Development of glass matrix for radioactive waste conditioning

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Abstract. Understanding of the incorporation of actinides in borosilicate matrix used for nuclear waste storage is of a great importance for radioactive waste immobilization. This study carried out on matrix glasses doped respectively with 30wt% UO₃ and CeO₂, Nd₂O₃ used for chemical modelling of the actinides. Neutron and X-ray diffraction measurements and Reverse Monte Carlo (RMC) simulations were performed. For several glasses, it was found that the basic network structure consists of tetrahedral SiO₄ units and of mixed trigonal BO₃ and tetrahedral BO₄. The BO₃ and BO₄ units are linked to SiO₄, forming mixed ^[4]Si-O-^[3]B and ^[4]Si-O-^[4]B bond-linkages. From significant second neighbour atomic pair correlations have been revealed that U, Ce, Nd accommodates in both silicate and borate site.

Introduction

The final and safe storage of radioactive waste materials is nowadays an existing and urgently to be solved problem. The most feasible and accepted way for storage of high-level radioactive waste (HLW) is the vitrification process, where the active elements are melted and poured into glass form, and thereafter deposited in the deep geological formation, where the objective is to retain the radionuclides in the host rocks, and to block access to the biosphere [1,2].

Borosilicate glass is a preferred and accepted waste form [3-6]. Vitrification plants are expected to be operational for the next 50 years, and a great number of relevant research to further enhance effectiveness and reduce cost being conducted in this area [7,8]. Future plans should reflect the best application of processing technologies and a knowledge of waste forms that reduces risk to the public and the environment while also avoiding unnecessary cost and delay.

Essentially the most important task in this area is to find a simple and well controllable process where we can immobilize the HLW's. The main problems are the high number of components, high melting temperature, crystallization, unknown basic processes and a high preparation costs.

Step by step we have made successful attempt to prepare borosilicate matrix glasses with the general composition of SiO₂-B₂O₃-Na₂O-BaO-ZrO₂. In this study we intend to explore basic network structure on the glasses by performing neutron- and X-ray diffraction experiments, which are complementary each other, X-ray diffraction data are dominated by contributions from heavier elements, while neutron diffraction gives information mainly on the light elements.

Our aim is to develop, optimize and compare the basic network structure of this glasses especially regarding the matrix glass with that of the uranium and lanthanides containing glassy network. In order to do this, simultaneous RMC simulation of the two data sets is applied to generate reliable 3-dimensional atomic configurations and to calculate the atomic parameters.

Experimental details

Samples

The composition of the investigated glassy specimens are 65SiO₂·10B₂O₃·25Na₂O (hereafter referred as SiB10NaO), 55SiO₂·10B₂O₃·25Na₂O·5BaO·5ZrO₂ (Matrix10), 70wt%[55SiO₂·10B₂O₃·25Na₂O·5BaO·5ZrO₂]+30wt%UO₃, CeO₂, Nd₂O₃ (Matrix10-U, Matrix10-

Ce, Matrix10-Nd, respectively). The investigations and results are presented parallel for the studied samples. The raw materials used were all of p.a. grade, SiO_2 , B_2O_3 are the basic glass forming oxides while Na_2O is glass modifier; while BaO , ZrO_2 serve both as network modifier, glass and hydrolytic stabilizers and UO_3 , CeO_2 , Nd_2O_3 . B_2O_3 was isotopically enriched with ^{11}B -isotope (99.6%) in order to reduce the influence of the high neutron absorption of ^{10}B present in natural boron. Actinides are not available, therefore for chemical modelling of the actinides we use lanthanides, as their complementary elements. Ce stays for the hazardous radioactive Pu, while Nd for Am and Cm. The glassy samples were prepared by melt-quenching technique, melted under atmospheric conditions, at temperatures between 1350-1450°C in Pt crucibles. The melted mixture has been kept at the melting temperature for 2 h, during which the melt was periodically homogenized by mechanical stirring. The melt was quenched by pouring it on a stainless steel plate.

