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# MEASURES FOR IMMOBILIZATION OF RADIOACTIVE WASTE IN THE STRUCTURE OF GLASS AND GLASS-CERAMICS UNDER MARTIAL LAW

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**Abstract.** The regulatory framework for radioactive waste management and its peculiarities in crisis situations are analyzed. The perspective directions of creation of high-tech materials for solid-state matrices for radioactive waste immobilization are determined. A methodological approach to the creation of high-strength glass-ceramic materials with high resistance to radiation, chemical, thermal, and mechanical effects has been developed. The choice of glass compositions for obtaining glass-ceramic materials and compositions based on them for the inclusion of radioactive waste in their composition is substantiated. The structure and the influence of phase composition on the functional properties of glass-ceramic materials are investigated. The prospects of using glass-ceramic materials based on anorthite and hydroxyapatite for long-term immobilization of radioactive waste in crisis situations are determined.

**Keywords:** immobilization, radioactive waste, glasses, ceramics, glass-ceramic materials, crisis situations.

## 1. Introduction

Nuclear security and the establishment of its regimes are the basic principles of compliance with the conditions for the physical protection of radioactive waste for the safety of future generations. Radioactive waste management activities are specialized. The source of ionizing radiation is always taken into account.

Given the special requirements for environmental safety in radioactive waste management, namely when it is placed in special storage facilities that must ensure safe storage, it is important to implement the best available technologies and management methods that are effective in terms of environmental protection.

Compliance with environmental safety conditions in these storage facilities is limited, and in today's realities, almost impossible, given the risks associated with the war. The need for their re-equipment and introduction of innovative technologies is caused by many factors, namely: the urgency of approximation of Ukrainian legislation on radioactive waste management to the international one, modernization and strengthening of physical protection of storage facilities from external influences, minimization of consequences in terms of radioactive waste reburial, creation and expansion of modern radioactive waste management infrastructure, *etc*.

Following the Concept of the National Target Environmental Program for Radioactive Waste Management[1], the strategic task of Ukraine is to ensure safety during radioactive waste management throughout the entire period of its potential hazard. The priority is to ensure the protection of life and health of the population and the protection of the environment from ionizing radiation. One of the main principles of the state policy in the field of radioactive waste management is compliance with radiation safety standards and requirements of Ukrainian legislation.

According to Ojovan and Yudintsev[1], the amount of radioactive waste in Ukraine will increase due to:

– operation of nuclear facilities, extension of their lifetime, and commissioning of new ones;

– management of temporarily stored spent nuclear fuel;

– decommissioning of nuclear facilities and facilities for radioactive waste management;

– decommissioning of the Chornobyl NPP;

– generation of own radioactive waste in the course of licensed activities at the state specialized enterprise Radon Association, as well as removal of radioactive waste from mothballed storage facilities and processing of liquid radioactive waste;

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– removal of radioactive waste from the most hazardous temporary containment sites, transport sanitation sites, and decontamination waste storage sites;

– operation of industrial enterprises, medical, research, and other institutions and establishments;

– carrying out activities on radioactively contaminated territories and facilities, in particular those related to transformation of the "Shelter" into an environmentally safe system, bringing the land into an environmentally safe condition, contaminated because of the Chornobyl accident and as a result of the liquidation of radioactive waste storage facilities resulting from the military programs of the former USSR.

Ensuring sustainable development of nuclear energy, proper protection of life and health of the population and protection of the environment from ionizing radiation, reducing the risk of radiation accidents, crisis situations or unauthorized access to radioactive waste and its possible use for terrorist purposes requires the development of technologies for safe and cost-effective radioactive waste management. To solve the problem, under the basic principles of radioactive waste management declared by the IAEA, it is necessary to lay the foundations and create conditions and technologies aimed at protecting human life and health and the environment from ionizing radiation through optimal radioactive waste management.

An important aspect of the current stage of civilization development is the search for ways to optimize waste management, including its subsequent reuse[1]. Waste inertness can be achieved by binding pollutants or encapsulating them in a monolithic solid with high structural integrity and stability. This will help reduce the potential hazards of toxic waste by converting pollutants into their most insoluble form. Inertness ensures minimal environmental impact of materials and is therefore very important for both reuse and waste disposal. Waste treatment technologies that use durable materials with minimal environmental impact are therefore the best option available.

Radioactive waste inerting is achieved through its immobilization, which the IAEA defines as the transformation of waste into a matrix (material) by solidification, filling, or encapsulation to reduce the potential for migration or dispersion of radionuclides during treatment, transport, storage, and/or disposal. Only the incorporation of radioactive waste into solid matrices, provided that a monolithic structure is obtained, ensures reliable environmental protection.

