Glass-ceramic matrices based on borosilicate and phosphate materials for the immobilization of radioactive waste

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The parameters for manufacturing of glass-ceramic materials based on borosilicate and phosphate compounds for further application as protective matrices for the immobilization of radioactive waste are presented in study. The chemical and phase compositions, microstructure and physic-mechanical properties of glass-ceramic samples were analyzed. Results shown, that obtained materials are characterized by homogeneous structure and high density, compressive strength and thermal shock resistance parameters, in accordance with the requirements to materials for radioactive waste immobilization. In addition, the influence of the temperature of glass heat treatment on the volatility of cesium compounds was analyzed. It was shown that in samples after treatment at 1150°C the amount of cesium in the glass ceramic samples was practically unchanged, in comparison with the amount of cesium in the initial mixture.

Keywords: radioactive waste immobilization, glass-ceramic materials, vitrification, borosilicate, phosphate compounds, phase composition, thermal shock resistance.

Показана возможность применения стеклокерамических материалов на основе боросиликатных соединений в качестве защитных матриц для иммобилизации радиоактивных отходов (РАО). Определены оптимальные параметры получения стеклокерамики, изучены их химический и фазовый составы, микроструктура и свойства. Показано, что полученные материалы характеризуются однородной структурой и высокими показателями плотности, прочности и термостойкости, которые соответствуют требованиям к материалам, предъявляемым для иммобилизации РАО. Проанализировано влияние температуры термообработки стекла на летучесть соединений цезия. Показано, что в образцах, полученных при температуре 1150°C, количество цезия практически не изменилось в сравнении с количеством цезия в исходной смеси.

Склокерамічні матриці на основі боросилікатних і фосфатних матеріалів для іммобілізації радіоактивних відходів. *С.Ю.Саєнко, Є.О.Світличний, В.А.Шкуропатенко, А.В.Зикова, О.Г.Ледовська, Л.М.Ледовська, Г.О.Холомєєв, А.Г.Миронова, М.О.Одейчук.*

На підставі виконаних досліджень показано можливість застосування склокерамічних матеріалів на основі боросилікатних та фосфатних сполук в якості захисних матриць для іммобілізації РАВ. Визначено оптимальні параметри отримання склокераміки, вивчено їх хімічний і фазовий склади, мікроструктуру і властивості. Показано, що отримані матеріали характеризуються однорідною структурою і високими показниками щільності, міцності і термостійкості, які відповідають вимогам до матеріалів, що пред'являються для іммобілізації РАВ. Проаналізовано вплив температури термообробки скла на летючість сполук цезію. Показано, що у зразках, отриманих при температурі 1150°C, кількість цезію практично не змінилася у порівнянні з кількістю цезію у вихідній суміші.

1. Introduction

Radioactive waste (RAW) poses a great danger to humanity around the world because of the radiation and toxic effects. Therefore, hazardous waste should be subject to conditioning, included volume reduction and transfer to a solid stable monolithic form, and followed by long-term storage of conditioned RAW for the time necessary to reduce the radioactivity to an acceptable level. One of the promising materials for the immobilization of such radioactive waste is glass. Glasses can serve as an ideal matrix for waste low and medium levels of radioactivity (LMAW), which are characterized by low heat dissipation [1, 2].

The environmental and economic benefits of low and medium levels waste vitrification are determined by the low solubility of vitrified waste in natural waters, a high degree of reduction in the volume of materials, and the possibility of vitrified waste disposal without additional surface engineering barriers in the geological environment. In the case that the chemical element concentration in the waste is higher than its solubility in glasses during vitrification, a crystalline phase forms and the matrix for such waste is glass ceramics containing, in addition to glass, mineral crystalline inclusions. The composition of the glass frit and its quantitative ratio with the waste are selected depending on the composition of the waste.

Currently, borosilicate glasses are mainly used in Russia, France, Great Britain, Germany, Japan, etc. as matrices for RAW immobilization [1–5]. The solubility of borosilicate glasses at low temperatures is low and glasses with relatively low stability are able to ensure the safety of underground storage of the LMAW without additional engineering barriers. At the same time, worldwide-used borosilicate glasses for nuclear waste vitrification are not suitable for immobilization of high content molybdenum, chromium, or salt waste because of the low solubility of such compounds in the borosilicate glasses. As alternative to borosilicate glasses phosphate glasses are proposed for further waste vitrification [6–10].