Neutron and X-ray diffraction experiments

Neutron diffraction (ND) measurements were performed in a broad momentum transfer range, combining the data measured by the 2-axis PSD monochromatic neutron diffractometer ($\lambda_0=1.068$ Å; $Q=0.45$ -9.8 Å⁻¹) [9] at the 10 MW Budapest research reactor and by the 7C2 diffractometer at the LLB-Saclay ($\lambda_0=0.726$ Å; $Q=0.52$ -16 Å⁻¹) [10]. The powder specimens of about 3-5 g/each were filled in cylindrical V-sample holder of 8 and 6 mm diameter for the two experiments, respectively. The structure factors, $S(Q)$'s were evaluated from the raw experimental data, using the programme packages available at the two facilities. The neutron $S(Q)$ data were obtained with a good signal-to-noise ratio up to $Q_{\max}=16$ Å⁻¹ in case of SiB10NaO and Matrix10 samples. Diffraction experiments performed up to high- Q values are important to obtain fine r -space resolution of the atomic distribution function analyses. Figure 1a shows the ND experimental $S(Q)$ data for the investigated samples together with the results of RMC simulation (details of the RMC modelling will be discussed in the next section). The overall run of the ND experimental curves is similar for the investigated samples, only slight differences may be observed, especially at low- Q values for the intensive first peak at 1.7-1.85 Å⁻¹. The high-energy X-ray diffraction (XRD) measurements were carried out at the BW5 experimental station [11] at Hasylab, DESY. The powdered samples were filled into quartz capillary of 2 mm in diameter. The energy of the radiation was 109.5 keV ($\lambda_0=0.113$ Å). Raw data were corrected for detector dead time, background, absorption, and variations in detector solid angle. The XRD structure factor for the SiB10NaO and uranium containing sample Matrix10-U was obtained up to 22 Å⁻¹, for higher Q -values the experimental data proved to be noisy. The reason for the worse data quality for the SiB10NaO sample is the lack of heavy element scatterer in opposite to Matrix10-U. Figure 1b shows the XRD experimental $S(Q)$ data for the investigated samples together with the results of RMC simulation.

Figure 1. a) ND and b) XRD total structure factors for SiB10NaO (red), Matrix10 (blue), Matrix10-U (green), Matrix10-Ce (magenta) and Matrix10-Nd (orange) glasses and RMC fits (solid line). (The curves are shifted vertically for clarity.)

It is obvious, that the XRD spectra are different from the ND ones and for the two studied samples. The differences in the overall run of the ND and XRD spectra lie in the different values of the weighting factors, w_{ij} , of the partial structure factors, $S_{ij}(Q)$, defined as:

$$S(Q) = \sum_{i,j}^k w_{ij} S_{ij}(Q) \quad (1)$$

$$w_{ij}^{ND} = \frac{c_i c_j b_i b_j}{\left[\sum_{i,j}^k c_i b_j \right]^2} \quad (2)$$

$$w_{ij}^{XRD}(Q) = \frac{c_i c_j f_i(Q) f_j(Q)}{\left[\sum_{i,j}^k c_i f_i(Q) \right]^2} \quad (3)$$

where c_i , c_j are the molar fractions of the components, b_i , b_j the coherent neutron and $f_i(Q)$, $f_j(Q)$ the X-ray scattering amplitudes, and k is the number of elements in the sample. The neutron scattering amplitude of an element is constant in the entire Q -range [12], while the X-ray scattering amplitude is Q -dependent [13] and for each atom in a somewhat different way.

Reverse Monte Carlo modelling and results

The experimental structure factors, $S(Q)$ data have been simulated by the RMC method [14] using the software package RMC⁺⁺ [15]. The RMC minimizes the squared difference between the experimental $S(Q)$ and the calculated one from a 3D atomic configuration. The RMC algorithm calculates the one-dimensional partial atomic pair correlation functions $g_{ij}(r)$, and they are inverse Fourier transformed to calculate the partial structure factors, $S_{ij}(Q)$:

$$S_{ij}(Q) = 1 + \frac{4\pi\rho_0}{Q} \int_0^{r_{\max}} r [g_{ij}(r) - 1] \sin Qr \, dr \quad (4)$$

where $r_{\max}$ is the half edge-length of the simulation box of the RMC calculation. The actual computer configuration is modified by moving the atoms randomly until the calculated $S(Q)$ agrees with the experimental data within the experimental error. Moves are only accepted if they are in accordance with certain constraints.