The physical condition and activity level of radioactive waste are of great importance when selecting materials. Waste, depending on the source of origin, can be liquid, solid and gaseous and differ in activity level: low-level, intermediate-level, and high-level waste, as well as waste and sources of ionizing radiation. For solid and liquid radioactive waste containing beta-gamma emitters, mainly $^{134}Cs$, $^{137}Cs$, $^{90}Sr$, $^{60}Co$ and impurities of alpha-emitting radionuclides, and consisting of chemically heterogeneous components, high-temperature matrices with high chemical, thermal, radiation resistance and mechanical strength are promising.

The most important requirements for the selection of optimal matrices for immobilization of high-level nuclear waste intended for final geological disposal are[2]:

– maximum waste utilization to minimize the disposal volume;

– manufacturability of production, which should be aimed at the implementation of resource and energy saving;

– durability aimed at minimizing the release of radioactive and chemical components;

– radiation resistance aimed at resistance to radiation effects from decay of radioactive components;

– chemical flexibility aimed at ensuring the disposal of a mixture of radioactive and chemical waste components;

– availability of natural analogues that provide a theoretical basis for long-term material characteristics;

– compatibility with the intended disposal environment of the facility for effective immobilization.

The most hazardous part of radioactive waste is associated with the presence of transuranic long-lived actinoids intended for incineration (transmutation) in a reactor or deep geological disposal in mine boreholes[1]. Separation of radioactive waste for the safe immobilization of the most hazardous long-lived actinoids and fission products in compact, capacious, and durable matrices increases the efficiency of using expensive geological repositories.

Today, the nuclear fuel cycle industry widely uses the technology readiness level (TRL) method, which covers the concept of development and proof-of-concept of radioactive waste immobilization techniques. Nuclear waste immobilization routes are assessed by their TRL: from the initial idea ($TRL = 1$), laboratory prototype ($TRL = 5$), to actual implementation in production ($TRL = 9$). Today, technologies for immobilization of highly radioactive waste weighing from 10 to 100 kg are already known, which correspond to $TRL = 7$, and in case they are produced in amount of more than 1 ton, $TRL = 8–9$[3].

Recently, silicate materials: glasses[4–6], ceramics[7, 8], and glass-ceramic materials[9, 10], due to their thermodynamic stability, chemical resistance, and mechanical strength, have been increasingly focused on by developers for their active use in immobilization of various types of nuclear waste. Thus, induction melting is industrially used for the synthesis of B-Si glasses with high-level and intermediate-level radioactive waste in France (Table 1) and already has

*TRL* = 9. In general, the readiness for immobilization of radioactive waste by melting or sintering of silicate materials can be assessed by TRL values from 7 to 9, since these methods are already used in the production of nuclear waste at semi-industrial and pilot plants. Let us consider the features and prospects of using silicate materials for radioactive waste immobilization.

The solution to the problem of radioactive waste immobilization is to incorporate it into glass, the structure of which is capable of accumulating ions of different radius and charge, including radionuclides. At present, the only matrices for radioactive waste that have found practical application are borosilicate and aluminophosphate glasses. The choice of the optimal matrix for intermediate-level waste is associated with the need to meet the requirements for chemical resistance and mechanical strength, on the one hand, and the technological and economic efficiency of their production, on the other.

The prospect of using glass as an immobilizing matrix is due to its high ability to incorporate elements regardless of the charge and size of their atoms; resistance to radiation damage due to the fact that their chaotic structure involves a large number of atomic movements; relative ease and low cost of production, as it does not require complex equipment; and proven production, casting, molding and firing technologies. The advantages of using glasses are that they are less sensitive to changes in composition in waste streams.

Borosilicate glasses have several advantages over aluminophosphate glasses: significant compositional flexibility, smoother changes in viscosity and electrical resistance with temperature, less corrosive effect on refractories, less susceptibility to devitrification, *etc.* Such glasses can be attributed to the $Na_2O$-CaO-$Al_2O_3$-$B_2O_3$-$SiO_2$ system. The content of CaO oxides in the glass is 30–35 wt. %. The leaching rate of Ca from these glasses at 20 °C in distilled water is $(2–5)\cdot10^{-2}$ g/($m^2$.day), Sr and Pu, respectively, are 1 and 2 orders of magnitude less. Borosilicate glass allows changes in the content of Fe, Al, Mn, Ca, and Ni by 2–3 times without a significant decrease in leaching.

Due to lower dose loads and heat release, the requirements for matrices for intermediate-level waste are more lenient than those for high-level waste, because they do not require high radiation resistance, thermal conductivity, and there is no need for the most homogeneous distribution of fissile materials to prevent the creation of conditions and maximum difficulty for the re-extraction of fissile uranium and plutonium isotopes and their use in terrorist activities. Thus, the necessary and sufficient requirements for glass for intermediate-level waste are: high chemical resistance (mainly to cesium and strontium radionuclides), maximum volume reduction, mechanical strength, simplicity, and reliability of the technology for their production. In addition, glasses in the liquid state should have certain viscosity values (3–6 Pa·s).

The authors of[11–13] analyzed in detail the effectiveness of different types of glasses (Table 1), which have already found their practical application in radioactive waste immobilization.