At the NSC KIPT, systematic studies are being conducted to obtain ceramic and glass-ceramic materials for immobilization of radioactive waste [11–13]. In [14–16], the prospects of using potassium — magnesium phosphate materials for the immobilization of liquid radioactive waste were shown.

The aim of the study was optimization of the parameters for the manufacturing of glass-ceramic materials based on borosilicate and phosphate compounds, which can be used as matrices for immobilization of radioactive waste.

2. Experimental

The following starting materials were used for the synthesis of potassium-magnesium phosphate $KMgPO_4 \cdot 6H_2O$: magnesium oxide MgO, potassium dihydrogen phosphate KH_2PO_4; distilled water.

For vitrification of the salt melt and its solidified form obtained by means of potassium-magnesium phosphate, mainly used borosilicate glass "Pyrex" of the composition: 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.

The vitrification of the samples was carried out in alumina crucibles in a high-temperature furnace Nabertherm P310 (Germany) at temperatures 900–1200°C, with heating rate 150–200°C/h, holding time 1 h. For mixing and grinding of the starting and synthesized materials, the planetary mill "Pulverisette 6" was used.

The phase composition of the materials before and after the heat treatment was studied by X-ray diffraction analysis (DRON — 1.5, Cu K_α with a nickel filter).

The microstructure of the samples was studied using a JSM-7001F scanning electron microscope (JEOL, Japan). The analysis of the composition of the samples was carried out by the method of energy dispersive X-ray microanalysis using an INCA Penta FETx3 analyzer (Oxford Instruments, United Kingdom).

Elemental analysis of the obtained glass ceramics was carried out on a double focusing EMAL-2 high-resolution laser mass spectrometer. The signal was recorded on the film, followed by photometry with an IFO-451 microphotometer.

The open porosity and apparent density of the samples were determined in accordance with standard 2409-95 by hydrostatic weighing.

The compressive strength of the samples was evaluated by the method of diametric compression [17].

To determine the thermal shock resistance, the standard EN 820-3:2004 was used. According to the standard requirements thermal shock resistance was characterized by a temperature difference ΔT, at which cracks appear in the samples.
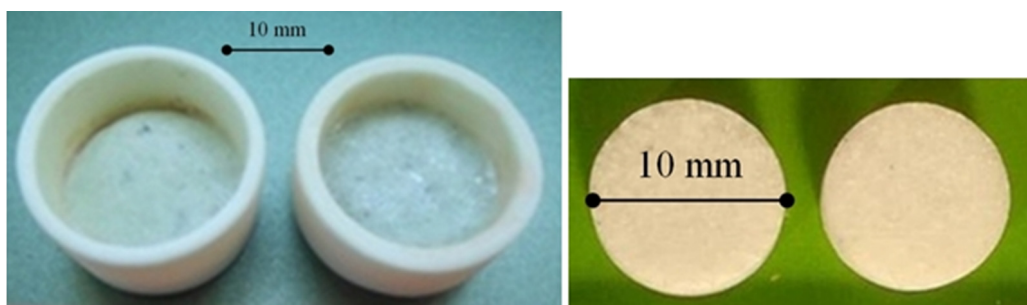
Fig. 1. Glass-ceramic samples obtained at a temperature of 1150°C in crucibles (left) and samples for physical and mechanical properties testing (right).

3. Results and discussion

Study was carried out on vitrification of a salt melt simulator, manufactured on the basis of its averaged chemical composition [18]. To obtain a solution of a salt melt simulator, the required amount of H_3BO_3, NaOH, Na_2SO_4, NaCl, KOH, $FeSO_4 7H_2O$ reagents was dissolved in distilled water, then cesium and cobalt salts were added to the resulting solution in a predetermined amount. The concentration of salts of the model solution, which according to the components corresponded to the real salt melt, amounted to 1600 g/l, at pH = 10.

