

Thermal properties of vitrified llw hospital waste incineration ash

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Abstract The low level nuclear waste (LLW) resulting from the use of radioactive isotopes in medicine, industry, laboratories, and other purposes can be immobilized by vitrification, using methods applied in the nuclear power industry. Borosilicate glass is providing the very suitable medium for the majority of the species present in these wastes. Management of LLW waste begins with combustion reducing their amount. The paper presents the results of model studies of vitrification of hospital waste by incorporating it into the composition of boro-aluminosilicate glass, similar to those used in nuclear power industry. The proposed borosilicate waste glass composition was: SiO₂-56.0, B₂O₃-15.0, Na₂O-21.0, and Al₂O₃-8.0 (mass %). The ashes were mixed in different amount with the glass frit and then remelted to obtain homogenous melt which was vitrified. The influence of the main ash components on the thermal properties of the vitrified waste was studied using DSC and heating microscopy methods. The glass transformation, crystallization and melting temperatures, and Hruby glass stability against crystallization parameter were determined. The correlations between ΔC_p , T_g , and K_H were observed and discussed.

Keywords LLW waste · Thermal properties · Borosilicate glass · Thermal stability

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Introduction

High level radioactive wastes from both the nuclear power industry and military nuclear programs are currently immobilized by vitrification. Borosilicate glass is providing the very suitable medium for the majority of species present in these wastes [1, 2]. It prevents leaching of radio nuclides by water—an immobilization effect. Environment protection and increase of disposal cost make that vitrification of the low level nuclear waste (LLW) lately is also finding favor [3].

The LLW resulting from the use of radioactive isotopes in medicine, industry, laboratories, and other purposes can be immobilized by vitrification. Immobilization of such waste begins with combustion reducing their amount. According to [4] paper, PCV, and cotton combustion ash containing radio isotopes are suitable for vitrification and ceramization by incorporating it into the composition of boro-aluminosilicate glass, 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].

The most durable matrix for waste vitrification would be pure silicate glass, but melting temperature of this glass is too high. Therefore glass composition is a compromise between glass durability and economics. As the primary choice of material for the immobilization of nuclear waste have become borosilicate glasses. They are characterized by a good glass-forming ability, chemical durability, thermal stability, and ability to incorporate many different kinds of waste elements. Among them the most frequently used are sodium borosilicate glasses with addition of other oxides like alumina, calcia and so on [1, 2].

The paper presents results of the studies of thermal properties of vitrified ash from hospital waste incineration plant with a borosilicate glass.

Table 1 Chemical composition of the hospital waste incineration ash (HWA), the base borosilicate glass (BS) and the vitrified products (BS10W, BS20W, BS30W, BS40W and BS50W)/mass %

Oxide	HWA/mass %	BS/mass %	BS10W/mass %	BS20W/mass %	BS30W/mass %	BS40W/mass %	BS50W/mass %
SiO ₂	22.2	56.0	52.6	49.2	45.9	42.5	39.1
B ₂ O ₃		15.0	13.5	12	10.5	9	7.5
Al ₂ O ₃	13.5	8.0	8.5	9.1	9.6	10.2	10.7
Na ₂ O	1.0	21.0	19.0	17.0	15.0	13.0	11.0
CaO	40.0		4.0	8.0	12.0	16.0	20.0
Fe ₂ O ₃	8.0		0.8	1.6	2.4	3.2	4.0
SO ₃	4.5		0.45	0.90	1.35	1.80	2.25
TiO ₂	3.0		0.30	0.60	0.90	1.20	1.5
P ₂ O ₅	2.6		0.26	0.52	0.78	1.04	1.3
Cr ₂ O ₃	1.0		0.10	0.20	0.30	0.40	0.5
Others	4.2		0.49	0.88	1.27	1.66	2.15

Experimental

The chemical composition of the base borosilicate glass applied in experiment was SiO₂-56.0, B₂O₃-15.0, Al₂O₃-8.0, and Na₂O-21.0 mass %.

The glass was obtained by melting of batch composed of quartz sand, Na₂CO₃, boric acid, and aluminum oxide of chemical grade purity. Then was melted at 1473 K for 2 h in an alumina crucible, cooled, and crushed into 0.3–0.1 mm grain size.

The obtained glass frit was mixed with ash from hospital waste incineration plant in Krakow (Poland). The mixtures were melted at 1473 K for 2 h in an alumina crucible and vitrified. The glass to the ash ratio was 10, 20, 30, 40, and 50 mass % and samples were designated BS10W, BS20W, BS30W, BS40W, and BS50W, respectively. The chemical composition of the ash, glass, and vitrified product is presented in Table 1.

