



Article

Glass-Containing Matrices Based on Borosilicate Glasses for the Immobilization of Radioactive Wastes

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Abstract: Glass-containing materials are widely considered among the most reliable materials for the immobilization of radioactive waste materials. The present work considers the synthesis of glass–ceramic and glass crystalline composite materials based on borosilicate glasses. The synthesis of glass–ceramic materials was carried out by a gradual temperature decrease, followed by crystallization for several hours. Sintering of crushed samples with crystalline components was carried out as an alternative procedure. Porous glasses were produced from glass melts by quenching. After impregnating the resulting porous materials with aqueous solutions of cesium nitrate, compaction of the glass was carried out to form glass crystalline composites. The thermochemical characteristics of the parent glasses were determined using the differential scanning calorimetry method. The phase composition and structure of the glass-containing materials were determined using X-ray phase analysis, X-ray spectral microanalysis, and Raman spectroscopy.

Keywords: glass–ceramics; glass crystalline composites; borosilicate glasses; immobilization; crystallization



Citation: Koroleva, O.N.; Nevolina, L.A.; Korobatova, N.M.

Glass-Containing Matrices Based on Borosilicate Glasses for the Immobilization of Radioactive Wastes. *J. Compos. Sci.* **2023**, *7*, 505. <https://doi.org/10.3390/jcs7120505>

Academic Editor: Aleksey A. Vedyagin

Received: 2 October 2023

Revised: 24 October 2023

Accepted: 1 November 2023

Published: 4 December 2023



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1. Introduction

The relevance of radioactive waste immobilization is due to an increase in spent nuclear fuel and the concomitant need to provide storage and reprocessing. Glasses have been demonstrated to be a rather flexible means of bonding many of the HLW (high-level waste) constituents (both radioactive and nonradioactive components) at an atomic level [1–4]. HLW has been incorporated into alkali borosilicate or phosphate vitreous materials for many years, with such vitrification approaches already representing an established technology in France, Japan, Russia, the USA, and the UK. However, existing vitrification approaches may not always represent the optimal method of immobilization due to the relatively low radionuclide loading of glasses and their tendency to crystallize, a process that can start immediately after pouring the melt into canisters as a result of its residual heat [5]. Matrix materials based on borosilicate glasses, representing the preferred form for the immobilization of highly radioactive waste, are currently under active development [6–8].

The increased interest in multiphase glass-containing materials is associated with their high chemical resistance, strength, thermal stability, and consequently, increased waste storage capacity. The leaching of actinide elements from glass–ceramic waste forms can be minimized by means of immobilizing actinides into more stable crystal structures by the crystalline phases, while the residual glass matrix can act as a secondary barrier [9]. The synthesis and processing conditions of such materials play a key role in predicting their stability, which also depends on external and geochemical conditions at underground waste disposal facilities. For the immobilization of radioactive waste, glass matrices must demonstrate chemical and physical stability under the influence of changing conditions over long periods of time.

In this study, we set out to investigate various approaches to the synthesis of multiphase glass-containing materials based on borosilicate glasses with two modifier cations.

In particular, we are interested in the possibility of controlled synthesis to ensure the immobilization of cesium by the crystalline phases into the predicted stable structures.

2. Materials and Methods

The initial glasses were synthesized by melting a charge with subsequent pouring in an air atmosphere. For the preparation of the charges, analytically pure dried reagents (sodium carbonate, silicon, boron, and germanium oxides) were used in appropriate proportions. To determine the weights, Sartogism CE224-C (Miass, Russia) laboratory scales having an accuracy of 0.1 mg were used. The prepared charges were fused in a platinum crucible in a muffle furnace SNOL 12/12 (Miass, Russia) in several stages. After maintaining the charges at temperatures of 700–800 °C for 1 h to decompose carbonates into oxides, they were then heated to 1100–1200 °C and exposed to the maximum temperature for 1.5 h to ensure complete homogenization of the melt (the temperatures varied depending on the composition). The melts were then poured into steel molds and cooled in air. The as-obtained glass compositions were tested using X-ray microanalysis on a CAMECA SX100 electron probe microanalyzer (Miass, Russia).

A Renishaw inVia Qontor confocal Raman microscope (Moscow, Russia) equipped with 50 mW 532 nm diode lasers was used in combination with a charged-coupled device (CCD) array detector. Baseline correction and intensity normalization procedures were performed for each recorded spectrum.

Differential scanning calorimetry (DSC) and thermogravimetric analysis (TG) were used to obtain information on the phase transition temperatures. Powdered glass placed in the holder of a Netzsch STA 449C Jupiter synchronous thermal analyzer (Chelyabinsk, Russia) was used for recording thermograms at a constant heating rate of 10 °C/min in a temperature range from 25 to 1000 °C.

Glass–ceramic samples were obtained using the petrological method by direct cooling of the melt. To that end, the glass powder was placed in quartz crucibles for remelting followed by a gradual reduction in temperature from 800 to 600 °C. After holding in the furnace at a temperature of 600 °C for another 24 h, the samples were cooled in the furnace to room temperature.

The synthesis of glass crystalline composites, including pyrochlore crystals, was carried out by annealing the tablets at a temperature of 600 °C for two hours. To prepare the tablets, crushed glass was mixed with crushed crystals of natural pyrochlore in a ratio of 4:1 followed by pressing at 200 bar.

The synthesis of porous glass crystalline composites involved exposing the initial glassy materials to a temperature of 610 °C for 24 h in the furnace. Following thermal treatment, the glasses acquired opalescence, thus indicating the completion of phase separation. At the next stage of processing, the original glasses were subjected to acid leaching in boiling 1N HCl for 2 h to produce porous glass samples. In order to study the characteristics of porous materials, a low-temperature nitrogen adsorption–desorption method based on an ASAP-2020 adsorption analyzer (Chelyabinsk, Russia) was used. The microstructure of the porous glasses was studied using a Jeol JSM-7001F scanning electron microscopy complex with an Oxford Instruments INCA X-max 80 EDX detector (Chelyabinsk, Russia). Impregnation of the glasses was carried out by sequential impregnation–drying of the porous material with 1M aqueous solution of cesium nitrate; this method earlier proved to be quite effective [10,11]. Drying was carried out at a temperature of 100 °C. Dry saturated glasses were pressed into tablets at a pressure of 200 bar; the tablets were then annealed to consolidate the pores. Heating was applied at a rate of 7 degrees per minute, then the glasses were kept at a temperature of 800 degrees for 1 h. The obtained materials were subsequently retrieved from the furnace for a short cooling in air to avoid crystallization of the matrix.

