

Cs containing borosilicate waste glasses

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Vitrification has been recognized as the best method of the neutralization and immobilization of the radioactive and toxic waste. Toxic elements are introduced into the structure of chemically durable glasses (waste glass). $\text{SiO}_2\text{-B}_2\text{O}_3\text{-Al}_2\text{O}_3\text{-Na}_2\text{O}$ glass is one of the most commonly used waste glass. Radioactive ^{137}Cs is often a dangerous contaminant of hospital and laboratory waste. Incineration of these waste and vitrification of ash by its co-melting with borosilicate glass is the perspective method of immobilization of this nuclide for safety waste storing. The influence of the partial substitution of Na by Cs and of the introduction of CaO as the main waste incineration ash component in the $\text{SiO}_2\text{-B}_2\text{O}_3\text{-Al}_2\text{O}_3\text{-Na}_2\text{O}$ waste glass on the change of its structure, crystallization ability, and physical properties were studied.

Keywords: waste glass, cesium borosilicate glass, cesium immobilization, glass crystallization.

1. Introduction

High level radioactive wastes (HLW) from both the nuclear power industry and military nuclear programmes are currently immobilized by vitrification. Borosilicate glass is providing the very suitable medium for the majority of the species present in these wastes [1, 2]. It prevents leaching of radio nuclides by water-immobilization effect. Environment protection and increase in disposal costs make that vitrification of the low level nuclear waste (LLW) is lately beginning to gain favour [3].

The LLW resulting from the use of radioactive isotopes in medicine, industry, laboratories and other purposes can be immobilized by vitrification. The management of such waste begins with combustion reducing their amount. The obtained ash, containing radio isotopes, is suitable for vitrification and ceramization by incorporating it into the composition of boro-aluminosilicate glass (the radio isotopes are similar to those used in nuclear power industry). The ash is mixed with glass powder and sintered or remelted at 1100–1300 °C [4, 5].

2. The aim of the investigations; materials and methods

In Poland, the waste resulting from the use of radioactive isotopes in medicine, industry, laboratories and other purposes, requires immobilization on an advanced

Table. The chemical composition of the investigated glasses.

Chemical composition [mass%]	Glass 1	Glass 2	Glass 3	Glass 4
SiO ₂	48.5	48.5	56	56
B ₂ O ₃	7.5	7.5	15	15
Al ₂ O ₃	8	8	8	8
CaO	18	18	—	—
Na ₂ O	18	13	21	16
Cs ₂ O	—	5	—	5

level. These are wastes which, to a great extent, can be subjected to the combustion process, and they comprise, among other things, linguine, rags, protective gloves, paper, plastic, syringes, glass, foil *etc.* Laboratory and hospital waste represents 77% of all volume of the low level waste. ¹³⁷Cs is one of their characteristic contaminants. The total radioactivity of waste of this type is about 7.5 GBq [6].

As the subject of investigations, the determination of the influence of Cs as a characteristic component of ash after combustion of the waste on the structure and properties of borosilicate glass has been chosen. The effect of introducing Cs₂O or Cs₂O and CaO on the properties of boro-aluminosilicate glasses is little known, as it is not used in traditional glass manufacturing.

These components have different crystallochemical parameters. Cesium is characterized by great ionic radius $r_{Cs} = 1.74 \text{ \AA}$ and by the coordination number in relation to oxygen CN = 8. Its ionicity of chemical bond with oxygen, according Görlich, is $i_G = 0.832$. Thus, it is considerably different from Na which shows $r_{Na} = 1.02 \text{ \AA}$, and CN = 6 in relation to oxygen and the ionicity of bond with oxygen Na–O, $i_G = 0.870$. The ionic radius of Ca²⁺ at CN = 6, $r_{Ca} = 1.00 \text{ \AA}$, and ionicity Ca–O bond $i_g = 0.707$ [7].

The chemical composition of the applied base glass is shown in the Table (glass 3). CaO is added to the composition of glasses 1 and 2 as it is a characteristic component of ash obtained from paper combustion. The other ash components: SiO₂, Al₂O₃ are already present in the base glass composition. In these glasses a part of Na₂O (5 mass%) is replaced by Cs₂O (glasses 2 and 4).

The glass batch components: quartz sand, and chemical grade calcium carbonate, aluminum oxide and cesium carbonate were mixed, and the batch was melted at 1200 °C for 2 hours in an alumina crucible, cooled and crushed into particles of suitable size.