Heating microscopy thermal analysis was carried out using compacted powder samples of cubic shape. Powdered samples prepared by milling of bulk samples in a ball mill were wetted in ethanol and compacted to cubes of 3 × 3 × 3 mm by a hand press. The changing of the samples' shape was conducted by Carls Zeiss MH01 microscope at heating rate 8 K min⁻¹. Data of the sample height were collected at intervals of 10 K during the experiment, and shrinkage curves were obtained. The beginning of sintering process temperature T_s as the onset of densification was determined from the shrinkage curve. The half sphere temperature T_{hs} which was the temperature at which the height of the sample was half the width of the base, the flow temperature T_f which was the first temperature at which the sample was melted to a third of its original height were observed.

Glass transformation T_g at the half of the specific heat capacity change step, crystallization T_C as the onset of the

first crystallization peak and melting T_m as the onset of the first melting peak temperatures were measured by differential scanning calorimetry (DSC) method at the heating rate 7 K min⁻¹. 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. Value of specific heat capacity change ΔC_p (J g⁻¹K⁻¹), accompanying glass transformation was determined using Perkin Elmer Pyris Thermal Analysis Software Library program.

Results and discussion

The shrinkage curve of the base borosilicate glass is presented in Fig. 1. Between 880 and 1000 K the first shrinkage is observed. In this region sample dimensions decrease, but the shape remains unchanged. This is the sintering stage ($T_s = 911$ K). Over 1000 K the sintering process is finished the maximum of densification is achieved and observed a plateau on the curve. The sample dimension persists unchanged. As the temperature increases the liquid phase appears on the surface of the sample which is observed as a smoothing and rounding of the corners (about 1050 K). Beyond this point the sample starts to behave like a liquid, begins the melting process, its viscosity decreases with temperature, a round sphere shape is formed, and the second shrinkage step on the curve (Fig. 1) is observed. The specimen shape becomes first spherical than semispherical ($T_{hs} = 1133$ K) until final melting point, the flow temperature ($T_f = 1200$ K) is achieved. All the investigated samples behave in the same manner with the short plateau on the shrinkage curve and melting like a typical glass (exhibits spherical shapes) what is the evidence of their low crystallization ability. The sintering, half sphere, and flow temperatures of the examined materials are presented in Table 2.

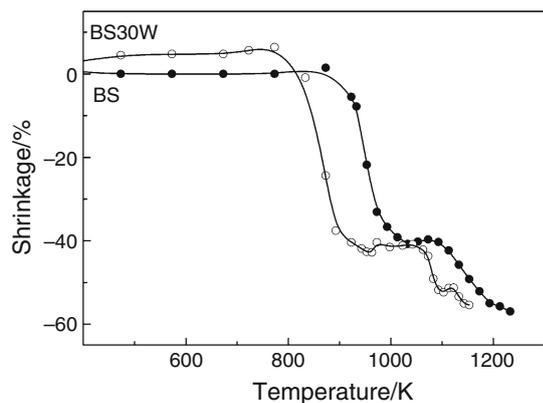


Fig. 1 Shrinkage curves of the BS and BS30W samples

Table 2 The sintering (T_s /K), half sphere (T_{hs} /K) and flow (T_f /K) temperatures

Sample	T_s /K	T_{hs} /K	T_f /K
BS	911(5)	1130(5)	1200(5)
BS10W	906(5)	1050(5)	1130(5)
BS20W	889(5)	1040(5)	1110(5)
BS30W	887(5)	1070(5)	1150(5)
BS40W	889(5)	1070(5)	1150(5)
BS50W	898(5)	1060(5)	1150(5)

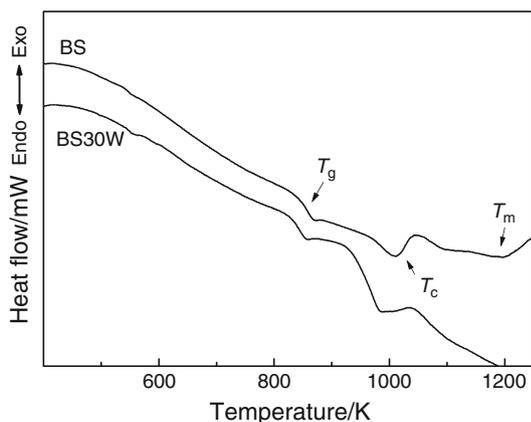


Fig. 2 DSC curves of the BS and BS30W samples

The sintering temperature is slightly reduced from above 900 K to about 890 K when the ash is added up to 20 mass % quantities and for higher waste concentrations the temperature is almost constant. In the similar way behave both T_{hs} and T_f —temperatures.