The solidification of the salt melt simulator using potassium magnesium phosphate was carried out by adding up to 35 wt.% of salt melt to a mixture of MgO and KH_2PO_4. The studies were carried out directly with heat-treated salt melt, as well as with solidified melt obtained using potassium-magnesium phosphate.

Figure 1 shows glass-ceramic samples treated at a temperature of 1150°C in crucibles (left) and samples for physic-mechanical properties testing (right).

In the Table 1 the physical characteristics of glass-ceramic samples obtained at various temperatures are presented. The table shows that the samples of both compositions obtained at temperatures of 900°C, 1000°C, 1100°C are characterized by high open porosity and low density, so further studies were carried out on samples obtained at temperatures of 1150°C and 1200°C.

According to X-ray phase analysis (XRD), after vitrification, the samples are represented by both crystalline and amorphous phases. Figure 2(a) shows the XRD patterns of the glass-ceramic sample of the composition: 70 wt.% borosilicate glass + 30 wt.% solidified simulator form. It should be noted that in the samples obtained at a temperature of 1150°C, there are a large number of elements and compounds with strong capacity to form various phase components during the interaction and subsequent crystallization. It can be seen that the peak of maximum intensity can belong to both the peak (104) of potassium-magnesium phosphate α-$KMgPO_4$ (ASTM 089-4675) and the peak (101) of cristobalite SiO_2 (ASTM 39-1425) and peak (201) of aluminosilicate potassium $KAlSi_3O_8$ (ASTM 31-0966). In addition, the phase of sodium-calcium-aluminum phosphate-silicate $Na_2Ca_3Al_2 (PO_4)_2(SiO_4)_2$ (ASTM 35-0327) and calcium carbonate $CaCO_3$ (ASTM 41-1475) are observed on the XRD patterns.

Table 1. Physical characteristics of glass-ceramic samples obtained at various temperatures

| Chemical composition	No.	Thermal treatment regime °C	Shrinkage, %	Open porosity, %	Apparent density, g/cm^3
70 % B−Si glass + 30 % solidified simulator form	1	900	0.3−0.9	29−32	1.95−2.04
	2	1000	1.2−1.4	21−22	2.15−2.18
	3	1100	1.8−2.4	13−15	2.22−2.24
	4	1150	2.3−3.0	2−4	2.30−2.33
	5	1200	2.5−3.2	2−3	2.32−2.36
60 % B−Si glass + 40 % solidified simulator form	6	900	0.3−0.8	27−28	2.02−2.10
	7	1000	0.9−1.3	22−24	2.17−2.20
	8	1100	1.6−1.8	14−15	2.22−2.25
	9	1150	2.0−2.7	3−5	2.33−2.36
	10	1200	2.2−2.9	2−3	2.35−2.38
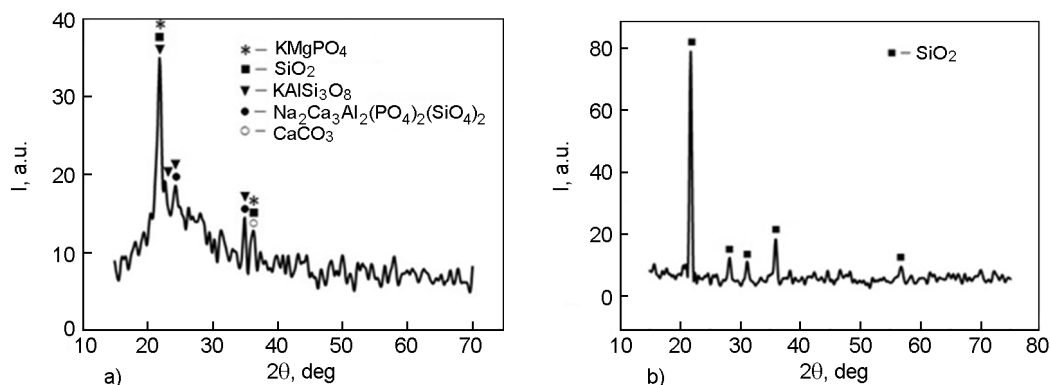
Fig. 2. XRD patterns of glass-ceramic samples: a — 70 wt. % borosilicate glass + 30 wt.% solidified simulator form of salt melt, b — borosilicate glass without additives.
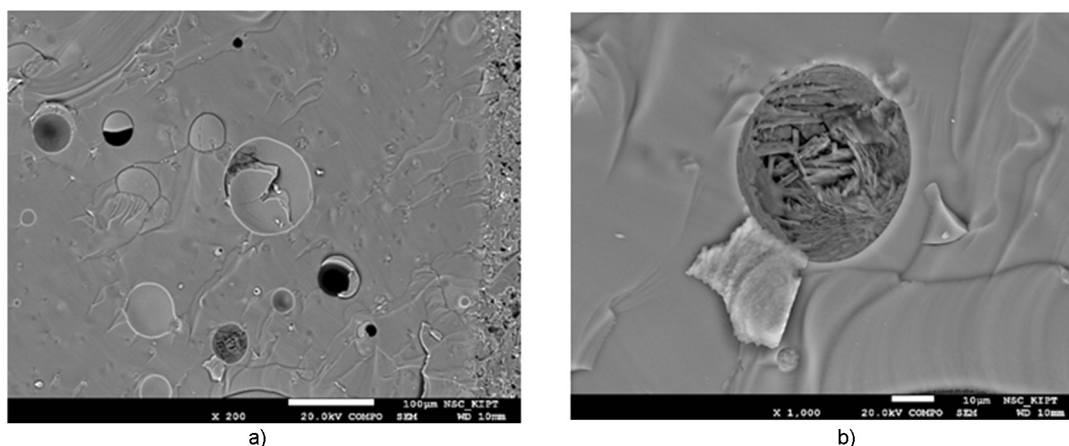