Glass thermal transformation was studied by differential scanning calorimetry (DSC) method. Measurements were carried out using Perkin Elmer DTA/DSC – 7 heat flow differential scanning calorimeter. Pure Al and Au were used for temperature and heat calibration. The powdered glass samples, of 0.1–0.3 mm grain size fraction, weighing 40–80 g, were heated in platinum containers, in nitrogen atmosphere, at the rate 10 °C/min. Obtained DSC curves indicate a heat flow (mW)

change vs. sample temperature ($^{\circ}\text{C}$). The transformation temperature T_g was measured at the half of the specific heat capacity change step, registered on DSC curve. The value of the specific heat capacity change ΔC_p ($\text{J g}^{-1} \text{K}^{-1}$), accompanying glass transformation, corresponds to the difference between C_p at the temperature of transformation step onset and C_p at offset temperature. It was calculated using Perkin Elmer Pyris Thermal Analysis Software Library programme.

Phase composition of crystallized glass was investigated by X-ray diffractometry (XRD) using DRON 1.5 apparatus and $\text{Cu K}\alpha$ radiation. Fourier transform infrared (FTIR) spectroscopy, scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS) were applied in glass thermal transformation study. Glass samples, heat treated at characteristic temperatures indicated by DSC curves, were the subject of investigations.

3. Results

The obtained investigation results have shown that the introduction of a relatively small amount of Cs_2O (5 mass%) instead of Na_2O induces considerable changes in the structure and the thermochemical properties of boroaluminosilicate $\text{Na}_2\text{O}-\text{B}_2\text{O}_3-\text{Al}_2\text{O}_3-\text{SiO}_2$ glass.

FTIR spectrum of $\text{Na}_2\text{O}-\text{B}_2\text{O}_3-\text{Al}_2\text{O}_3-\text{SiO}_2$ glass is characterized by an intensive band of Si-O-Si bridges of silicate network at 1000 cm^{-1} , 729 cm^{-1} , and a band 1407 cm^{-1} of $[\text{BO}_3]$ groups which occur in its structure. The band connected with

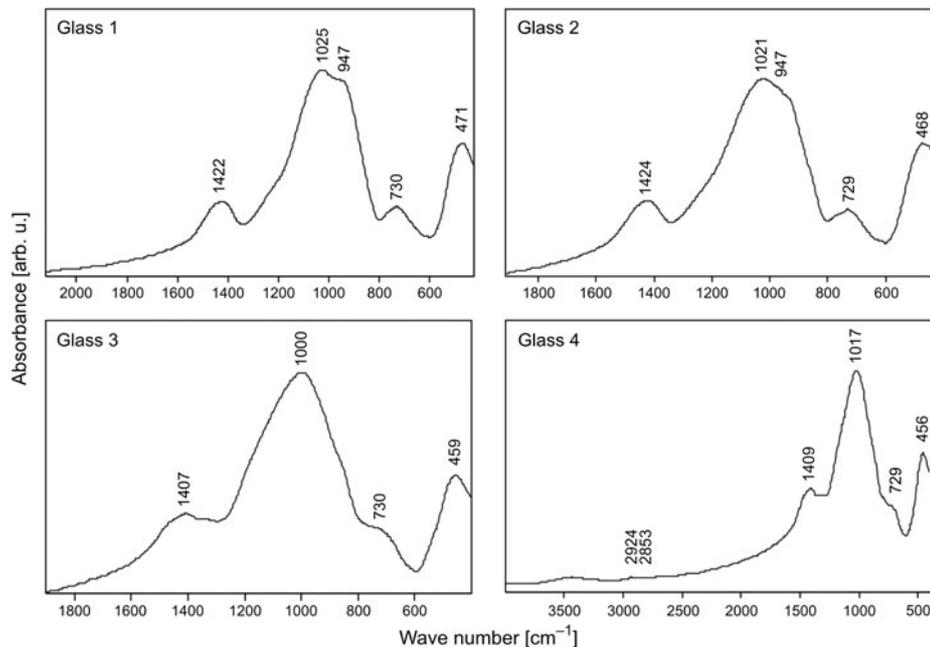


Fig. 1. FTIR spectra of investigated glasses.

the cation modifier Na^+ occurs at 458.8 cm^{-1} (Fig. 1, glass 3). The introduction of Cs_2O causes the shifting of the main band to 1017 cm^{-1} and the glass modifiers band to 455.9 cm^{-1} . It means that the presence of Cs^+ influences the increase of the degree of polymerization of the network (Fig. 1, glass 4).

