

RADIATION STABILITY OF NATURAL ALUMINOSILICATES VARIOUS STRUCTURAL TYPES BY ELECTRONS AND GAMMA QUANTUM

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The analysis of the properties of natural aluminosilicates in the conditions of various physical loadings and thermal factors are carried out. Microcline and clinoptilolite are inorganic materials having sorption opportunities to radionuclides. It is shown that under the effects of electrons, gamma quanta and thermal factors in natural aluminosilicates of various structures take place different radioaction stimulation of transformation which can be using for future perspective developments.

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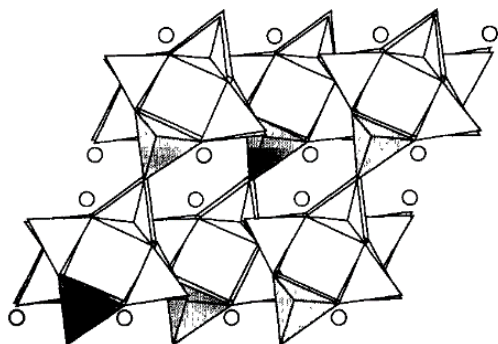
INTRODUCTION

With deep disposal of radioactive waste, the stability of the geological environment will be determined mainly by its radioaction resistance and the value of the absorbed dose of ionizing radioaction from the radioactive waste located in it. To solve the problem of safe isolation of radioactive waste, it is necessary to evaluate the radioaction resistance of natural minerals depending on the mineral composition, rock structure, selectivity, isomorphous capacity, etc. in order to select the varieties of minerals that are most resistant to radiation exposure [1-5].

There are a sufficient number of publications on the effect of irradiation on the structure of the natures of minerals, but data on radiation-stimulated transformations of the structure and phase composition of rock-forming silicates that are part of the rocks of radioactive waste, promising for the creation of radioactive waste storages, are not enough.

The main rock-forming minerals of granitoid rocks are aluminosilicates. The content of aluminosilicates is ~ 80%. The basis of the structure of silicates is a silicon-oxygen tetrahedron, in the center of which there is a silicon ion (Si^{4+}), and at the peaks, there are oxygen ions (O^{2-}), which create tetravalent radicals (SiO_4).

The partial replacement of tetravalent silicon ions by trivalent aluminum ions leads to the appearance of an additional negative charge in the compound. Fig. 1 shows the microcline structure.



*Fig. 1. Ordered microcline structure:
Al is located at one tetrahedral site (shaded),
Si is located at three other sites. Circles – location K*

In this work, attention was paid to two minerals: potassium feldspar – microcline $(\text{K, Na})\text{AlSi}_3\text{O}_8$, which is the main rock-forming mineral that is part of granitoids and clinoptilolite $[(\text{NaK})_4\text{CaAl}_6\text{Si}_{30}\text{O}_{72} \cdot 24\text{H}_2\text{O}]$ – high-siliceous natural zeolite [6].

The microcline studied in the work has an inclined symmetry, but its crystal lattice can have a different degree of deviation from monoclinic symmetry.

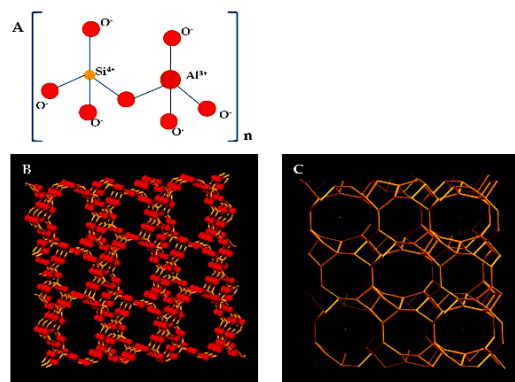


Fig. 2. The structure of clinoptilolite

A wide variety of properties of clinoptilolite is due to its structural features Fig. 2. The crystalline framework of clinoptilolite consists of $[(\text{Si,Al})\text{O}_4]$ octahedra combined into simple, double, and more complex rings, has a sublayer structure, and a two-dimensional system of channels. Since some of the Si^{4+} ions are replaced by Al^{3+} ions, this framework has a negative charge, which is compensated by the presence of Na^+ , K^+ , Ca^{2+} , etc. cations. The total volume of cavities and connecting channels filled with “zeolite water” is ~ 50% of the crystal volume. The channel diameter varies from 0.26 to 0.8 nm.