The obtained samples were examined for the distribution and content of cesium using a Jeol JSM-7001F scanning electron microscopy complex with an Oxford Instruments INCA X-max 80 EDX detector (Chelyabinsk, Russia). In order to determine the form of the presence

of cesium in the samples, a Rigaku Ultima IV diffractometer X-ray diffraction (Tokyo, Japan) operating with Cu K α radiation (wavelength = 0.154 nm) was used.

3. Results

3.1. Petrurgic Method

Synthesis was carried out by directional crystallization from a model sodium–cesium borosilicate melt. The composition of the initial synthesis glass was as follows: Na₂O—7.5 mol.%; Cs₂O—22.5 mol.%; B₂O₃—20 mol.%; SiO₂—50 mol.% (1Na3Cs50 sample). For crystallization from the melt, the glass powder was placed in quartz crucibles, remelted, and then the temperature was reduced to 800 °C by natural cooling. The results of differential scanning calorimetry of the parent glass are given in Figure 1. The temperature of annealing was chosen according to the results of DSC. Namely, the longest period of heat treatment should be in the temperature region between the glass transition temperature and the melting point. Special attention was paid to slow cooling in the region of crystallization temperatures. The 1Na3Cs50 sample was kept at temperatures of 800, 750, 700, and 650 °C for 30 min. After subsequently holding the sample at 600 °C for an additional 24 h to stabilize the system, it was cooled in the furnace to room temperature. Thus, the synthesis of glass–ceramics can be presented as follows: melting glasses in Pt crucibles, crushing, thermal treatment, and crystallization in quartz crucibles.

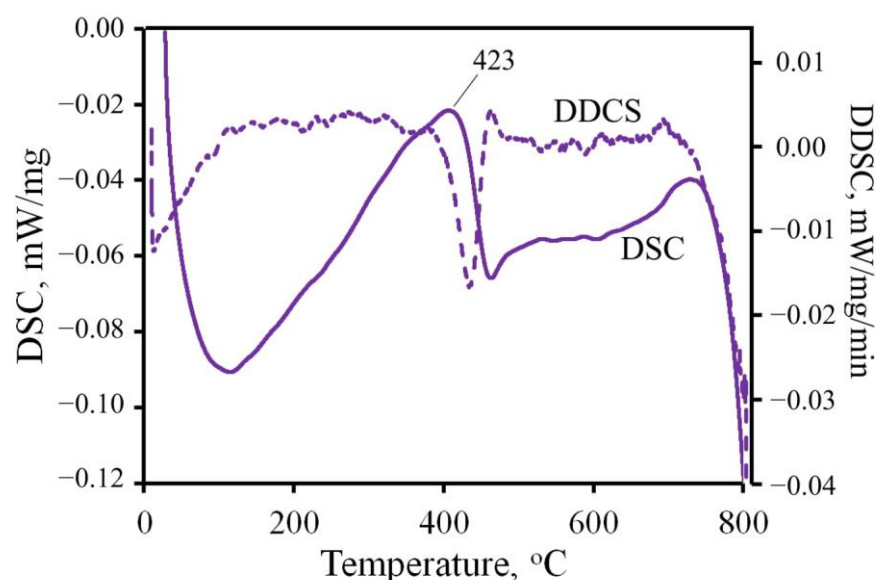


Figure 1. DSC of the initial glass 1Na3Cs50.

SEM results of the glass–ceramic material obtained under the described heat treatment conditions are given in Figure 2a. During electron microscopic study of the glass–ceramic (Figure 2a,b), streak-forming skeletal crystals were discovered. The size of crystals and their intergrowths was up to 30 μ m. To distinguish the mineral, the composition of the crystalline phase was determined. The stoichiometric composition of the crystalline phase calculated from the SEM results corresponds to (Na_{0.09}Cs_{1.10})B_{0.93}Si_{1.92}O₆. The formula unit was calculated on the basis of six atoms of oxygen. A TEM image of the glass–ceramic material is demonstrated in Figure 2b.

The results of the X-ray spectral microanalysis are presented in Figure 3. The characteristic peaks for orthorhombic phase CsBSi₂O₆ taken from [12] are shown in comparison with the diffractogram of the obtained glass–ceramics. It can be concluded that the heat treatment of 1Na3Cs50 glass results in the formation of a crystalline phase as represented by CsBSi₂O₆.

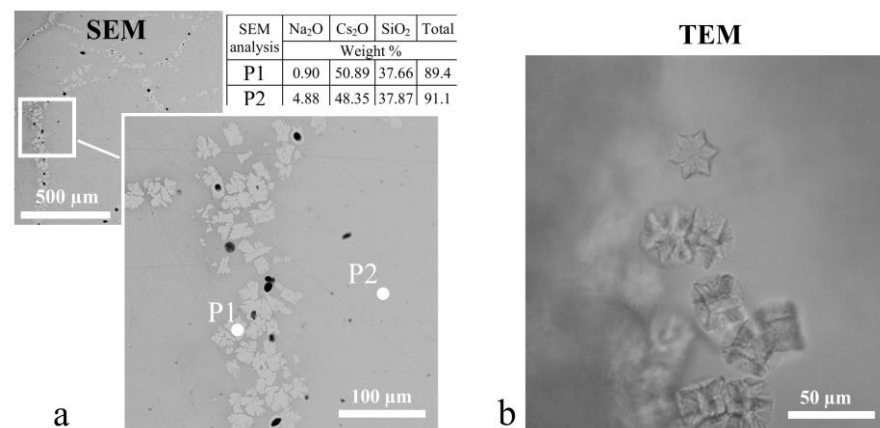


Figure 2. Images from scanning electron microscopy (a) and transmission electron microscopy (b) of 1Na3Cs50 glass–ceramics.