The effect of addition of ash 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. An exemplary DSC curve for the base glass is presented in Fig. 2. The glass shows a broad effect on the plateau above the transformation step,

Table 3 The transformation (T_g /K), crystallization (T_c /K), melting (T_m /K) temperatures, (ΔC_p /J $\text{g}^{-1}\text{K}^{-1}$), Hruby's parameter (K_H)

Sample	T_g /K	T_c /K	T_m /K	ΔC_p /J $\text{g}^{-1}\text{K}^{-1}$	K_H
BS	858(5)	1028(5)	1163(5)	0.26(2)	1.26
BS10W	846(5)	1007(5)	1166(5)	0.27(2)	1.01
BS20W	842(5)	995(5)	1174(5)	0.36(2)	0.85
BS30W	840(5)	995(5)	1179(5)	0.32(2)	0.84
BS40W	835(5)	995(5)	1193(5)	0.41(2)	0.80
BS50W	838(5)	997(5)	1189(5)	0.38(2)	0.82

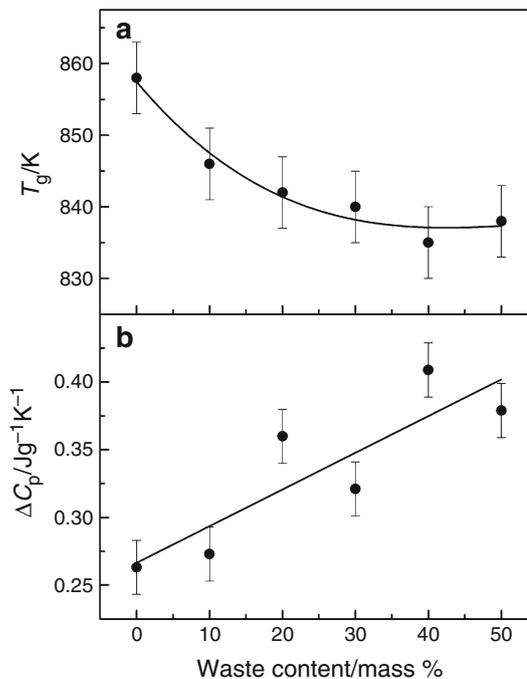


Fig. 3 Transformation temperature T_g (a) and the specific heat capacity ΔC_p accompanying the glass transformation (b) as the waste content function

which is indication of the low degree of chemical homogeneity of the glass. Just behind there appears a poor effect of crystallization and then melting process occurs. The similar curves are observed for the rest of the measured samples. The obtained transformation, crystallization, and melting temperatures for all of the investigated materials are presented in Table 3.

Influence of the ash content on transformation temperature T_g is presented in Fig. 3a. The T_g —temperature is reduced with the ash addition. According to previous studies [6] this effect should not be connected only with replacing Na_2O by CaO , which is the main ash component in the glass structure. On the other hand, addition of the ash to the glass is causing decrease of the number of network forming cations which leads to reduction of the directional covalent bonds and at the same time increase the

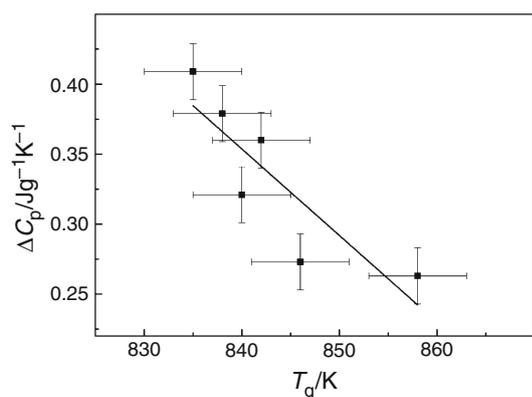


Fig. 4 Specific heat capacity change ΔC_p as the transformation temperature T_g function

proportion of ionic bonds and broken network oxide bridges. On the other hand increasing number of ionic bonds indicate that the structure becomes more flexible, cations could move easier and decomposition of the structure could take place in a lower temperatures leading to reduction of the T_g [7].

The ash increases the change of the specific heat capacity ΔC_p accompanying the glass transformation.

(Fig. 3b), the value of which can be the index of the degree of structural changes accompanying the transformation (number and force of the broken bonds, components rearrangement). As was previously observed [7, 8] change of the modifier cation e.g., replacement of sodium by calcium is connected with increase of the ΔC_p value which forms a less ionic bonds with oxygen than sodium.

DSC curve with its coordinate dH/dT , and $T(t)$ where H —enthalpy, T —temperature and t —time, makes possible to measure ΔC_p $Jg^{-1}K^{-1}$ at T_g temperature accompanying the glass transformation, it is transition from glass as solid body to its visco-elastic state at T_g temperature. It can be used as an indicator of the configuration entropy change connected with degree of the glass structure rebuilding at T_g temperature and its energetic measure supplementing the molar volume ΔV $cm^3 mol^{-1}$ and viscosity change as the internal structure rebuilding characteristics [8, 9]. Usefulness of the ΔC_p of glass transition in the structural consideration was confirmed several times [7, 10].