**Table 1.** Oxide compositions of HLW (high-level waste) glasses, wt. %

| Country | $SiO_2$ | $P_2O_5$ | $B_2O_3$ | $Al_2O_3$ | $Fe_2O_3$ | $TiO_2$ | CaO | MgO | PbO | MnO | $Na_2O$ | Misc |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Belgium | – | 70.7 | – | 7.1 | 22.2 | – | – | – | – | – | – | – |
| Belgium | 52.7 | – | 13.2 | 2.7 | – | – | 4.6 | 2.2 | – | – | 5.9 | 18.7. |
| France | 46.6 | – | 14.2 | 5.0 | 2.9 | – | 4.1 | – | – | | 10.0 | 17.2 |
| France | 54.9 | – | 16.9 | 5.9 | – | – | 4.9 | – | – | | 11.9 | 5.5 |
| Germany | 60.0 | – | 17.6 | 3.1 | – | – | 5.3 | – | – | | 7.1 | 6.9 |
| India | 30.0 | – | 20.0 | – | – | – | – | – | 25.0 | | 5.0 | 20.0 |
| India | 34.1 | – | 6.4 | – | – | 6.2 | – | – | – | 9.3 | 0.2 | 43.8 |
| Japan | 46.7 | – | 14.3 | 5.0 | – | – | 3.0 | – | – | – | 9.6 | 21.4 |
| UK | 47.2 | – | 16.9 | 4.8 | – | – | – | 5.3 | – | – | 8.4 | 17.4 |
| Hungary | 78.9 | | 11.30 | 2.83 | | | 0.10 | 0.10 | | | 6.25 $K_2O$ 0.52 | – |
| China | 54.43 | | 6.57 | 14.41 | 0.34 0.12 FeO | 0.33 | 22.57 | 0.64 | | | 0.36 $K_2O$ 0.23 | – |
| US | 49.8 | – | 8.0 | 4.0 | – | – | 1.0 | 1.4 | – | – | 8.7 | 27.1 |
| US | 45.8 | – | 8.4 | 6.1 | 11.4 | – | | 1.4 | – | – | 9.1 | 17.8 |
| US | 50.0 | – | 20.0 | 5.0 | – | – | | – | – | – | 25.0 | – |

Boron-free glasses based on the $Na_2O$-$Al_2O_3$-$Fe_2O_3$-$SiO_2$ system also meet all these requirements, but they are "shorter" (they retain technological parameters in a narrow temperature range) and have less compositional flexibility for radioactive waste components, both in terms of the content of radioactive waste oxides in general and the maximum content of such components as sulfates and chlorides that are poorly soluble in silicate glasses.

About vitrification of radioactive waste (both intermediate-level waste and high-level waste) with a high content of sulfates and chlorides (as well as molybdates, chromates, uranates, fluorides and iodides), the maximum total concentration (in terms of $SO_3$ and NaCl) that can be achieved in glasses without phase separation (crystallization or liquation) varies between 0.8–1.2 wt. %.

It is known that phosphate systems are much more compatible with sulfate and chloride systems than silicate and borosilicate systems in terms of crystal chemistry[13], and the content of $SO_3$ and NaCl in phosphate-based glasses can reach 20–30 wt. %. The chemical resistance of such glasses is lower than that of aluminophosphate-based glasses used for immobilization of high-level waste, but is quite sufficient for solidified intermediate-level waste. The leaching rate of Ca is ~2–$10^{-2}$ g/($m^2$·day) at 20 and 50 °C; 3.5–$10^{-2}$ g/($m^2$·day) at 100 °C, and increases by another 6 times when the leaching temperature is increased to 150 °C. One of the most promising areas is the use of production waste and/or rocks such as basalt as an additive to the batch during processing. Natural silicate-based glasses (obsidians, basalt glass, tektites) have proven to be stable over geological periods.

The main disadvantage of glass is its thermodynamic instability, which manifests itself in the crystallization of glass under the influence of high temperatures caused by radioactive decay. The phenomenon of vitrification worsens the initial properties of the product, in particular, the rate of its leaching increases. However, vitrification is considered the most effective method of solidification of liquid radioactive waste.

The advantage of ceramics is their thermodynamic stability and higher hydrothermal and radiation resistance, especially for actinides. However, the use of ceramics as a waste form is limited by their composition, for example, in terms of silicon content due to the formation of the glass phase, and by the small number of crystal structures capable of adapting to compositional changes.

There is a significant amount of minerals in nature containing uranium, thorium and their daughter products and ranging in age from hundreds of thousands to hundreds of millions of years, which have demonstrated high stability in geological conditions, including stability during radioactive decay of uranium and thorium isotopes. The most promising phases for binding actinide and rare earth elements are those with a fluorite-derived structure (tageranite / fianite, pyrochlore, murataite, various modifications of zirconolite), as well as some orthophosphates and silicophosphates, zircon and perovskite (the latter mainly for rare earth elements and strontium). To predict the behavior of preservation matrices in real conditions of storage over geological periods for different types of radioactive waste, modeling of the behavior of matrices and radionuclides is necessary. This requires knowledge of the main immobilizing parameters of the matrices when calculating dose rates.