For the RMC starting model a disordered atomic configuration was built up with a simulation box containing 10.000 atoms with density data 0.078, 0.073, 0.08, 0.065 and 0.069 atoms·Å⁻³ and $r_{\max}$ =25.21, 20.55, 19.84 Å, 26.79 Å and 26.26 Å for the SiB10NaO, Matrix10, Matrix10-U, Matrix10-Ce and Matrix10-Nd glasses, respectively. Two types of constraints were used, the minimum interatomic (cut-off) distances and coordination constraints. For the starting configuration we have used the results based on the literature and our previous results for binary SiO₂-Na₂O [16] and B₂O₃-Na₂O [17] glasses. We have been used the cut-off distances were chosen to avoid unphysical overlapping of the atoms. We apply two types, a positive and a negative coordination constrains for the two network former atoms, for the Si and B atoms. Based on the literature and our previous results [18,19] it is reasonable to suppose that silicon has a 4-fold oxygen coordination as a positive constrain, and a negative constrains that not coordinated 1 and/or 2 O atoms. While B atoms were constrained to be not coordinated both by 1 and 2 O atoms.

Several RMC runs have been completed by modifying the cut-off distances in the way, that the results of each run have been carefully checked to obtain reliable data for each partial pair correlation functions (PPCF) and coordination number (CN) distributions.

Figure 2. The a) Si-O, b) B-O and c) U,Ce,Nd-O PPCF's, SiB10NaO (red), Matrix10 (blue), Matrix10-U (green), Matrix10-Ce (magenta) and Martix10-Nd (orange) glasses.

Results for the most important partial pair correlation functions obtained from the RMC simulation are displayed in Fig. 2. For Si-O a covalent bond length at 1.60 Å was revealed for all studied glasses, showing an excellent agreement within limit of error (see Table 1.). This is a somewhat shorter value than that in ν -SiO₂ (1.615 Å) or in 70SiO₂-30Na₂O (1.62 Å) [16 and references therein]. The coordination number distribution shows that Si atoms are surrounded by 4 oxygen atoms. The actual average coordination numbers are 3.98, 3.8, 3.9, 3.84 and 3.88 (± 0.15) for the SiB10NaO, Matrix10, Matrix10-U, Matrix10-Ce and Matrix10-Nd, respectively (see Fig. 3a).

Table 1. Most important oxygen-linked atomic distance, r_{ij} (Å) obtained from RMC simulation.

Sample	Interatomic distances, r_{ij} (Å)						
	Si-O	B-O	O-O	Na-O	U-O	Ce-O	Nd-O
SiB10NaO	1.60 $\pm$ 0.01	1.30/1.55 $\pm$ 0.05	2.40/2.60 $\pm$ 0.05	2.25/2.5 $\pm$ 0.05	-	-	-
Matrix10	1.60 $\pm$ 0.01	1.40/1.60 $\pm$ 0.01	2.30/2.60 $\pm$ 0.05	2.20/2.60 $\pm$ 0.05	-	-	-
Matrix10-U	1.60 $\pm$ 0.01	1.50 $\pm$ 0.05	2.50 $\pm$ 0.1	2.10 $\pm$ 0.1	1.82/2.22 $\pm$ 0.1	-	-
Matrix10-Ce	1.60 $\pm$ 0.01	1.35 $\pm$ 0.05	2.25/2.60 $\pm$ 0.05	2.20/2.60 $\pm$ 0.1	-	2.13 $\pm$ 0.1	-
Matrix10-Nd	1.60 $\pm$ 0.01	1.33 $\pm$ 0.05	2.20/2.60 $\pm$ 0.05	2.55 $\pm$ 0.1	-	-	2.00 $\pm$ 0.1

For the B-O network we have established two distinct first neighbour distance at 1.30 Å and 1.55 Å for the SiB10NaO and at 1.40 Å and 1.60 Å for the Matrix10 glasses, in agreement with our previous high resolution neutron diffraction study [17], while from the Matrix10-U, Matrix10-Ce and Matrix10-Nd only one broad peak at 1.50 Å, 1.35 Å and 1.33 Å, respectively could be determined. Taking into consideration the low resolution of the present ND experiment, the agreement is reasonable reported for alkali diborate glasses [20-23]. RMC calculations have revealed that for all studied glassy compositions the B atoms are 3-fold and 4-fold coordinated by O atoms, as it is illustrated in Fig. 3b. The B-O average coordination number varying as 3.45, 3.1, 3.5, 3.6 and 3.63 (± 0.15) atoms for the SiB10NaO, Matrix10, Matrix10-U, Matrix10-Ce and Matrix10-Nd compositions, respectively.

Figure 3. a) Si-O and b) B-O CN's distributions from RMC modelling: SiB10NaO (red), Matrix10 (blue), Matrix10-U (green), Matrix10-Ce (magenta) and Matrix10-Nd (orange) glasses.