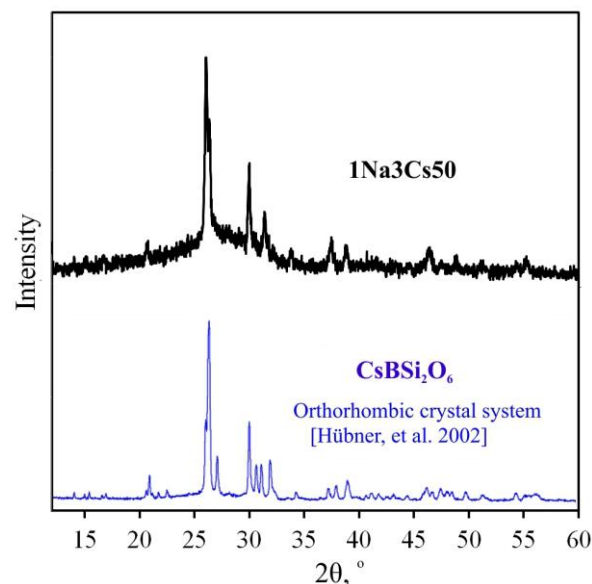


Figure 3. X-ray spectral microanalysis of 1Na3Cs50 glass–ceramics ; XRD of orthorhombic CsBSi₂O₆ [12].

The results of electron microscopy showed that the content of cesium oxide in the crystalline phase (point P1) exceeds its content in the amorphous phase (point P2) by 2.5 wt.% (Figure 2a). Conversely, sodium oxide is five times more prevalent in the glass than in the crystalline phase. According to these results, it can be concluded that cesium passes from the melt into the crystalline phase. It is apparent that the formation of CsBSi₂O₆ led to changes in the structure of the glass, which are also observed in the Raman spectra. The change in the glass structure before and after crystallization can be noted based on a comparison of the Raman spectra of the original glass and the glass in the glass–ceramic sample (Figure 4). Interpretation of the bands can be carried out based on the literature data. In the low-frequency region, there are bands corresponding to vibrations of bridging oxygen atoms in the borate and silicate network. The medium-frequency region is characterized by vibrations of nonbridging oxygen atoms in the structural units Q³ and Q². The high-frequency region is characterized by vibrations of borate triangles [13,14]. A decrease in the intensity of the oscillation bands of structural units Q² and borate triangles BO_{3/2} can be noted during the transition from glass to glass–ceramic phases. At the same time, the band corresponding to the bridging bonds between borate and silicate Si–O–B tetrahedra grows [15]. These changes correspond to the formation of borosilicate structural groupings, which are absent in the parent glass.

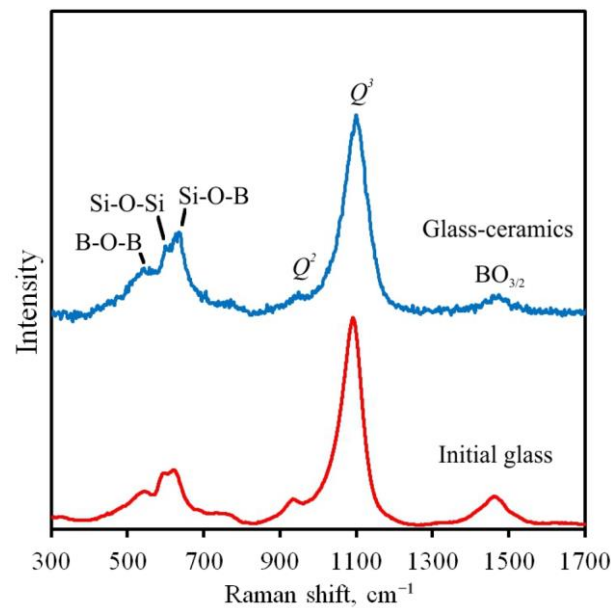


Figure 4. Raman spectra of the initial glass and an amorphous phase of the 1Na3Cs50 glass–ceramics.

Thus, a glass–ceramic sample was obtained by the peturgic method from sodium and cesium borosilicate glass with a ratio of $\text{Na}_2\text{O}/\text{Cs}_2\text{O}$ equal to 1/3. The synthesis of glass–ceramics was carried out according to the scheme in Figure 5. The formation of an orthorhombic crystalline phase CsBSi_2O_6 not matching the stoichiometric composition of the original glass resulted in a changed composition of the amorphous part of the glass–ceramic material.

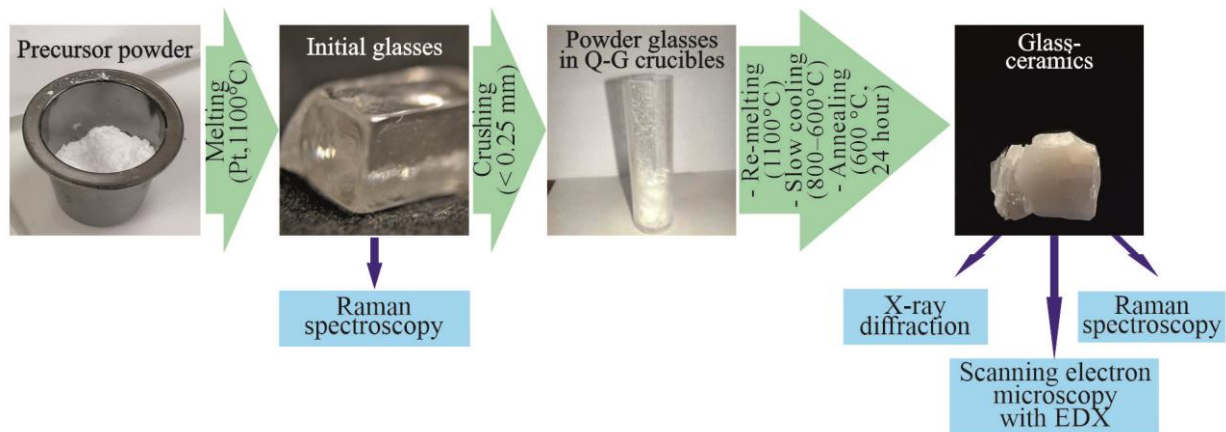


Figure 5. Scheme of glass–ceramic production by the peturgic method.