Crystalline ceramics are being intensively studied as an effective material in various nuclear power applications[14]. Ceramic materials for radioactive waste immobilization, similar to minerals, are characterized by different structures, including simple oxides with fluorite structure, complex oxides (pyrochlore, murataite, zirconolite, perovskite, hollandite, garnet, crichtonite, freudenbergite and P-pollucite), simple silicates (zircon/thorite/coffinite, titanite (sphen), britholite), framework silicates (zeolite, pollucite, nepheline / leucite, sodalite, cancrinite, micas structures), phosphates (monazite, xenotime, apatite, kosnarite (NZP), langbeinite, thorium diphosphate, struvite), and aluminates with the structure of magnetoplumbite $LnPO_4$[15]. These materials can contain various cations in different combinations and ratios: Li-Cs, Tl, Ag, Be-Ba, Pb, Mn, Co, Ni, Cu, Cd, B, Al, Fe, Ga, Sc, Cr, V, Sb, Nb, Ta, La, Ce, rare-earth elements (REEs), Si, Ti, Zr, Hf, Sn, Bi, Nb, Th, U, Np, Pu, Am, and Cm. They can be produced in the form of powders, including nanopowders, as well as monolithic ceramics. Cold pressing and sintering, hot pressing, hot isostatic pressing, and spark plasma sintering (SPS) can be used to produce ceramics. The SPS method is currently considered one of the most promising for use with real radioactive substances, allowing for a compaction of up to 98–99.9 % in a few minutes. However, the use of ceramics is significantly limited by the complexity of the technology and significant energy costs for obtaining a monolithic form, which significantly increases the cost of this technology.

Glass-ceramic materials not only combine the advantages of using glasses and ceramics for radioactive waste immobilization[16], but also, due to the formation of a nanostructured texture under low-temperature synthesis conditions, allow for a lower solidification temperature, increase shape flexibility to changes in waste composition, while maintaining high stability.

The idea behind the immobilization of various radioactive wastes into glass-ceramics or ceramics is based on the use of minerals that are stable in the Earth's crust, the bulk of which is well understood. Radionuclide ions are incorporated into the crystal lattice in the form of solid solutions that are thermodynamically stable under disposal conditions. When immobilizing waste in single-

phase glass-ceramics, radiologically inert materials are used as matrices: silica, alumina, α-quartz, mullite, rutile, pollucite, zeolite, feldspar, apatite, sphen, *etc*.[17–19]. Using rocks containing mullite, glass-ceramic materials designed for radioactive waste isolation were obtained. The introduction of aluminum oxide additives into granite-based compositions, firing, and hot isostatic pressing (HIP) made it possible to create glass-ceramic materials with a predictable composition and glass phase content[20].

To date, special materials based on borosilicate[21] and alumina-borosilicate glass-ceramics containing barium[22], magnesium[23], and calcium oxides[24] are known. Aluminosilicates and spinels may include activated corrosion products (iron group elements). Phosphate and silicophosphate glass-ceramics based on the crystalline phases $Ca_3(PO_4)_2$ – $Ca_5(PO_4)_2(SiO_4)$, $Ca_7(PO_4)_2(SiO_4)_2$, $Ca_2SiO_4$ are becoming increasingly used. At the same time, calcium phosphates are matrix phases for immobilization of radioactive strontium, REE and actinoids due to the ability of calcium ions to undergo isomorphic exchange according to the following scheme:

$$Sr^{2+} + Ca^{2+} + P^{3+} = REE^{3+} + Si^{4+},$$

$$Ca^{2+} + P^{5+} = An^{4+} + Me^{3+}.$$

Some of the cesium and strontium enter the crystalline phases, as indicated by a decrease in their leaching rates of approximately the order of magnitude of $10^{-3}$ g/(m$^2$·day), compared to borosilicate glass.