Similar crystal-chemical features of these minerals, their ability to cation exchange, loss, and absorption of water without destroying the structural framework, allow us to consider them as natural matrix materials and sorbents for long-term storage of radioactive waste in Ukraine. In this regard, it is necessary to study the resistance of these minerals to radiation exposure.

The purpose of this work was to determine the features of the influence of radiation and thermal factors on the properties of natural aluminosilicates necessary for the safe immobilization of radionuclide.

1. MATERIALS AND METHODS

The following objects were chosen as objects of study: 1. white microcline fraction selected from granitoids; 2. clinoptilolite of the Sokirnitskoe deposit with a high SiO₂ content (~70%) and the highest Si/Al ratio ≥ 5.

The samples were irradiated on linear electron accelerator with the following parameters: electron energy $E \approx 7$ MeV, average beam current $I = 500 \mu\text{A}$, temperature of the irradiated samples $T \sim 40^\circ\text{C}$, absorbed dose $D_{\text{abs}} = 10^7$ Gy at electron fluence $\Phi = 3 \cdot 10^{16} \dots 3 \cdot 10^{17} \text{ cm}^{-2}$. The indicated dose range was chosen because it is known that the maximum dose of external radiation from radioactive waste, that can be collected by the geological environment for 1000 years, is $\sim 3.5 \cdot 10^7$ Gy. Irradiation of the samples was carried out in sealed copper containers (copper foil thickness 0.5 mm) with water cooling.

Gamma-activation analysis was used to determine the element content in the samples. The samples were irradiated by bremsstrahlung from the linear accelerator electron NSC KIPT with energy 23 MeV and current 500 μA . Activation of samples was carried out on air, the temperature of samples in the course of activation did not exceed 40°C. Gamma activation analysis is indestructible for native samples.

The determination of elements content in samples performed by gamma-spectrometer method in Ge(Li) - detector with the volume of 50 cm³ and resolution of 3.2 at 1332 keV line. To reduce the influence of background, the detector is equipped with a three-layer Pb-Cu-Al protection. The errors of measurements were from 7 to 25 %. The limit of detection elements for photo activation analysis was $10^{-4} \dots 10^{-7}$ wt. %.

Heat treatment of clinoptilolite was carried out at 260 and 750°C for 6 h to dehydrate and remove non-zeolite components.

The structure and phase composition of samples were investigated by infrared (IR) spectroscopy (IRS-29, LOMO) in the frequency 400...4000 cm⁻¹ with a measurement error of $\pm (2 \dots 7) \text{ cm}^{-1}$. For IR spectroscopy analysis the samples were prepared in the form of transparently compressed tablets from a mixture of KBr and the test substance in an amount of 1% (100 mg sample). The pressing pressure was 9200 kg/cm². To eliminate matrix absorption bands, a tablet of pure potassium bromide preliminarily dried at 180°C for 10 h was placed in the comparison channel of the device. The powders were ground in agate mortars to a size of $\sim 1 \dots 10 \mu\text{m}$ and mixed in a special closed box; pressing was carried out immediately before the spectra were recorded. Graduation in the range of 4000...700 cm⁻¹ was carried out according to the spectrum of polystyrene with known frequencies of absorption maxima, and in the range of 700...400 cm⁻¹ according to the bands of atmospheric water and CO₂. The correction averaged 15...5 cm⁻¹.

Crystal optical studies were carried out on polarizing microscope POLAM-L211 using immersion liquides.

2. RESULTS AND DISCUSSION

Fig. 3 shows microphotographs of grains of the initial ordered microcline before and after irradiation to $D = 10^8$ Gy. Without analyzer.