Fig. 3. SEM microstructure of the cleavage of the sample with composition 70 % B–Si glass + 30 % salt melt simulator using potassium magnesium phosphate after heat treatment at 1150°C.

At the same time, a significant part of the amorphous component is noticeable.

To determine the effect of the solidified salt melt simulator on the phase composition of the obtained samples, XRD of borosilicate glass was carried out without additives after heat treatment at the same temperature of 1150°C. After holding the samples for 1 h at 1150°C and slow cooling with the furnace, intense crystallization of glass samples with the formation of cristobalite SiO_2 (Fig. 2b) was detected. Therefore, on the one hand, in the samples of 70 % B–Si glass + 30 % solidified form of the simulator, in addition to cristobalite, the phase of calcium carbonate, as a part of the mixture of borosilicate glass, and potassium-magnesium phosphate, as the main phase component of the solidified salt melt simulator, were revealed. On the other hand, as a result of the interaction of the constituent parts of solidified salt melt simulator using potassium magnesium phosphate with borosilicate glass, phases of potassium alumi-

nosilicate and sodium-calcium-aluminum phosphate-silicate were appeared.

Figure 3 shows the microstructure of the cleavage of the sample with composition 70 % B–Si glass + 30 % salt melt simulator using potassium magnesium phosphate after heat treatment at 1150°C. It can be seen that the obtained material mainly consists of glass with crystalline inclusions of various shapes. Some of the inclusions are consisted directly of potassium-magnesium phosphate, and others are represented by magnesium oxide, which did not react during the solidification of salt melt simulator. The inclusions sizes were in the range 100–150 μm in diameter (Fig. 3a). Spherical inclusions with a diameter of 40–50 μm consist of needle crystals of ~ 1 μm (Fig. 3b) were also observed. According to the XRD data, the crystals may belong to cristobalite, calcium carbonate, potassium aluminosilicate and sodium-calcium-aluminum phosphate-silicate.