The authors of[25, 26] investigated the parameters of manufacturing glass-ceramic materials based on boro-silicate and phosphate compounds for further use as protective matrices for radioactive waste immobilization. Magnesium oxide MgO, potassium dihydrogen phosphate $KH_2PO_4$, and distilled water were used as starting materials for the synthesis of potassium-magnesium phosphate $KMgPO_4 \cdot 6H_2O$. The borosilicate glass of the following composition wt. %: $SiO_2$ – 78.90 %; $B_2O_3$ – 11.30 %; $Na_2O$ – 6.25 %; $Al_2O_3$ – 2.83 %; $K_2O$ – 0.52 %; MgO – 0.10 %; CaO – 0.10 % was used for vitrification of salt melt and its solidified form. The glass-ceramic materials were obtained by heat-treatment at 1150 °C of the composition of 70 wt. % borosilicate glass + 30 wt. % potassium magnesium phosphate with Cs. These materials were represented by potassium-magnesium phosphate $K_{1-x}Cs_xMgPO_4$, cristobalite $SiO_2$, and potassium-magnesium silicate $K_2MgSi_5O_{12}$. The analysis of the chemical and phase composition, microstructure, and physical and mechanical properties of the glass-ceramic samples showed that the obtained materials are characterized by a homogeneous structure and high parameters of density 2.32–2.36 g/cm$^3$, compressive strength σ = 30 MPa, and thermal shock resistance $\Delta T \geq 550$ °C, which meets the requirements for materials for radioactive waste immobilization according to ASTM C1285-21. It has been shown that after treatment at 1150 °C, the amount of cesium in the glass-ceramic samples remained virtually unchanged compared to the amount of cesium in the original mixture.

Numerous studies of the use of calcium phosphate and calcium aluminosilicate glass-ceramics confirm their effectiveness in the immobilization of radioactive waste due to the peculiarities of structure formation and the ability to retain lanthanides (Ce, Nd, Eu, Gd, Yb) in the structure[27].

An important task of reliable immobilization of radioactive waste in critical situations (military operations, natural disasters, and catastrophes) is to ensure high mechanical and thermal stability, in particular, when hit by high-efficiency firearms and missiles. However, currently known matrices for this purpose are not strong enough to be used in high-risk areas.

This study aims to establish the prospects for the development of high-strength glass-ceramic materials for radioactive waste immobilization in crisis situations.

## 2. Experimental

### 2.1. Materials and methods

To achieve this goal, the following tasks were set:

– analysis of the regulatory framework for radioactive waste management and its specifics in crisis situations;

– analysis of the accumulated experience in the development of silicate materials for radioactive waste immobilization;

– development of a methodological approach to the creation of solid-state matrices for radioactive waste immobilization;

– substantiation of the choice of glass compositions for obtaining high-strength glass-ceramic materials;

– determining the influence of phase composition on the functional properties of glass-ceramic materials.

In the work, physico-chemical methods of research of the obtained model glasses were used, which made it possible to study the processes occurring in glasses during heat treatment, in particular X-ray phase (DRON-3M diffractometer), differential-thermal (Q-1500D Paulik-Paulik-Erday derivatograph), and electron-microscopic analyses (scanning electron microscope SEM with a maximum resolution of 1 nm). Indicators of hardness and crack resistance were determined according to ISO 9385-2013, compressive strength according to EN 1748-2-1-2016, and the modulus of elasticity of glass-ceramic materials was determined by the acoustic resonance method. The method for determining the hydrolytic resistance of glass grains at 98 °C is based on the action of distilled water at 98 °C on crushed glass and the determination of the volume (mL) of 0.01 M HCl required for titration.

## 3. Results and discussion

### 3.1. Development of a methodological approach and justification of the choice of glass compositions for glass-ceramic materials

The main idea in the development of new generation high-strength glass-ceramic materials for radioactive waste immobilization is to simultaneously ensure high mechanical strength, thermal and chemical resistance of materials using directed catalyzed crystallization of the amorphous phase of a certain chemical composition to provide a densely packed homogeneous high-strength structure with the formation of nano- and submicron crystals under low-temperature short-term heat treatment.

The development of high-strength glass-ceramic materials should take into account the requirements for multiphase glass-ceramics used for nuclear, hazardous, and mixed waste according to ASTM C1285-21[28]: chemical resistance (leaching rate of cesium and strontium $\leq 10^{-3}$ g/(m$^2$·day); thermal resistance $\Delta T \geq 550$ °C; mechanical compressive strength $\sigma \geq 9$ MPa.

To ensure the durability of the material and its resistance to ballistic weapons and blast waves, open flames, the following are required: fire resistance RE45($h$) – RE80($h$); fracture toughness > 3.0 MPa·m$^{1/2}$, Young's modulus > 100 GPa; impact strength > 5.0 kJ/m$^2$; Vickers hardness HV = 7000–11000 MPa.

Taking into account that calcium silicophosphate glass-ceramic materials are characterized by insufficient mechanical and thermal properties, it is necessary to select glass compositions based on the calcium aluminosilicate system.

Considering previous studies[23, 24, 29, 30], calcium silicophosphate

$RO$=CaO, $R_2O$=$Na_2O$, $RO_2$= $\sum TiO_2$+$ZrO_2$

and calcium aluminosilicate glasses

($RO$=$\sum$CaO+MgO+SnO+ZnO, $R_2O$=$K_2O$,

$RO_2$= $\sum TiO_2$+$ZrO_2$) (Table 2)

were selected to develop a glass composite material with increased strength properties.