As was mentioned above introduction of the ash to the glass structure reduces the number of covalent bonds. These bonds because of its directional nature could lead to higher internal structural strains. The strains may cause the cracking of the bonds, what is less probable in the case of bonds of high ionicity. More the internal strain the higher energy is accumulated in the glass network and lower energy is needed to break the bonds at the glass transition temperature. It is supported by the fact that the transition of a pure silicate glasses take place with the very small

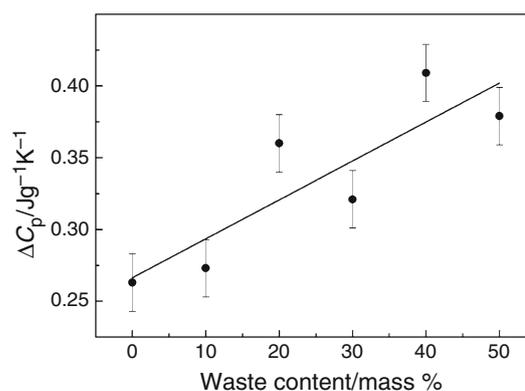


Fig. 5 The Hruby parameter K_H as the waste content function

change in C_p [8]. Thus increase in ΔC_p with the ash (modifiers) concentration is observed (Fig. 3b).

It is interesting to notice in case of the investigated glasses exist a relation between the glass transition temperature T_g and the specific heat capacity change ΔC_p accompanying this transition (Fig. 4). The lower T_g temperature and higher the ΔC_p value is the case with the high concentration of the glass network modifiers and more elastic ionic bonds, less rigid covalent bonds and less the internal strains it means more flexible the glass structure. The higher flexibility gives possibility to move the cations at lower temperatures and bending the whole glass structure and because of the lower internal energy the higher energy should be set to break the covalent bonds leading to the higher ΔC_p .

One of the important parameter in case of waste vitrification is a thermal stability of the vitrified product. The glass stability of the investigated materials was evaluated using Hruby criterion. According to [11] the higher K_H value the greater would be its stability against crystallization. The K_H value was evaluated according to the formulae:

$$K_H = \frac{T_c - T_g}{T_m - T_c} \quad (1)$$

The obtained K_H parameters are summarized in Table 3 and Fig. 5.

All of the investigated glasses evidenced high glass stability with the K_H parameter over 0.8. The values of K_H parameters for silicate glasses varied from 0.14 to about 1.3 [12–14]. The increasing of the ash concentration is causing decrease of the K_H parameter and thus it lowers the glass stability against crystallization on heating and in the same way the glass ability to vitrify on cooling [14].

The existence of a relation between ΔC_p and the ability of a glass to crystallize was observed previously [8]. Glasses crystallizing easily are characterized by a greater value of ΔC_p as compared with glasses that crystallize with

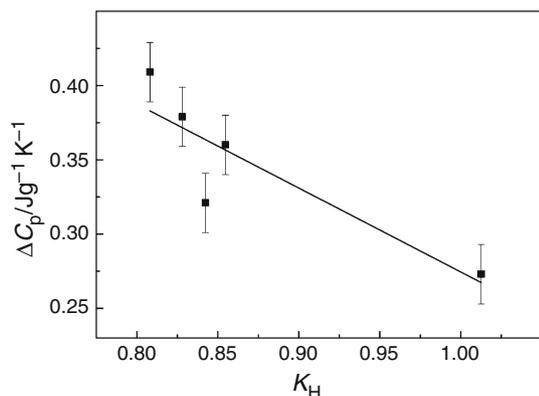


Fig. 6 Dependence of specific heat capacity change ΔC_p versus the K_H parameter

difficulty. As the ΔC_p and the K_H parameter could describe glass stability against crystallization there should exist relation between them. Such the relation is presented in Fig. 6. As can be clearly seen the higher ΔC_p value means lower glass structure stability its deeper destruction at the T_g temperature and in the same way the lower the K_H parameter. That proves the ΔC_p value obtained by DSC method could be also used as glass stability against crystallization parameter. The ΔC_p value is related to the change of entropy accompanying glass transition and considered as the structure modification degree indicator [9].

Conclusions

The conventional borosilicate waste glass was used to vitrify ashes from a hospital waste incineration plant. The influence of the ash addition on thermal properties of the obtained materials was investigated. The addition of the ash is causing only slightly reduction of the all characteristic temperatures like sintering, transformation, crystallization, and melting. On the other hand increases the ΔC_p which is correlated with the glass transition temperature T_g and glass stability K_H parameter. The ash constituents increase elasticity of the glass structure and thus reduce T_g and decrease stability of the product against crystallization on heating. Nevertheless, the thermal stability of proposed glass containing even considerable quantities of the ash is good, which makes the proposed glass suitable to vitrify such a waste.

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