The uranium and lanthanides surroundings has been obtained with a great stability especially the U-O pair distribution, due to its relatively high 17% weight in the XRD experiment. The U-O, Ce-O and Nd-O partial pair correlation functions are illustrated in Figure 2c. The U-O correlation function shows two well resolved peaks at relatively short distances, centred at 1.82 Å and 2.24 Å. The first peak positions were possible to determine with a relatively high accuracy, because they do not overlap with other atomic pair distributions. For UO₃ containing glasses it has been reported that prefers to form uranyl ions with a short bond 1.8(3) Å and a some longer 2.2(6) Å [4,24]. The Ce-O distribution function shows a broad peak at 2.13 Å. The Nd-O shows characteristic first neighbour distance at 2.00 Å. However the intensity of Nd-O peak distribution is significantly higher than the

Ce-O peak intensity, suggested that Nd atom shows better tendency to incorporate on the network structure.

Significant correlations may be observed at higher r -values, finding that U, Ce and Nd atoms are in correlations with the network former Si and B atoms. This is a fingerprint for strong atomic correlations and indicate the existence of a pronounced intermediate-range ordering.

Discussion

For the investigated borosilicate glassy system a possible atomic configuration was obtained by the application of RMC computer simulation of neutron and X-ray diffraction experimental data. Here we focus our interest on the investigations of basic network structure and the possible incorporation of uranium and lanthanide ions.

The Si-O coordination number distributions show mainly 4-fold coordinated oxygen atoms, the number of different types of neighbours is below ~5%. Taking into consideration the $g_{\text{Si-O}}(r)$ distribution (see Fig. 2/a and Table 1), it is reasonable to suppose that the distance at 1.60 Å can be attributed to the SiO₄ units. It can be concluded that tetrahedral SiO₄ units are formed, what is in good agreement with the findings in the literature for glassy systems. [19,23]

For B-O distributions both 3- and 4-fold coordinated oxygen surroundings have been revealed, connected to formation of trigonal BO₃ and tetrahedral BO₄ units [25]. The fraction of BO₃ and BO₄ to the total number of B-O neighbours depends on the boron concentration and on their compositions. In this case the nominal boron concentration is constant, but the composition is really changed. In case of SiB10NaO, Matrix10 and Matrix10-U samples the fraction of BO₃ units are higher than BO₄ units. In the Matrix10-Ce and Matrix10-Nd glasses the ratio is changed, obtained higher number of BO₄ units than BO₃ units. The fraction of BO₃ and BO₄ to the total number of {BO₃+BO₄} is an important structural characteristics.

In the multi-component matrix glasses we have a compact structure, where the network former atoms as Si and B atoms play an important role. Based on our RMC calculations basic network structure was established formed by mixed ^[4]Si-O-^[3]B and ^[4]Si-O-^[4]B linkages [26,27] and is stable for all studied samples, for the simple 4-components sample as well as for the multi-component samples. The Si-O-B network structure is illustrated in Fig. 4 for Matrix10-U sample.

Figure 4. The Si-O-B network illustrated for 500 atoms.

The RMC modelling provides information on the second coordination sphere. The analysis of the silicon-metal and boron-metal pair correlation functions show pronounced peaks. The relatively shortest second neighbour distances are obtained for the Si,B-U, Si,B-Ce and Si,B-Nd pair correlation functions, suggests that uranium and lanthanide ions take part as partly as network former in the structure. These characteristic correlations shows that U, Ce and Nd atoms can incorporate on the matrix glass structure. This results also leads to the compact glassy structure possessing ability to include with high stability uranium and lanthanide ions.

Conclusions

We have performed ND and XRD measurements on simple SiB10NaO sample and a multi-component Matrix10 borosilicate host glass and the same composition loaded with 30wt% UO₃, CeO₂, Nd₂O₃ in order to get structural information on the basic network structure and on the incorporation of U, Ce, Nd ions.

It was established that the basic network structure consists mixed ^[4]Si-O-^[3]B and ^[4]Si-O-^[4]B linkages, the formation is stable, and is similar for the simple and matrix glasses than doped glasses. For the U-O correlations two distinct peaks were resolved at 1.8 Å and 2.2 Å. For the Ce-O and Nd-O correlations characteristic distribution was detected at 2.13 Å and 2.00 Å, respectively. Furthermore, significant second neighbour atomic pair correlations have been revealed between U,

Ce, Nd and the network former (Si,B) atoms. From these results we may conclude that also for the doped glasses we have a stable basic network structure and U, Ce, Nd accommodates in both silicate and borate site. This may be the reason of the observed good glassy stability and incorporation ability of the ions.

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