**Table 2.** Chemical composition of model glasses of the ASK and BS series and temperature conditions of melting and heat treatment

| Glass marking | Chemical composition of model glasses, wt. % | | | | | | | Temperature modes of melting and heat treatment, °C | | Crystalline phase |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | Melting | Heat treatment I / II stages | |
| | $SiO_2$ | $Al_2O_3$ | RO | $R_2O$ | $P_2O_5$ | $B_2O_3$ | $RO_2$ | | | |
| Calcium aluminosilicate glasses | | | | | | | | | | |
| ASK-1 | 35.0 | 30.0 | 23.5 | 2.5 | – | – | 9.0 | 1650 | 860/ 1200 | $CaAl_2Si_2O_8$ |
| ASK-2 | 37.0 | 30.0 | 23.0 | 2.5 | 3.0 | – | 4.5 | 1650 | 920/ 1200 | $CaAl_2Si_2O_8$ |
| ASK-3 | 46.0 | 27.0 | 17.0 | 2.5 | – | – | 7.5 | 1600 | 860/ 1200 | $CaAl_2Si_2O_8$ |
| ASK-4 | 40.0 | 26.0 | 25.0 | – | – | 5.0 | 4.0 | 1600 | 900/ 1250 | $CaAl_2Si_2O_8$ |
| ASK-5 | 43.0 | 23.0 | 24.0 | 1.5 | 1.0 | 4.0 | 3.5 | 1550 | 800/ 1000 | $CaAl_2Si_2O_8$ |
| Calcium silicophosphate glasses | | | | | | | | | | |
| BS-1 | 50 | 5 | 15 | 15 | 10 | – | 5 | 1400 | 980 | $Ca_5(PO_4)_3OH$ |
| BS-2 | 45 | 5 | 16 | 16 | 8 | 5 | 5 | 1370 | 960 | $Ca_5(PO_4)_3OH$ |
| BS-3 | 50 | – | 15 | 15 | 10 | 5 | 5 | 1400 | 950 | $Ca_5(PO_4)_3OH$ $TiO_2$ |
| BS-4 | 50 | 5 | 15 | 15 | 10 | 5 | – | 1400 | 950 | $Ca_5(PO_4)_3OH$ |
| BS-5 | 50 | – | 15 | 15 | 10 | 5 | 5 | 1450 | 1000 | $Ca_5(PO_4)_3OH$ $CaZr4(PO4)_6$ |
| BS-6 | 45 | – | 15 | 15 | 10 | 5 | 5 | 1450 | 1000 | $CaZr_4(PO_4)_6$ |
| BS-7 | 50 | – | 15 | 15 | 10 | – | 10 | 1400 | 1000 | $Ca_5(PO_4)_3OH$ $ZrTiO_4$ $SiO_2$ |
| BS-8 | 55 | 5 | 25 | 10 | 5 | – | – | 1450 | 1000 | $Ca_5(PO_4)_3OH$ |
| BS-9 | 55 | 5 | 25 | 5 | 10 | – | – | 1450 | 1000 | $Ca_5(PO_4)_3OH$ |
| BS-10 | 55 | 5 | 20 | 10 | 5 | – | 5 | 1450 | 1000 | $Ca_5(PO_4)_3OH$ |
| BS-11 | 55 | 5 | 20 | 10 | 5 | 5 | – | 1400 | 1000 | $Ca_5(PO_4)_3OH$ |
| BS-12 | 55 | – | 20 | 10 | 5 | 5 | 5 | 1450 | 1000 | $Ca_5(PO_4)_3OH$ $ZrTiO_4$ |

Natural mineral raw materials (Novoselivsky sand, alumina, zircon, chalk), oxides with ChP markings (ZnO, $TiO_2$), and other chemical compounds (boric acid, potash, strontium carbonate and magnesium carbonate, and disubstituted ammonium phosphate) were used to make the glass batch. The glasses were synthesized in the temperature range of 1370–1650 °C in corundum crucibles in an electric furnace with molybdenum disilicide heaters with gradual cooling in the furnace (12 h).

The glass-ceramic materials of the ASK and BS series were obtained using ceramic technology: grinding the mixture in a laboratory ball mill until it passes through a sieve No. 063 with a mesh size of no more than 63 μm; heat treatment (HT) according to a two-stage mode for calcium aluminosilicate glasses: stage I – $T$ = 800–920 °C (2 hour), stage II – $T$ = 1000–1250 °C (4 hours) and in a one-stage mode for calcium silicophosphate glasses at 950–1000 °C (2 hours).

The composite glass-ceramic material of the ABSK-1Z series was obtained based on ASK and BS glasses in a ratio of 50:50 and 5 wt. % of zirconia stabilized with yttrium oxide and heat-treated in a single-stage mode at 1050 °C (2 h).

## 3.2. Study of the influence of phase composition and structure on the performance properties of glass-ceramic materials

According to the results of X-ray phase analysis, it was established that ASK-5 and BS-11 glasses are characterized by the highest content of the crystalline phase after heat treatment among the experimental glasses. The content of the crystalline phase of calcium anorthite and calcium hydroxyapatite is an important condition for ensuring high chemical resistance of glass-ceramic materials. The high resistance of the glass phase is provided by the presence of four-coordinated boron and aluminum by oxygen, and the formation of a single aluminoborophosphosilicate glass framework with high chemical resistance.

