3. IR absorption spectra of K-Mg phosphate in the frequency range 400...1300 cm<sup>-1</sup>.

Curve 1 – initial sample; curve 2 – sample after irradiation to a dose of 1.35·10<sup>5</sup> Gy

The sample microstructure changes significantly after irradiation to a dose of 1.35·10<sup>5</sup> Gy. The sample contains a smaller amount of isotropic amorphous phase

and is more crystalline. The boundaries between the grains of individual phases become more distinct (Fig. 5).

The form of the IR spectrum of the irradiated sample reveals that irradiation does not lead to a change in the basic phase composition of the substance since the quantity and the positions of all bands in the spectrum remains invariable (see Figs. 3 and 4, curve 2). Changes in the spectrum are related only to the intensity of the bands, which directly depends on the degree of crystallinity and orderliness of the structure of the substance, as well depends on the quantity of individual phases of which the sample consists.

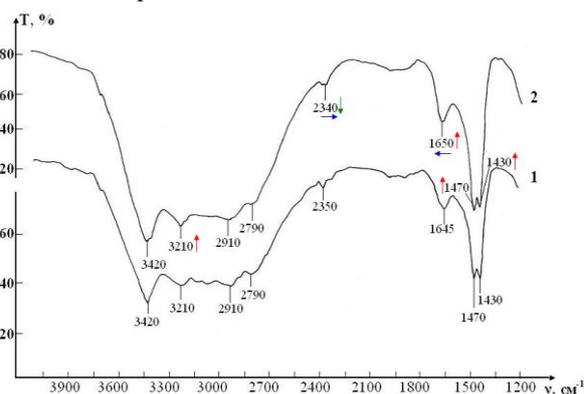


Fig. 4. IR absorption spectra of K-Mg phosphate in the frequency range 1200...4000 cm<sup>-1</sup>. Curve 1 – initial sample; curve 2 – sample after irradiation to a dose of 1.35·10<sup>5</sup> Gy

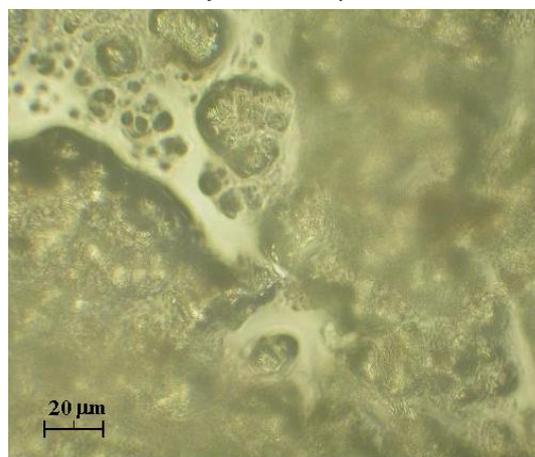


Fig. 5. A microphotograph of the immersion preparation of the irradiated sample KMgPO<sub>4</sub>·6H<sub>2</sub>O (D=1.35·10<sup>5</sup> Gy) in transmitted light. Without analyzer

We can note the following changes in the shape and intensity of the bands:

1. The intensity of all bands associated with the bending oscillations of M-O (M-metal) in the phosphate structure: 570, 630 and 760 cm<sup>-1</sup> is increasing. Strengthening of these bonds is caused by a structural ordering of KMgPO<sub>4</sub>·6H<sub>2</sub>O.

2. The shape of the main band in the region 1100...950 cm<sup>-1</sup> varies: the maxima are smoothed out and the intensity of the bands of amorphous phosphate components (950 and 980 cm<sup>-1</sup>) is decreased. The general form of the given band becomes closer to that kind which is characteristic of crystal phase KMgPO<sub>4</sub>·6H<sub>2</sub>O [13].

3. The intensity of the bands which were associated with the vibrations of C-O in the structure of magnesite ( $\text{MgCO}_3$ ) (870, 1430, 1470 and  $1650 \text{ cm}^{-1}$ ) markedly increases. We can conclude that the strengthening of bonds in this structure occurs.

4. The intensity of the doublet  $405$  and  $425 \text{ cm}^{-1}$  ( $\text{MgO}$ ) increases. Perhaps, irradiation leads to an increase in the size of  $\text{MgO}$  crystals or their quantity.

5. The shift of a whole series of bands in a spectrum, which concern different phases, into the low – frequency area of a spectrum ( $475 \rightarrow 470$ ,  $765 \rightarrow 760$ ,  $880 \rightarrow 870$ ,  $2350 \rightarrow 2340$ ) is observed. This also confirms the fact that the structure of all the phases which belong to composition of the sample becomes more perfect. Such a shift indicates a strengthening of the bonds in the crystal lattice [14].

6. It should be noted that the shape of the wide band of H-O-H vibrations in the  $\sim 3500 \dots 2800 \text{ cm}^{-1}$  region and the quantity of peaks remain practically unchanged. Obviously, the radiation effect did not have a significant effect on the structured or adsorbed water, which is contained in the various phases that make up this sample.

### CONCLUSIONS

1. The initial sample of K-Mg phosphate consists of four main phases: Struvite-K ( $\text{KMgPO}_4 \cdot 6\text{H}_2\text{O}$ ), semi-amorphous phosphate phase, magnesite and single grains of magnesium oxide ( $\text{MgO}$ ) (no more than 5 vol. %).

2. The phase composition of the sample does not change significantly after irradiation by bremsstrahlung to a dose of  $1.35 \cdot 10^5$  Gy. Crystallization of amorphous phosphate and the structural ordering of struvite-K and magnesite occurs.

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### ВЛИЯНИЕ ГАММА-ИЗЛУЧЕНИЯ НА СТРУКТУРУ СТРУВИТА-К

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Анализируется влияние гамма-излучения на функциональные характеристики наноструктурного струвита-К. Были измерены спектры поглощения струвита-К в инфракрасной области. Описаны результаты микроструктуры образцов после гамма облучения до дозы  $1.35 \cdot 10^5$  Град. Было показано, что после гамма-облучения фазовый состав образца существенно не меняется, а происходит кристаллизация аморфного фосфата и структурное упорядочение струвита-К и магнетита.

### ВПЛИВ ГАММА-ВИПРОМІНЮВАННЯ НА СТРУКТУРУ СТРУВІТУ-К

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Аналізується вплив гамма-випромінювання на функціональні характеристики наноструктурного струвіту-К. Були виміряні спектри поглинання струвіту-К в інфрачервоній області. Описано результати микроструктури зразків після гамма-опромінення до дози  $1.35 \cdot 10^5$  Град. Було показано, що після гамма-опромінення фазовий склад зразка істотно не змінюється, а відбувається кристалізація аморфного фосфату і структурне впорядкування струвіту-К і магнетиту.

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