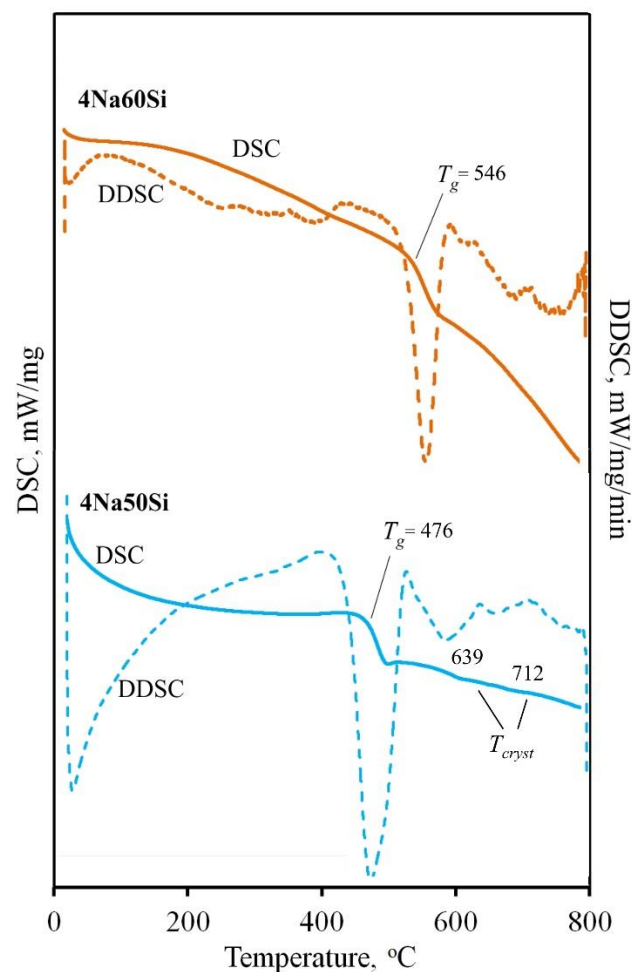
3.2. Powder Method

The powder method was the second approach applied to the synthesis of glass crystalline composites. Due to its excellent high-temperature resistance, flexible structure, and complex chemical composition, pyrochlore has attracted extensive attention as a potential matrix for immobilizing actinide nuclides [16]. A possible method for the neutralization of compounds of highly active radionuclides having a pyrochlore structure consists of encapsulating them in a glass matrix. In this work, the glass crystalline composite material was obtained by simple annealing from a mixture of glass powder of two compositions (Table 1) with natural pyrochlore $(\text{Na, Ca})_2\text{Nb}_2\text{O}_6(\text{OH, F})$.

Table 1. Composition of glasses synthesized for powder method.

Glasses	Na ₂ O, mol.%	B ₂ O ₃ , mol.%	SiO ₂ , mol.%
4Na50Si	30	20	50
4Na60Si	30	10	60

The results of the DSC of parent glasses, which show the influence of the composition on thermal characteristics, are given in Figure 6. The subsequent heat treatment mode was selected in accordance with the DSC data. The treatment temperatures were selected to be above the glass transition temperature T_g , but lower than the temperature of crystallization T_{cryst} . There are no obvious crystallization peaks in the DSC curves of the 4Na50Si and 4Na60Si glasses. However, if we examine the DDSC curves over time, peaks are visible at temperatures of 639 and 712 °C for 4Na50Si glass and 716 °C for 4Na60Si glass, respectively. Therefore, presumably, these temperatures correspond to the crystallization process.

**Figure 6.** DSC curves of borosilicate glasses indicating glass transition temperature.

Raman spectra of parent glasses 4Na50Si and 4Na60Si, which can demonstrate the influence of the composition on the structure, are given in Figure 7. Spectra have a broad band near low frequencies (400–700 cm^{-1}) with a maximum near 625 cm^{-1} for 4Na50Si glass. An increase in the Si content in glasses resulted in the bifurcation of this band. At the same time, there is a decrease in the bandwidth of 625 cm^{-1} , characteristic of the vibrations of B–O–Si bonds and the appearance of the band at 550 cm^{-1} in the Raman spectrum of 4Na60Si glass. The latter band is characteristic of Si–O–Si bond vibrations in the silicon–oxygen framework. In the midfrequency region, two main bands are observed, i.e., an intense band with a maximum of 1090 cm^{-1} and a weaker band of about 945 cm^{-1} ,

corresponding to vibrations of nonbridge oxygen atoms in silicon–oxygen tetrahedra Q^3 and Q^2 , respectively. The ratio of these bands varies in the spectra of glasses with an increase in the Si/B value from 2.5 to 6, which indicates a change in the ratio of the content of SiO_4 tetrahedra with two and three nonbridging oxygen atoms. A wide band with a maximum of about 1460 cm^{-1} , characteristic of the oscillation of borate triangles, is observed in the high-frequency region. Its intensity also depends on the Si/B ratio. From the interpretation of the Raman spectra of glasses 4Na50Si and 4Na60Si, it can be unambiguously concluded that the degree of polymerization of the silicate network, as well as borate, changes when the Si/B ratio changes against the background of a constant content of the modifier cation in the glass.

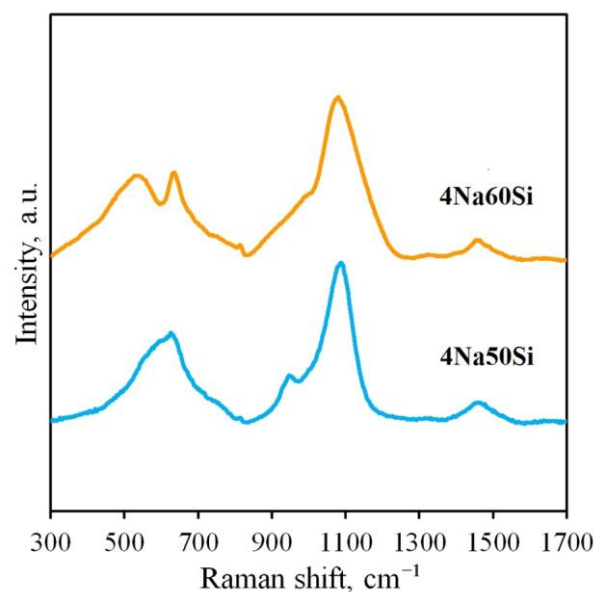


Figure 7. Raman spectroscopy of initial glasses showing differences in structure of glasses.