According to the differential thermal analysis, intensive nucleation for these glasses is observed in the low temperature region $T$ = 700–800 °C. However, the crystallization differs due to the different thermal prehistory of the glasses. Thus, the significant content of crystallization catalysts $RO_2$ and $P_2O_5$ for BS-11 glass affects the formation of a crystalline phase of ≈20 vol. % after melting. For the glass material, the high-viscosity glass framework formed during melting and cooling due to the high crystalline phase content inhibits the process of nucleation at the softening temperature. This, in turn, leads to the glass sitallization with a crystalline phase content of only 50 vol. %, which is insufficient for the formation of a hardened structure.

Gradual change in the character of the thermogram in the temperature range of 720–980 °C and a decrease in the height of the echo-effect peak indicate some enlargement of the crystalline phase in these temperature intervals, which can lead to hardening of the structure and a decrease in mechanical stability (Fig. 1). For ASK-5 glass, which is X-ray amorphous after melting, the formation of a finely dispersed synthesized structure is confirmed by the presence of a rapid echo-effect at a temperature of 1050 °C (Fig. 1) and the formation of a crystalline phase in the amount of 70 vol. %. The significant amount of the crystalline phase formed during the heat treatment is evidenced by the large area of the endo-effect at $T$ = 880 °C, which precedes the echo-effect at $T$ = 1050 °C (Fig. 1).

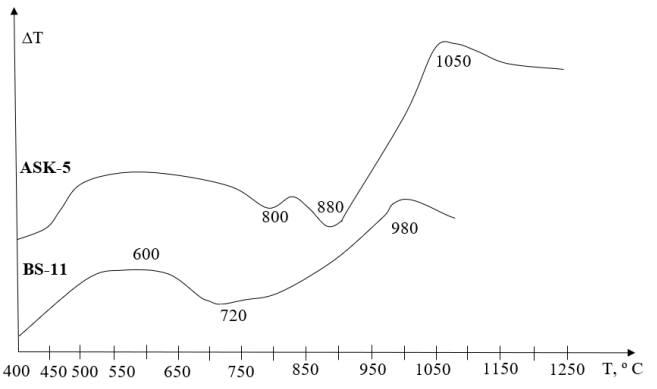



**Fig. 1.** Thermograms of the experimental glasses

The study of the glass structure by scanning electron microscopy made it possible to establish a significant difference in the formation of the structure of calcium aluminosilicate and calcium aluminophosphate glasses.

The study of the chemical resistance of the experimental glass-ceramic materials ASK-5, BS-11, and ABSK-1Z made it possible to establish that the developed materials belong to the I hydrolytic class with losses of 0.015, 0.08, and 0.04 mg/mL. The high chemical resistance of the developed glass-ceramic materials is determined by their nanostructured glass-ceramic structure with the content of anorthite and hydroxyapatite crystal phases in the amount of 50–70 vol. %. The study of the glass structure by the method of scanning electron microscopy allowed us to establish a significant difference in the formation of the structure of calcium aluminosilicate and calcium aluminophosphate glasses.

The structure of the ASK-5 glass-ceramic material after low-temperature two-stage heat treatment is a glass phase, in which scaly crystals of triclinic anorthite ≈1 μm

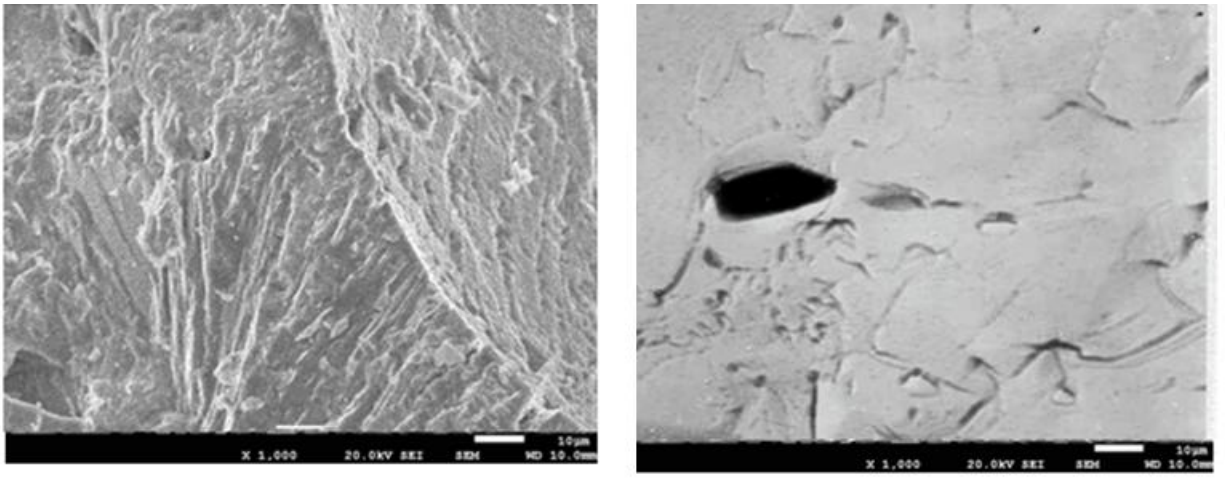
in size are evenly distributed, which form longitudinal protrusions and furrows oriented in the same direction (Fig. 2, *a*) and strengthen the structure of the material.