The introduction of Ca into the glass causes the appearance (besides the Si–O–Si band (1021 cm^{-1})) of the band at 946 cm^{-1} (Fig. 1, glasses 1 and 2), which is characteristic of silicate and aluminate glasses containing calcium [8], and it indicates that in the network form the domains containing this element. In the similar way, the shifting of the band $[\text{BO}_3]$ to 1422 cm^{-1} may be interpreted. The band connected with the cation modifiers also shifts to 471 cm^{-1} . This means that the presence of Cs_2O , even in the amount of 5 mass%, causes the modification of the glass structure. It is stronger when Cs_2O and CaO are introduced simultaneously; then, the degree of polymerization of the silicate network increases, which is observed as the shifting of the band Si–O–Si toward higher values (from 1000 to 1021 cm^{-1}).

The effect of additions to the $\text{Na}_2\text{O}-\text{B}_2\text{O}_3-\text{Al}_2\text{O}_3-\text{SiO}_2$ glass on its thermochemical properties is demonstrated by the DSC curves (Fig. 2). The glass shows a broad double effect on the plateau above the transformation step, which is an indication of the low degree of chemical homogeneity of the glass structure. Just after that there appears a poor effect of crystallization. The addition of CaO does not change T_g , but it increases the change in the specific heat capacity ΔC_p accompanying the glass transformation, the value of which can be the index of the structural changes accompanying the transformation (number and force of the broken bonds, components rearrangement) [9]. ΔC_p of glass 3 and CaO containing glass 1 have values of $0.718 \text{ Jg}^{-1} \text{ K}^{-1}$ and $0.887 \text{ Jg}^{-1} \text{ K}^{-1}$, respectively. The addition of Cs_2O increases T_g

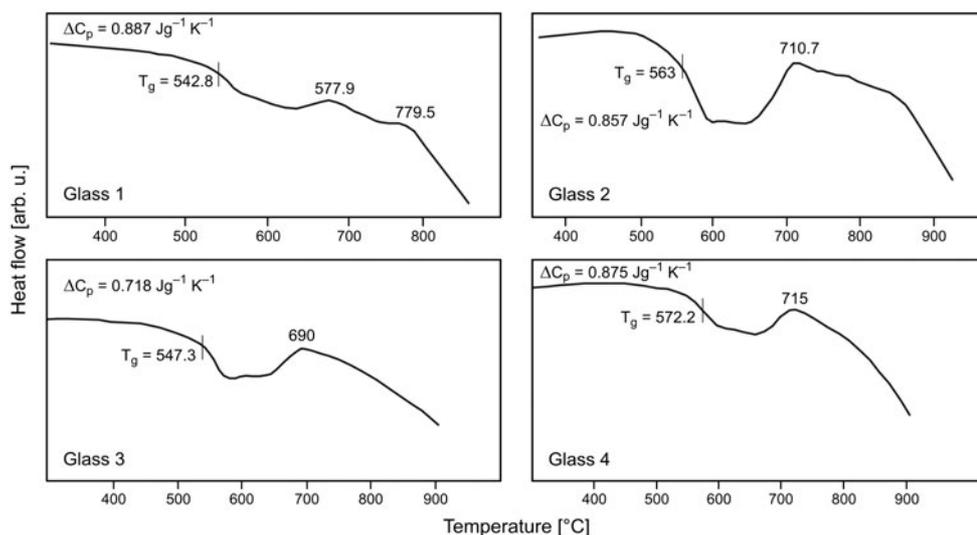


Fig. 2. DTA curves of glasses.

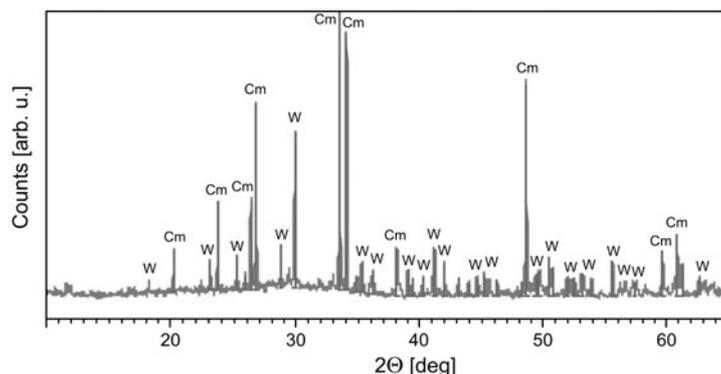


Fig. 3. X-ray pattern of glass 1 heated at 780 °C (Cm – columbeite $\text{Na}_4\text{Ca}_2(\text{Si}_6\text{O}_{18})$, W – wollastonite CaSiO_3).