The next steps of the synthesis involved crushing to a grain size of less than 0.25 mm, mixing with pyrochlore crystals in a ratio of 4:1, tablet pressing at 200 bar, and subsequent annealing at $600\text{ }^{\circ}\text{C}$ for 2 h. The final samples of 4Na50Si-pcl and 4Na60Si-pcl glass crystalline composites were studied using scanning electron microscopy (Figure 8). Pieces of pyrochlore crystals can be observed in the formed glass-containing materials. It can be noted that, in the case of the 4Na50Si-pcl composition, the edges of the crystals are melted, whereas in the 4Na60Si-pcl sample, they remained sharp. Hence, it can be concluded that the annealing temperature regime of the second sample requires adjustment.

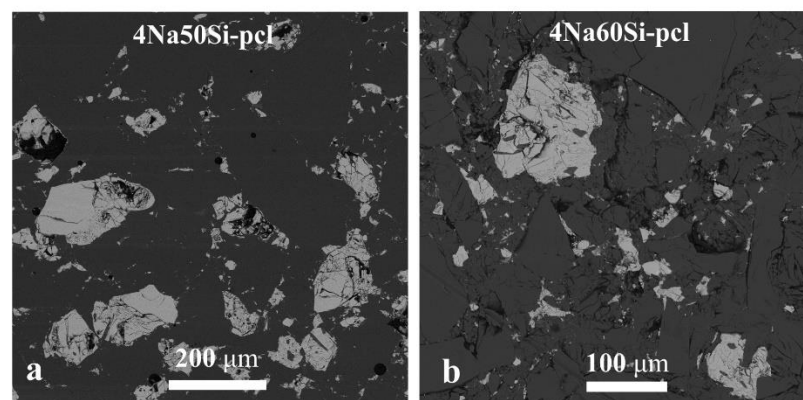


Figure 8. SEM images of 4Na50Si-pcl (a) and 4Na60Si-pcl (b) samples.

From the results of EDX spectroscopy, the elemental composition of the glass phase of the glass crystalline composite material corresponds to the composition prior to annealing. Thus, the applied synthesis mode does not affect the stability of the crystalline phase of pyrochlore but allows homogeneous glass to be obtained as a secondary matrix barrier, implying an optimal selection of the heat treatment mode. One thing that can be noted is that the 4Na0Cs60-pcl sample is characterized by its greater resistance to temperature, which is due to the peculiarities of the anionic structure. Accordingly, the synthesis of glass crystalline composites by the powder method can be carried out according to the scheme shown in Figure 9.

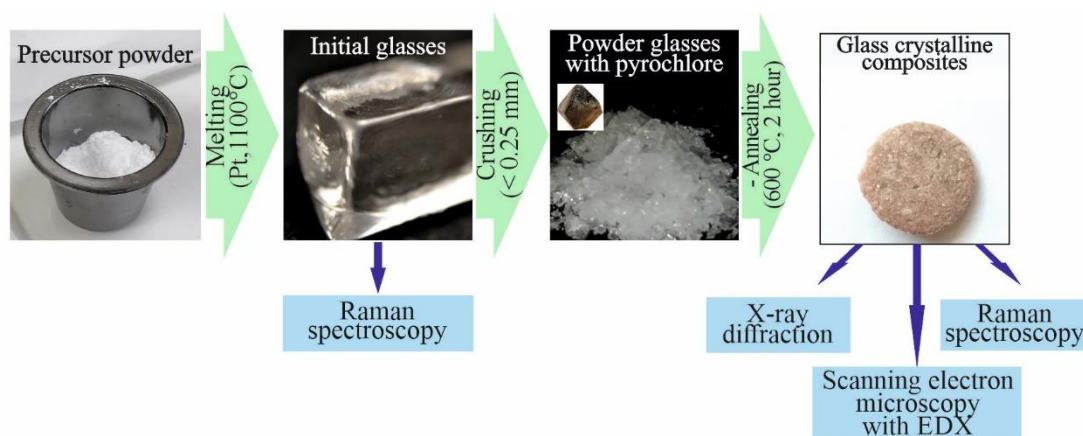


Figure 9. Scheme of glass crystalline composite production by the powder method.

3.3. Sintering of Impregnated Porous Glasses

Porous glasses were produced from initial glasses according to the phase separation method [11,17–20]. The composition of the initial synthesis glasses was as follows: M_2O —7.6 mol.%; B_2O_3 —39.9 mol.%; SiO_2 —42.5 mol.%; GeO_2 —10 mol.%, where $M = Na/K$ (Table 2). The ratios of sodium and potassium oxides were 0Na/1K, 1Na/2K, 1Na/1K, 2Na/1K, and 1Na/0K, respectively. Germanium oxide was added to this system in order to reduce the melting point of the charge. On the other hand, this was made for the convenience of comparing the results obtained by different synthesis approaches. We determined earlier that the addition of up to 14 mol.% of germanium oxide in the initial composition did not significantly affect the characteristics of porous glasses, since germanium atoms do not significantly affect the structure of the initial glass [21]. These conclusions were made based on the results of Raman spectroscopy of Na_2O – B_2O_3 – SiO_2 – GeO_2 glasses and the study of porous glasses by low-temperature adsorption/desorption nitrogen.

Table 2. Initial compositions of glasses.