In the case of the content of solidified salt melt simulator using potassium magne-
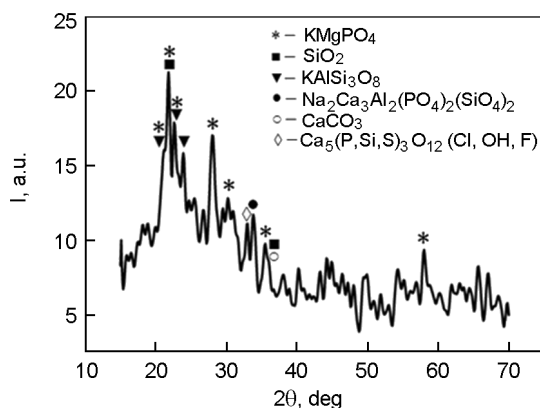
Fig. 4. XRD patterns of glass-ceramic samples 60 wt.% borosilicate glass + 40 wt.% solidified simulator form of salt melt.

sium phosphate increasing up to 40 wt.% there was an increase in the peaks of potassium-magnesium phosphate (Fig. 4). This fact indicates the increase in the content of the crystalline phase of the potassium magnesium phosphate in comparison with the sample composition: 70 wt.% borosilicate glass + 30 wt.% solidified salt melt simulator. In addition, after heat treatment at 1150°C for 1 h, 60 wt.% B–Si glass + 40 wt.% solidified salt melt simulator samples contained phases of calcium carbonate and cristobalite, observed during crystal-

lization of borosilicate glass. Moreover, phases of potassium aluminosilicate and sodium-calcium-aluminum phosphate-silicate were detected. When 40 wt.% of the solidified salt melt simulator was introduced into borosilicate glass, a new phase of chlorostadite $Ca_5(P,Si,S)_3O_{12}(Cl,OH,F)$ was appeared (ASTM 25-0167) (Fig. 4) as a result of solid-phase reactions during heat treatment.

The XRD results were confirmed by energy dispersive X-ray microanalysis of samples with composition of 60 % B–Si glass + 40 % solidified simulator of salt melt.

Figure 5 shows the microstructure of the cleavage of the sample with composition 60 % B–Si glass + 40 % salt melt simulator using potassium magnesium phosphate after heat treatment at 1150°C. The elemental composition of sample was obtained by energy dispersive X-ray microanalysis. According to the elemental analysis of the spectrum 2 site, it can be objectively concluded that the inclusion of a spherical shape with a diameter ~ 50 μm contains potassium-sodium-magnesium phosphate $(K,Na)MgPO_4$ and cristobalite SiO_2 (Fig. 5a). Irregular inclusions with sizes of 3–5 μm (spectrum 9) consist of calcium carbonate $CaCO_3$, potassium aluminosilicate $KAlSi_3O_8$ and cristobalite SiO_2 (Fig. 5b). Despite the fact that ^{137}Cs and ^{134}Cs isotopes make the main contribution to the ac-
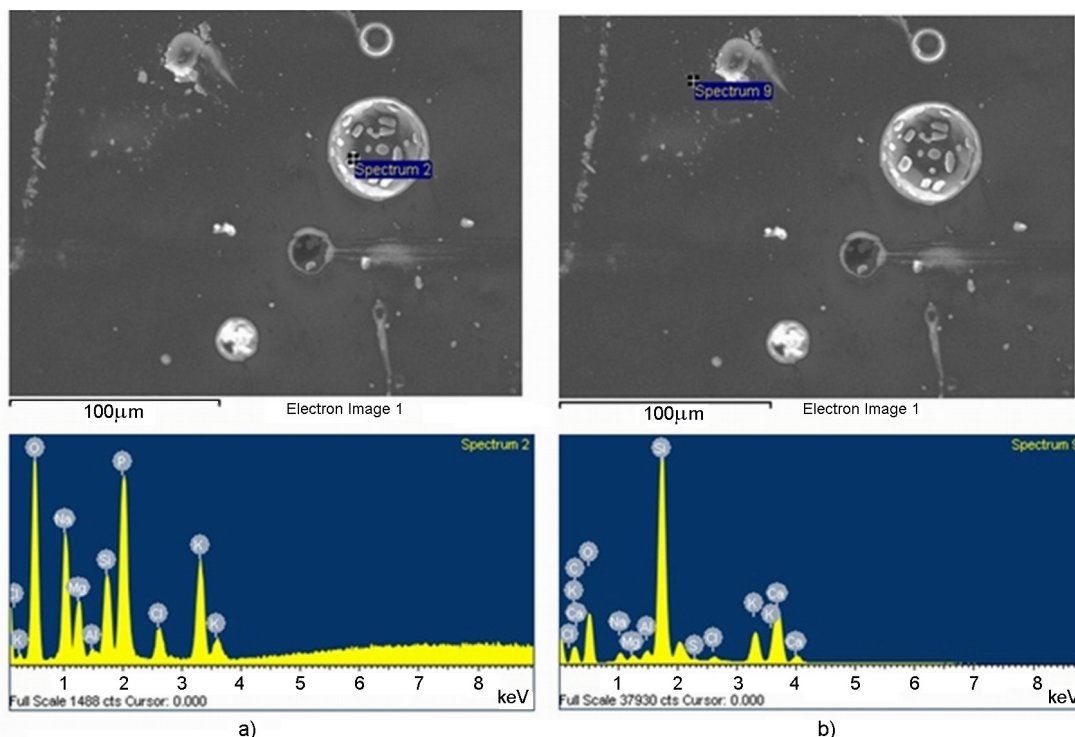