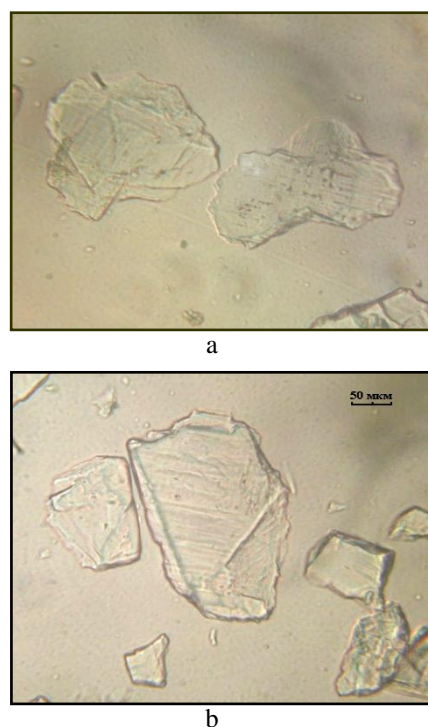


Fig. 3. Microphotographs of an immersion preparation of initial microcline and after irradiation to $D = 10^8$ Gy, in transmitted light, view without an analyzer. a – initial microcline; b – after irradiation to $D = 10^8$ Gy

The preparation of the initial microcline is represented by pure grains with a characteristic lattice structure with a small amount of secondary products of pelitization up to 10% by volume.

Crystal optical studies of the microcline after irradiation showed that with an increase in the irradiation dose from 10^7 to 10^8 Gy, there is a gradual decrease in the refractive index and a decrease in the birefringence value to 0.003 (compared to the initial 0.008) due to the formation of secondary products of pelitization and disorder of the crystal lattice.

The IR spectrum of the initial microcline (Fig. 4) contains absorption maxima characteristic of this mineral: a strong intensity band at 440 cm⁻¹ and a group of bands in the region of 1040...1150 cm⁻¹ (Si-O and Si-O-(Al) Si), as well as the bands of average intensity 545, 595, 645, 735, 776 cm⁻¹, characteristic for the combined vibrations of Al-O-Si, Al-O, Si-O-Si bonds.

The obtained γ -spectrum of activated clinoptilolite revealed the presence of impurity radioactive isotopes ⁵⁵Fe, ⁵⁴Mn, ⁸⁹Zr, ²³⁷U, ^{92m}Nb, ⁸⁸Y, etc., which have a significant output of Auger electrons with energy from 2 to 6 keV from the reactions ⁵⁶Fe(γ, n)⁵⁵Fe, ⁵⁵Mn(γ, n)⁵⁴Mn (Fig. 5).

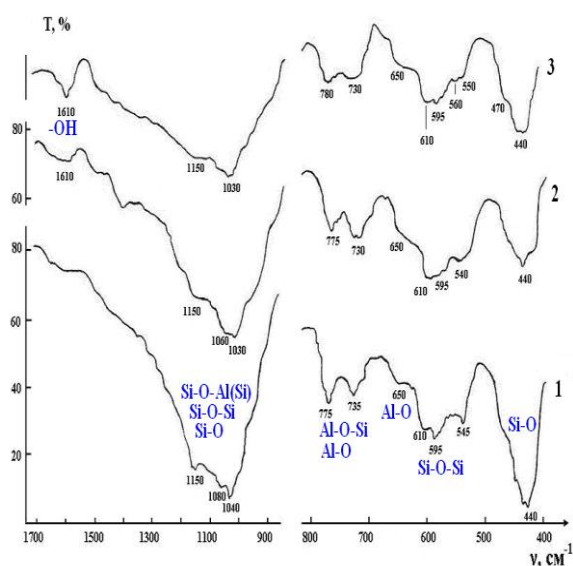


Fig. 4. IR spectra of 1 – initial microcline; 2 – after irradiation to $D=5 \cdot 10^7$ Gy; 3 – after irradiation to $D=10^8$ Gy