Designation	The Content of Oxides, mol.%					Na_2O/K_2O
	Na_2O	K_2O	B_2O_3	SiO_2	GeO_2	
P2(0Na/1K)	0.0	7.6	39.9	42.5	10.0	0/1
P2(1Na/2K)	2.5	5.1	39.9	42.5	10.0	1/2
P2(1Na/1K)	3.8	3.8	39.9	42.5	10.0	1/1
P2(2Na/1K)	5.1	2.5	39.9	42.5	10.0	2/1
P2(1Na/0K)	7.6	0.0	39.9	42.5	10.0	1/0

The Raman spectra of the initial glasses are given in Figure 10. The changes in the structure of glasses were obtained according to the spectral forms. Here, changes in the borate network and germanate components were observed with composition changes. The boron structure of germanosilicate glasses was interpreted on the basis of studies of germanosilicate and borosilicate systems conducted earlier [22]. The wide band at about 460 cm^{-1} represents a superposition of bands corresponding to the vibrations of Si–O,

B-O, and Ge-O bridge bonds. The band appearing on the spectra of P2(1Na/2K) and P2(0Na/1K) glasses at about 590 cm^{-1} corresponds to the oscillation of six-coordinated germanium atoms. The bands at about 720 cm^{-1} , 770 cm^{-1} , and 800 cm^{-1} describe vibrations in the bonds in the metaborate, triborate, and boroxole groups, respectively. Lines 910 and 1070 cm^{-1} describe vibrations of nonbridging oxygen atoms in silicate tetrahedra Q^2 and Q^3 . Vibrations of B-O⁻ bonds in BO_3 triangles correspond to a broad band around $1300\text{--}1500\text{ cm}^{-1}$. It can be seen from any Raman spectrum in Figure 10 that the bands corresponding to vibrations of bridging Si-O bonds are characterized by a much greater intensity than those describing the nonbridging oxygen atoms in SiO_4 tetrahedra. Such a qualitative ratio of the intensity of the bands shows that the silicate network is characterized by a high degree of polymerization. At the same time, it can be noted that the band of about $1300\text{--}1500\text{ cm}^{-1}$ has an intensity higher than that of the bands corresponding to the vibrations of nonbridging oxygen atoms in the silicate network. Since the line in the high-frequency region describes vibrations of B-O⁻ bonds in BO_3 triangles, it can be concluded that the modifier cations (Na, K) coordinate the boron-oxygen network to a greater extent, which corresponds to the theory of porous glass synthesis [17,20].

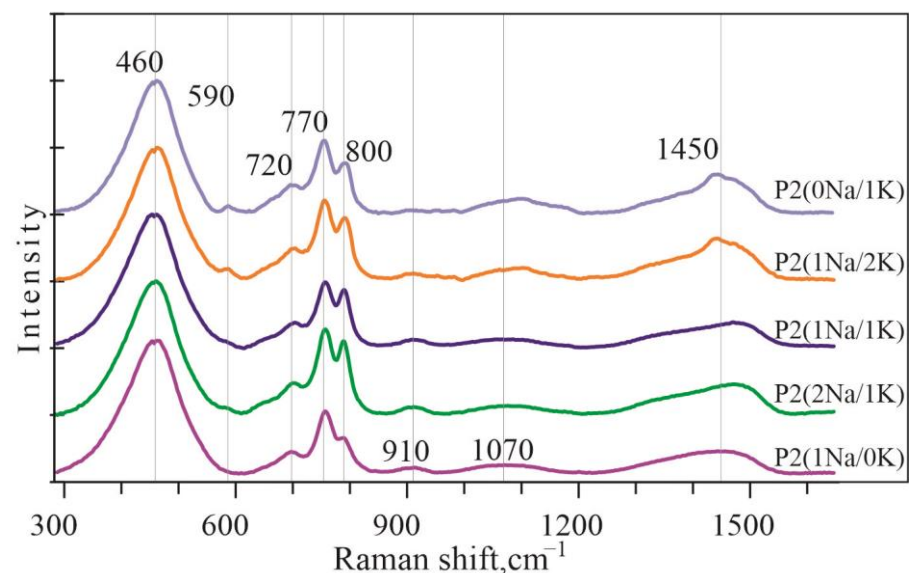


Figure 10. Raman spectra of initial glasses.

The synthesis scheme of impregnated porous glasses consists of melting of initial glasses, heat treatment, etching, impregnation, tableting, and annealing for pore consolidation. The processing modes were selected based on the literature and the experience of our previous studies [21,22]. The resulting porous materials were studied by the low-temperature nitrogen adsorption/desorption method. Nitrogen adsorption/desorption isotherms are shown in Figure 11. The common distinguishing features of all isotherms are a sharp rise in isotherms at low pressures, indicating the presence of micropores (pores smaller than 2 nm), and the horizontal shape of isotherms at high relative pressures, which indicates the absence of macropores in the structure of materials (pores larger than 50 nm). Adsorption isotherms for all porous glasses except P2(0Na/1K) have a hysteresis loop, which indicates the presence of mesopores (pores with sizes from 2 to 50 nm). At the same time, when potassium is added to the system, the hysteresis loop decreases. Since the P2(0Na/1K) porous glass isotherm has no hysteresis loop, this material can be classed as microporous. Based on this, it can be concluded that the mesoporosity of the resulting materials declines with the complete replacement of sodium by potassium in glasses.

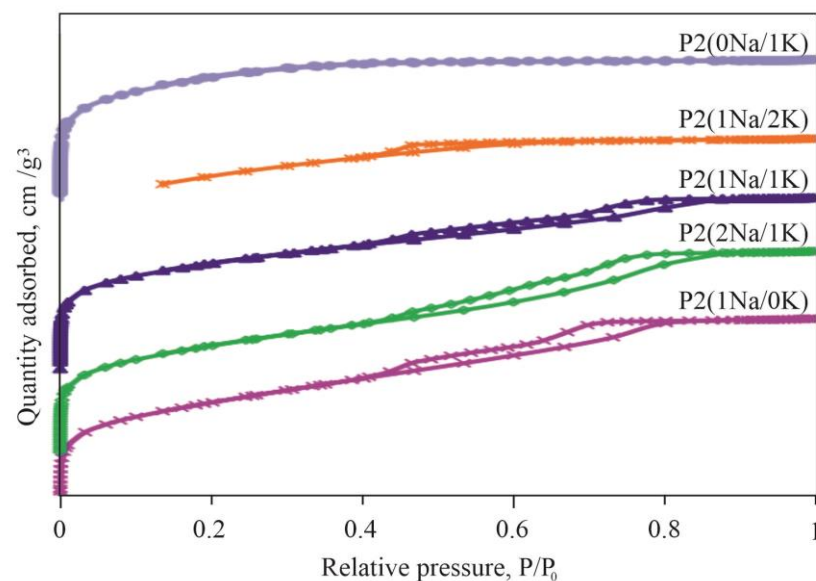


Figure 11. Isotherms of adsorption–desorption of nitrogen porous glasses.