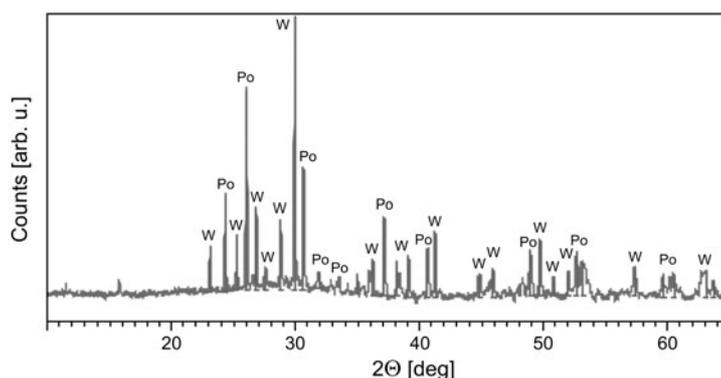


Fig. 4. X-ray pattern of glass 2 heated at 715 °C (Po – pollucite $\text{Cs}(\text{AlSi}_2\text{O}_6)$, W – wollastonite CaSiO_3).

of the basic glass (Fig. 2, glass 3), and ΔC_p of the transformation value increases from $0.718 \text{ Jg}^{-1}\text{K}^{-1}$ to $0.875 \text{ Jg}^{-1}\text{K}^{-1}$ for Cs_2O containing glass 1. The temperature of the DSC crystallization peak increases from 690 °C to 715 °C (Fig. 2). The presence of Cs_2O in glass containing Ca contributes also to the increase in T_g and ΔC_p of the transformation. In general, the replacement of a part of Na by Cs, especially together with the introduction of Ca, increases the thermal stability of the primary glass structure, which is in agreement with its modification indicated by the changes in FTIR spectra.

Moreover, the introduction of Ca^{2+} increases the glass tendency to crystallization above the temperature of transformation T_g . As the first, at 690 °C, *i.e.*, at the stage of glass softening, the ring silicate $\text{Na}_4\text{Ca}_4[\text{Si}_6\text{O}_{18}]$ (columbeite) is formed and at 780 °C the wollastonite CaSiO_3 crystallizes (Fig. 3). The introduction of Cs_2O changes the course of crystallization, which becomes a single stage crystallization; then, pollucite $\text{Cs}[\text{AlSi}_2\text{O}_6]$ with wollastonite crystallize (Fig. 4).

In calcium-free base glass (the Table, glass 3) the high temperature variety of quartz stabilized by Al and Na admixtures and nepheline $\text{Na}[\text{AlSiO}_4]$ crystallizes. The presence of Cs_2O increases the temperature of crystallization and increases its intensity.

SEM investigations and EDS spectra have confirmed the results of XRD studies. According to EDS in the basic calcium-free glass, Cs is incorporated as an admixture into the structure of the newly formed crystal phases (high quartz and nepheline). In CaO containing glass, Cs is localized in wollastonite and pollucite structure.

Crystal phases in which Cs is present as a chemical durable increase the Cs immobilization ability of the material, thanks to introducing it into their structure.

Observations of the behavior of glass samples in a heating microscope show that the introduction of Cs_2O into the glass increases a little its softening as well as the melting temperature, whereas it reduces the flow temperature, which means faster depolymerization of the network resulting in the drop in the molten glass viscosity at high temperatures. The presence of CaO makes flowing interval longer. It is the effect of the stiffening of the primary structure of the glass. Crystallochemical parameters of Ca^{2+} ($r_{\text{Ca}} = 1.00 \text{ \AA}$, $\text{CN} = 6$, $i_g = 0.707$) cause that it forms more covalent and less flexible bonds with Si^{4+} through the oxygen bridge than Na^+ and Cs^+ . It means that oxide bridges in the glass structure become more rigid but at the same time more susceptible to breaks, what is the result of the network de-polymerization effect. Diminishing of viscosity, visible as flowing of the sample, is the result of this.

4. Conclusions

The introduction of Cs into the basic glass $\text{Na}_2\text{O}-\text{B}_2\text{O}_3-\text{Al}_2\text{O}_3-\text{SiO}_2$ (waste glass) in order to immobilize its radioactive isotope induces changes in the structure and in the properties of the glass. This results from considerable crystallochemical differences between Cs^+ and Na^+ as the glass structure modifiers. In the presence of even a relatively small amount of Cs_2O (5 mass%) the degree of polymerization of the glass network and its stability increase, which means, simultaneously, the increase in the chemical durability of the glass. On the other hand, above the glass transformation temperature T_g , cesium acts as the strong depolymerizer of network, increasing the tendency to crystallization of the basic glass. It becomes incorporated into the structure of the newly formed crystal phases such as the chemically resistant aluminosilicates (pollucite, nepheline). Similar changes are induced by the introduction of CaO into the glass. It confirms and explains the suitability of borosilicate glass to inactivate the hospital and laboratory waste incineration ashes contaminated with radioactive ^{137}Cs demonstrated in [4].

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