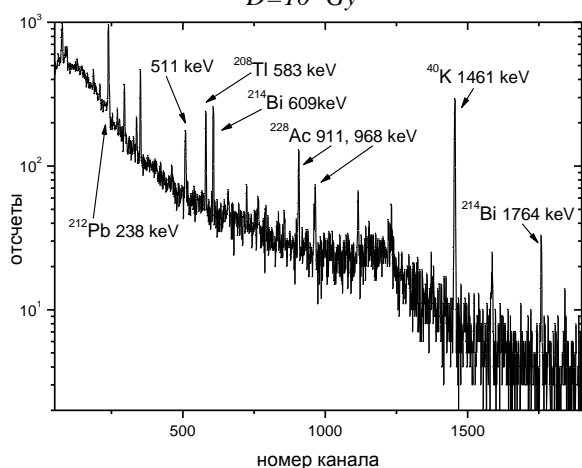


Fig. 5. Gamma-spectrum of clinoptilolite

Having a high specific activity, Auger electrons can form a significant number of electron-hole pairs ($e-h^+$) in a sample of clinoptilolite. Holes are able to split water molecules in water-cationic subsystems, and electrons that interact with dissolved oxygen molecules generate highly reactive radicals such as singlet oxygen (1O_2), hydroxylic, etc., which, in turn, interact with H^+ and form radical HO_2^- and peroxides H_2O_2 . The presence of Fe in the “redox state” of aluminosilicates increases the activation of the “Fenton reaction”, which is accompanied by the release of hydroxyl radicals (OH^\cdot) and peroxide forms. A significant number of highly reactive forms (oxygen atoms $10^{19} \dots 10^{21} \text{ cm}^{-3}$), which were formed under the influence of ionizing radiation, can form bonds with vacancies and interassemblies atoms, which creates conditions for additional active centers that play a positive role in sorption of radionuclides and immobilization of radioactive waste.

Thus, γ -activation by bremsstrahlung on LAE on porous aluminosilicates preserves chemical resistance to leaching and stability of the crystal structure, but at the same time realizes additional active centers of sorption, which is the main high capacity.

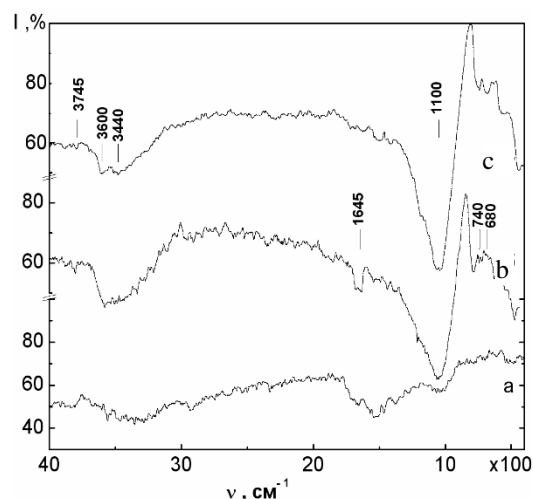


Fig. 6. IR spectra of clinoptilolite samples before (a) and after heat treatment at 260°C (b) and 700°C (c)

IR spectra of clinoptilolite samples before and after heat treatment at 260 and 700°C are presented in Fig. 6. The spectrum of the initial sample (see Fig. 6, curve a) is significantly different from the two almost identical spectra of the samples after heat treatment (curves b, c). In the IR spectrum of the initial sample, the wide, smoothing contours of the bands, characteristic of the water-saturated variety of clinoptilolite, attract attention [6]. On the contrary, in the spectra of heat-treated samples, intense absorption bands of lattice vibrations of Si-O-Al tetrahedral bonds, typical for crystalline monomineral zeolites, are observed]. It can be noticed that the contour of each of the wide bands in the spectrum of the original sample almost completely corresponds to the total envelope for the individual narrow bands of the series of frequencies in the spectra of heat-treated samples.

A more detailed consideration in Fig. 6 spectra show that the main bands relate to the valence bonds of silicon and aluminum with oxygen and hydrogen with oxygen. In the far IR region ($\nu \leq 1150 \text{ cm}^{-1}$), absorption bands at 680, 740, and $1060 \dots 1120 \text{ cm}^{-1}$ associated with lattice vibrations of external tetrahedral Si-O-Al bonds are observed [7]. Along with this, the IR spectrum contains bands at $1640 \dots 1650$ and $3620 \dots 3440 \text{ cm}^{-1}$, corresponding to vibrations of OH bonds in zeolite water and hydroxyl groups – Si-ON, K-OH, Na-OH, Ca-(OH) 2 . In the region of 1340 cm^{-1} , a band corresponding to vibrations of Si-O bonds in crystalline quartz appears. In the samples, there is also an insignificant amount of amorphous silica – an absorption band at 805 cm^{-1} . In the region of $420 \dots 1150 \text{ cm}^{-1}$, small maxima corresponding to vibrations of Me-O bonds in oxides of impurity metals (hematite, rutile, etc.) are observed.