All porous glasses have a sufficiently large volume of micropores. Pores with a diameter of up to 2 nm have a monomodal distribution, and the maximum for all materials is located at 0.95 nm. The volume of micropores also increases with an increase in the potassium content in the glasses. The maximum volume of micropores has a P2(0Na/1K) sample, while the minimum volume has a P2(1Na/0K) sample. The diameter of mesopores in the glasses can be estimated as 2–8 nm. It can be noted that porous glasses with a large amount of sodium have a large pore volume of this size, reaching a maximum in the P2(2Na/1K) sample. The volume of mesopores decreases significantly with an increase in potassium, and pores with a diameter of more than 2 nm are practically absent in P2(0Na/1K) glass.

The largest volume of mesopores, according to the results of the low-temperature adsorption/desorption of nitrogen, has a porous glass P2(2Na/1K). Based on this, we propose an example of the impregnation of P2(2Na/1K) porous glass with an aqueous solution of cesium nitrate as the most indicative. The image from a scanning electron microscope of P2(2Na/1K) samples is presented in Figure 12. Here, the microstructure of porous glasses is heterogeneous and spongy, while the particle size of the glass matrix is about 100 nm.

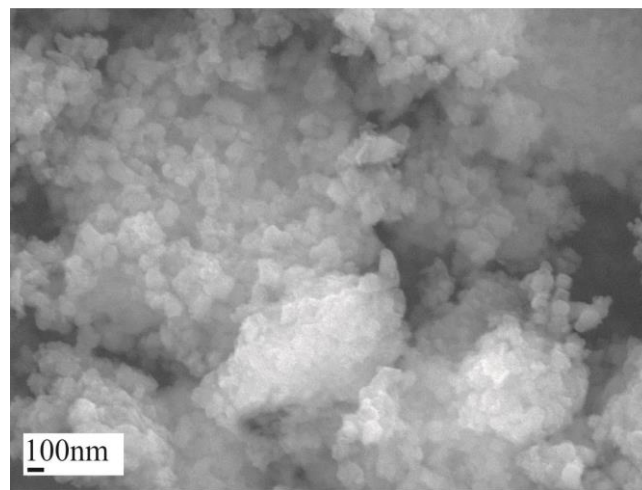


Figure 12. SEM image of porous glass P2(2Na/1K).

Porous glasses were impregnated in a cesium nitrate solution. Several stages concluding with alternating impregnation and drying for 1 h at a temperature of 110 °C were carried out. Tablets with a diameter of 1.8 cm were pressed. In the next step, the tablets were heat-treated to consolidate the pores and encapsulate cesium. Heating was carried out at a rate of 7 °C per minute, then exposure at 800 °C for 1 h. After that, the materials were taken out of the furnace for rapid cooling.

The distribution of cesium in the final material was determined using an electron microscope (Figure 13). Here, cesium is shown to be distributed fairly evenly over the volume of the matrix. According to the results of the EDX analysis, the cesium content in this material is about 3 at.%. Radiographs and Raman spectra of tablets after sintering were also obtained to clarify the form of cesium deposited in porous glass and exclude the crystallization of the matrix. The results of the XRD analysis and Raman spectroscopy of impregnating glasses and examples of spectra are shown in Figures 14 and 15, respectively. The crystalline phase in the matrix is observed against the background of a large halo corresponding to the amorphous phase. Accordingly, the radiographs peaks can be attributed to the crystalline phase of cesium nitrate.

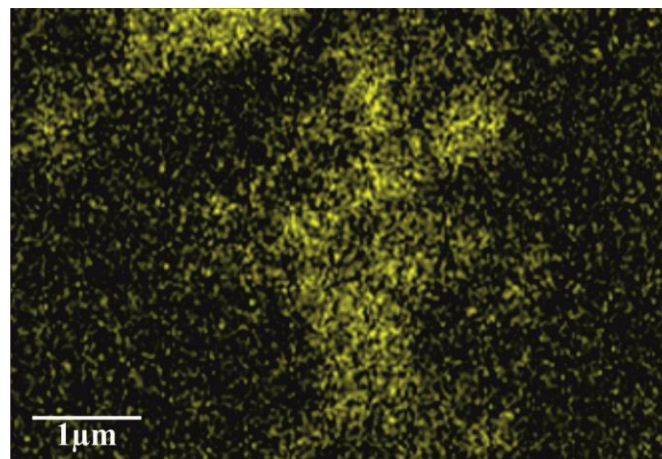


Figure 13. Cs distribution map of impregnating porous glasses of composition P2(2Na/1K).

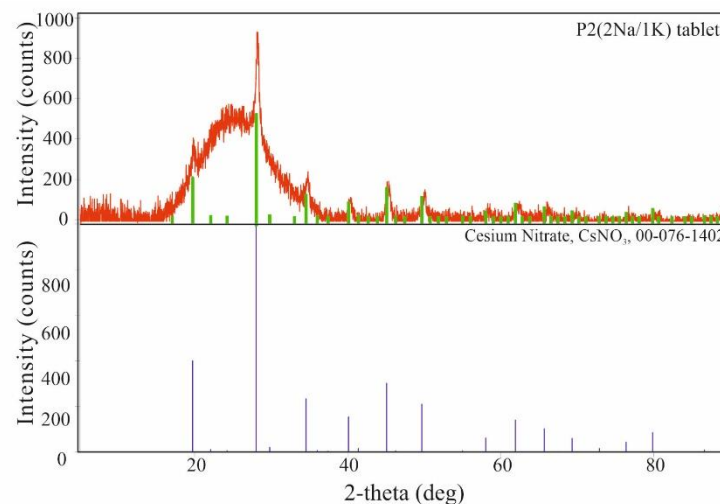


Figure 14. Radiographs of sintered porous glasses of P2(2Na/1K) composition impregnated by Cs.