Fig. 5. SEM images and EDX spectra of spectrum 2 site (a) and spectrum 9 site (b) of the sample 60 % B–Si glass + 40 % solidified simulator form of salt melt.

Table 2. The elemental composition of the samples of the initial composition of 70 wt.% borosilicate glass + 30 wt.% potassium magnesium phosphate and with the addition of 1 and 10 wt.% CsCl before and after heat treatment at a temperature of 1150°C and 1200°C

Sample composition	Element, content, wt.%											
	B	O	Na	Mg	Al	Si	P	S	Cl	K	Ca	Cs
Initial (1 % CsCl)	2.32	49.65	3.11	2.84	1.05	31.26	3.31	0.016	0.21	5.98	0.076	0.17
Heat treated at 1150°C (1 % CsCl)	2.57	50.0	2.92	1.80	2.29	35.3	0.95	0.004	0.25	3.64	0.11	0.16
Heat treated at 1200°C (1 % CsCl)	2.13	50.17	2.73	0.83	1.73	37.98	0.68	0.002	0.06	3.49	0.013	0.17
Initial (10 % CsCl)	2.27	49.70	2.68	3.16	0.87	29.14	3.11	0.002	1.00	6.37	0.01	1,58
Heat treated at 1150°C (10 % CsCl)	2.62	50.40	5.68	0.63	1.28	34.16	0.31	0.002	0.12	3.45	0.006	1.34
Heat treated at 1200°C (10 % CsCl)	2.74	49.63	3.78	1.13	1.43	35.49	0.45	0.002	0.19	3.85	0.01	1.29

tivity of salt melt, the elements concentration was insignificant. Therefore, in order to study the volatility of cesium compounds during vitrification of hardened melt simulators, samples of composition 70 wt. % borosilicate glass + 30 wt.% potassium-magnesium phosphate with the addition of 1 and 10 wt.% CsCl after subsequent heat treatment at 1150 and 1200°C with exposure for 1 hr were manufactured.

The results of elemental analysis of the initial samples of composition 70 wt.% borosilicate glass + 30 wt.% potassium magnesium phosphate and with the addition of 1 and 10 wt.% CsCl before and after heat treatment at a temperature of 1150°C and 1200°C are presented in Table 2. It can be seen from the presented data that at the samples with the addition of 1 wt.% CsCl in comparison with the initial samples the amount of Cs did not change after heat treatment both at temperature of 1150°C and 1200°C. On the other hand, at the samples with the addition of 10 wt.% CsCl in comparison with the initial samples the amount of Cs decreased in the samples after heat treatment at temperatures of 1150°C and 1200°C.

According to the fact, that the amount of cesium in the heat treated at temperatures of 1150°C samples (Table 2) was remained practically unchanged, the temperature 1150°C was defined as optimal.