For the BS-11 glass material, the presence of phase separation at the initial stages of nucleation in the conditions of a highly viscous melt leads to the appearance in it at the final crystallization temperature of 1000 ºC of 1–3 micron in size of hydroxyapatite crystals and in the amount of ~ 50 vol. % (Fig. 2, *b*). However, the presence of a small amount of crystals > 1 μm can lead to a decrease in the mechanical properties of the glass-ceramic material. This is a significant obstacle for the use of calcium silicophosphate glass materials for the immobilization of radioactive waste in crisis situations.

In general, the investigated glass-ceramic materials are characterized by a dissipative structure due to the formation of fluctuations that have a composition corresponding to the equilibrium at the nucleation temperature, followed by their stabilization due to the ordering of the structure and further self-organization of the finely dispersed bulk crystallized glass structure under low-temperature heat treatment.

The formation of a strengthened structure allows to ensure high values of mechanical properties for the glass-ceramic material ASK-5. This is related to the structural characteristics of sitalls, namely the formation of a nanostructure and the blocking of microcracks by the crystalline phase.

To ensure reliable immobilization of radioactive waste in critical situations, a high-strength composite material ABSK-1Z was developed. A characteristic feature of the developed material is its high mechanical properties (Table 3). The high hardness and fracture toughness of the developed material determine the durability of radioactive waste immobilization, in particular, when hit by high-yield firearms and missiles.



a b

**Fig. 2.** Structure of glass-ceramic materials ASK-5 (a) and BS-11 (b)

**Table 3.** Mechanical properties of glass-ceramic materials

| Material | Mechanical properties | | | |
|---|---|---|---|---|
| | *HV*, MPa | $K_{1C}$, MPa·m$^{1/2}$ | $\sigma_{copmr}$, MPa | *E*, MPa |
| BS-11 | 6290 | 2.22 | 100 | 100 |
| ASK-5 | 10000 | 4.2 | 400 | 250 |
| ABSK-1Z | 9000 | 5.5 | 300 | 240 |

## 4. Conclusions

The main trends in the environmental direction of radioactive waste conversion into a long-term inert physicochemical form stable to radiation and thermal effects, and promising directions for the creation of solid-state inert matrices for radioactive waste incorporation were analyzed. The main advantages of glass-ceramic materials were established, and a methodological approach to the creation of high-strength glass materials for radioactive waste immobilization in crisis situations was developed. The compositions of glass-ceramic materials based on anorthite and calcium hydroxyapatite were selected, and the compositions and technological modes of composites based on them with high strength characteristics (*HV* = 9000 MPa; $K_{1C}$ = 5.5 MPa·m$^{1/2}$;

$\sigma_{compr}$ = 300 MPa; $E$ = 240 MPa) and high chemical resistance (0.015–0.08 mg/ml) were developed. It has been established that the creation of a new type of nanostructured self-organized glass-ceramic materials will solve the problem of reliable long-term involvement of radioactive waste in high-strength solid-state matrices resistant to environmental factors, man-made factors, and the effects of armed aggression.

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## ЗАХОДИ ЩОДО ІММОБІЛІЗАЦІЇ РАДІОАКТИВНИХ ВІДХОДІВ У СТРУКТУРІ СКЛА ТА СКЛОКЕРАМІКИ В УМОВАХ ВОЄННОГО СТАНУ

***Анотація.*** *Проаналізовано нормативну базу щодо поводження з РАВ та її особливості в умовах кризових ситуацій. Визначено перспективні напрями створення високотехнологічних матеріалів для твердотілих матриць для іммобілізації РАВ. Розроблено методологічний підхід до створення високоміцних склокристалічних матеріалів із високою стійкістю щодо радіаційного, хімічного, термічного і механічного впливу. Обґрунтовано вибір складів стекол для одержання склокристалічних матеріалів і композицій на їхній основі для введення до їхнього складу РАВ. Досліджено структуру та визначено вплив фазового складу на функціональні властивості склокристалічних матеріалів. Визначено перспективність застосування склокристалічних матеріалів на основі анортиту та гідроксіапатиту для довготривалої іммобілізації РАВ в умовах кризових ситуацій.*

***Ключові слова:*** *іммобілізація, радіоактивні відходи, стекла, кераміка, склокристалічні матеріали, кризові ситуації.*