Heat treatment at 260 and 700°C leads to significant changes in the IR spectra of clinoptilolite, indicating dehydration processes occurring in the samples. However by the intensity of the band of deformation vibrations of water (1645 cm^{-1}), it can be said that the main mass of molecularly sorbed water is lost already after heat treatment at 260°C . However, the intensity of this band decreases to zero only after

holding the samples at 700°C. Additionally, both spectra show a significant decrease in the intensity of the bands associated with the valent vibrations of free water in zeolites (3600 and 3440 cm⁻¹) and the absorption bands corresponding to the valent vibrations of hydroxyl groups (3750...3450 cm⁻¹).

Moreover, the absorption bands of hydroxyl groups are observed after heat treatment at 260 and 700°C: both spectra are characterized by a typical set of bands – 3745, 3635, and 3580 cm⁻¹. Hydroxyl groups, corresponding to the absorption band at 3745 cm⁻¹, can be attributed to Si-OH groups, usually localized on structural defects. This band is the weakest and is observed in almost all spectra of natural zeolites, regardless of the type of cations. On the contrary, the intensity of absorption bands in the region of 3500...3600 cm⁻¹ depends on zeolites of cation composition – the strong in the spectra of heylandite and the weak in the spectra of clinoptilolite, which corresponds to a decrease in the concentration of divalent cations in clinoptilolite. In the context of this fact, the noticeable decrease in the intensity of the broad band in the interval 3650...3450 cm⁻¹ can be explained mainly by the effect of the reduction of Ca-(OH)₂. Note that the Ca²⁺ cation released from the hydroxide, along with other cations (K⁺, Na⁺, etc.), easily migrates and is incorporated into the structure of clinoptilolite.

Changes in IR spectra in the region of 3750...3450 cm⁻¹ are especially clearly manifested in the spectrum of the sample processed at 700°C (see Fig. 6, curve c). It is possible to state that only structural OH groups and their dehydroxylation products are present in the sample after treatment at 700°C. Moreover, OH groups are groups formed during dehydration, and not the original molecular “zeolite” water. These groups are connected to the framework of the zeolite and therefore are more heat-resistant than the original crystalline hydrate water.

CONCLUSIONS

The study of changes in the structure and phase composition of the main rock-forming aluminosilicates under the influence of different types of irradiation

(electron and gamma quanta) showed: 1) as a result of electron irradiation of the microcline, the formation of structural defects and a gradual decrease in the cationic orderliness occurs, which leads to the transition of the microcline from an ordered to an intermediate state at the maximum radiation dose up to D = 10⁸ Gy. There is also a decrease in the degree of triclinicity and the disordering of the microcline due to the monoclinization of the structure with the formation of weakly crystallization products of secondary pelitization; 2) a comparison of the radiation and thermal effects on the structural-phase state of clinoptilolite made it possible to establish the unidirectional (towards a positive change) nature of both processes.

These results are well comparable with numerous new data on the high thermal and radiation stability of aluminosilicates and on the possibility of using this advantage for future promising developments.

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РАДІАЦІЙНА СТІЙКІСТЬ ПРИРОДНИХ АЛЮМОСИЛІКАТІВ РІЗНИХ СТРУКТУРНИХ ТИПІВ ПІД ВПЛИВОМ ЕЛЕКТРОНІВ ТА ГАММА-КВАНТІВ

М.П. Дикий, О.П. Березняк, Ю.В. Ляшко, О.П. Медведєва, Д.В. Медведєв

Проведено аналіз властивостей природних алюмосилікатів в умовах дії різних фізичних навантажень та термальних факторів. Мікроклін та кліноптилоліт – неорганічні матеріали, які мають сорбційні можливості до радіонуклідів. Показано, що під впливом електронів, гамма-квантів та термальних факторів у природних алюмосилікатах різної структури виникають різноманітні радіаційно-стимульовані трансформації, які можуть бути використані для майбутніх перспективних розробок.