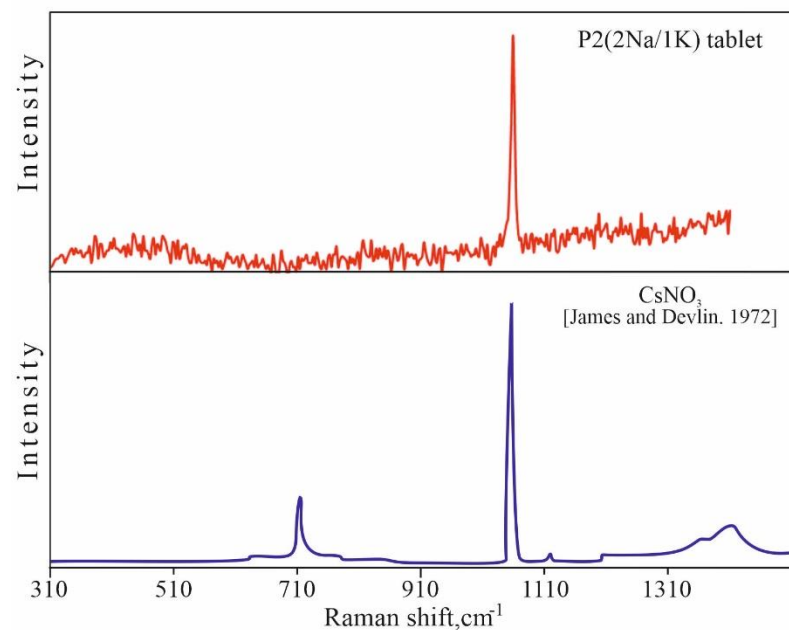


Figure 15. Raman spectrum of sintered porous glasses of P2(2Na/1K) composition impregnated by Cs compared to the spectrum of CsNO_3 [James and Devlin, 1972].

Samples of glass crystalline composite were obtained by the impregnated porous glass sintering method. The compositions and regimes of synthesis, annealing, etching, saturation, and sintering were selected according to the scheme shown in Figure 16.

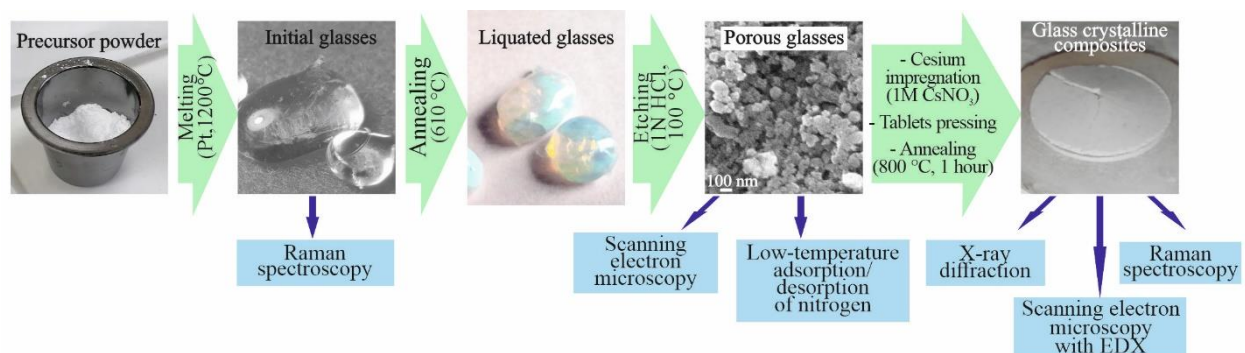


Figure 16. Scheme of glass crystalline composite production using sintering of impregnated porous glasses method.

4. Conclusions

A variety of matrix materials and techniques is available for the immobilization of radioactive waste materials. However, the choice of immobilization technology depends on the physical and chemical nature of the waste and the acceptance criteria for the long-term storage and disposal facility to which the waste will be consigned. Three different approaches for producing glass-containing materials with simulators of radioactive nuclides were selected and tested: the petrugic method, the powder method, and the sintering of impregnated porous glasses method. Synthesis, annealing, etching, saturation, and sintering regimes were selected along with the compositions. The structure and properties of the initial glasses and resulting materials were studied. The powder XRD pattern and Rietveld refinements showed that CsBSi_2O_6 is the main crystalline phase in the $1\text{Na}3\text{Cs}50$ glass crystalline composite prepared by the one-step slow-cooling petrugic method. In the case of the powder method, the $4\text{Na}60\text{Si}$ -pcl sample is characterized by greater resistance to temperature than the $4\text{Na}50\text{Si}$ -pcl sample, which is due to the peculiarities of the anionic structure. Glass-containing materials obtained by the sintering of impregnated porous glass

are characterized by a fairly even distribution of cesium over the volume of the matrix. In all the obtained materials, the characteristics of the crystalline phase and the glassy matrix were determined. Finally, three developed schemes of synthesis and study of glass–ceramic and glass crystalline composite materials were presented, which can be finalized in the future in accordance with the tasks and conditions.

Author Contributions: Conceptualization, O.N.K. methodology, L.A.N., N.M.K. and O.N.K. investigation, L.A.N. and N.M.K., writing—original draft preparation, O.N.K., visualization, L.A.N. and N.M.K.; supervision, O.N.K.; project administration, O.N.K.; funding acquisition, O.N.K. All authors have read and agreed to the published version of the manuscript.

Funding: This work was supported by a grant from the Russian Science Foundation No. 22-17-20005 (<https://rscf.ru/project/22-17-20005/> accessed on 31 October 2023).

Data Availability Statement: Data are available upon reasonable request from the authors.

Acknowledgments: This work was supported by a grant from the Russian Science Foundation No. 22-17-20005 (<https://rscf.ru/project/22-17-20005/> accessed on 31 October 2023). The analysis of spectroscopic data was performed by O.N.K. within the Project of the State Assignment (Vernadsky Institute of Geochemistry and Analytical Chemistry of Russian Academy of Sciences, Moscow, Russian Federation).

Conflicts of Interest: The authors declare no conflict of interest.

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