Figure 6 shows the XRD patterns of heat-treated at 1150°C samples of composition 70 wt.% borosilicate glass + 30 wt.% potassium magnesium phosphate with Cs. Presented data demonstrate that the phase composition was represented by potassium-magnesium phosphate $K_{1-x}Cs_xMgPO_4$, cristobalite SiO_2 and potassium-magnesium silicate $K_2MgSi_5O_{12}$ (ASTM 45-1499).
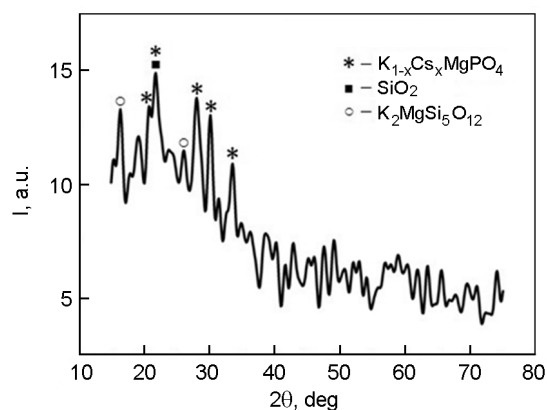

Fig. 6. XRD patterns of glass-ceramic samples of the composition 70 wt.% borosilicate glass + 30 wt.% solidified simulator form of potassium-magnesium phosphate with cesium after heat treatment at 1150°C.

Figure 7 shows the microstructure of cleaved samples of composition 70 wt.% borosilicate glass + 30 wt.% potassium magnesium phosphate with Cs after heat treatment at 1150°C. The samples are characterized by a dense homogeneous structure and a very uniform distribution of finely dispersed inclusions. The inclusions are presented both by particles of introduced potassium-magnesium phosphate with cesium, and a mixture with other elements formed as a result of reactions between the components of borosilicate glass and potassium-magnesium phosphate.

Table 3 shows the properties of glass ceramic samples. It can be seen from the presented data that the obtained samples of both compositions are characterized by high density, compressive strength, and thermal shock resistance in accordance with the requirements for materials for RAW immobilization (Standard 50926-96).

Table 3. Properties of glass ceramic samples

Properties	Sample composition	
	70 wt.% B–Si glass + 30 wt.% solidified simulator form	60 wt.% B–Si glass + 40 wt.% solidified simulator form
Apparent density, g/cm^3	2.32–2.36	2.35–2.38
*Compressive strength, σ, MPa	26–30	22–25
*Thermal shock resistance, ΔT, C	≥ 550	≥ 550

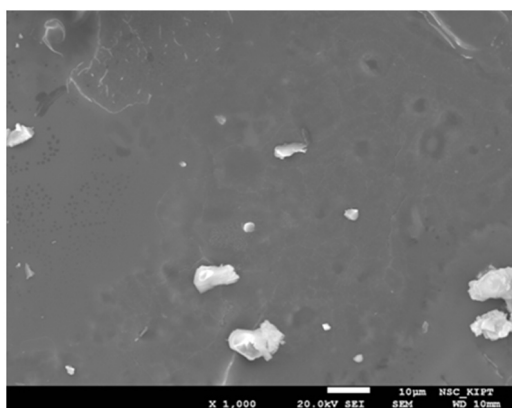*Requirements (Standard 50926-96) σ =≥ 9 MPa, ΔT ≥ 550°C

Fig. 7. SEM microstructure of the cleavage of the sample with composition 70 % B–Si glass + 30 % salt melt simulator using potassium magnesium phosphate with cesium after heat treatment at 1150°C.

4. Conclusions

The possibility of application of glass-ceramic materials based on borosilicate compounds as protective matrices for immobilization of radioactive waste was presented. The optimal parameters for the manufacturing of glass ceramics such as the chemical and phase compositions, microstructure and properties were determined. Results show that the obtained materials are characterized by a homogeneous structure and high density, compressive strength and thermal shock resistance, according with the requirements for materials proposed for RAW immobilization.

In addition, the effect of glass heat treatment temperature on the volatility of cesium compounds was analyzed in study. It was shown that the amount of cesium in the samples heat treated at temperature of 1150°C was remained practically unchanged compared with the cesium amount in the initial mixture.

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