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Neutron diffraction structure study of borosilicate based matrix glasses

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Abstract. We have performed structure study on a newly synthesized sodium borosilicate matrix glass system with general composition of $65SiO_2*5B_2O_3*25Na_2O*5BaO$ *(mole%)* doped with CeO_2 and ZrO_2 with the aim to model radioactive PuO_2 and also, to increase the hydrolytic and network stability of the glasses. Neutron diffraction experiments have been performed and reverse Monte Carlo modelling was applied to obtain the partial atomic pair correlation functions. We have established that ZrO_2 is an effective glass stabilizer, and the short-range structure of the CeO_2 doped samples preserves the basic network configuration of the matrix glasses, making them suitable for radioactive waste material storage.

Introduction

Borosilicate glasses are of significant current interest as suitable materials for isolating host media for radioactive waste material storage [1-4]. Although the investigation of boron containing matrix glasses is challenging, only a few neutron diffraction studies have been reported in the literature so far [5].

The aim of the present study was to investigate the network glass configuration of a newly synthesized sodium borosilicate glass system doped with CeO_2 and ZrO_2. Matrix glass with the general composition of $65SiO_2*5B_2O_3*25Na_2O*5BaO$ was prepared, where *BaO* serves as glass stabilizer. Radioactive waste material PuO_2 was modelled by addition of CeO_2 to the host glass. Since *Pu* and *Ce* coordinations are rather similar in complex oxide environments, it can be expected that *Pu* coordination in a glass network is properly simulated by *Ce*. In order to increase both the hydrolytic and network stability of the matrix glass, ZrO_2 was added.

Here we present our neutron diffraction experiments and results obtained by reverse Monte Carlo (RMC) modelling, characterizing the short-range structure of the investigated glass system. Details of sample preparation and sample characteristics are also described.

Experimental

Sample preparation

Host glass compositions were synthesized by melting 50 g quantities of previously homogenized powder mixtures obtained from the properly weighed dry starting components: SiO_2, Na_2CO_3, BaO, H_3BO_3, and ZrO_2 in platinum crucible at 1300-1450 ºC in atmospheric conditions. The raw materials used were: SiO_2, Na_2CO_3 and H_3BO_3 as supplied by Reactivul (Bucuresti), BaO and ZrO_2 by Merck (Darmstadt).

The sample series with different ZrO_2 content was prepared with the general composition of $(65-x)SiO_2*5B_2O_3*25Na_2O*5BaO*xZrO_2$ *(mole%)* $x=0,1,2,3,4,5$. The melt was quenched by pouring it on a stainless steel plate.

The second sample series was prepared by re-melting 90 wt% of the corresponding host glass with addition of *10 wt%*CeO_2 supplied by Fluka (Darmstadt). It was homogenised for several hours at high temperature as described above, and thereafter quenched. The general composition of the five samples is:

$90\ wt\%\{(65-x)SiO_2*5B_2O_3*25Na_2O*5BaO*xZrO_2\}+10\ wt\%CeO_2$..

Powder samples for neutron diffraction measurements were prepared by powder milling of the quenched glasses in an agate mill.

Neutron diffraction measurements

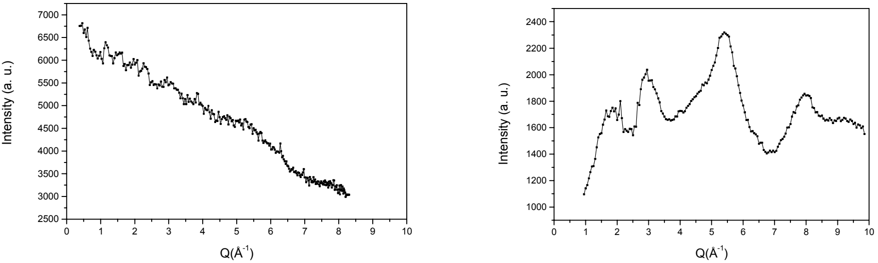
Neutron diffraction measurements were performed at the 10 MW Budapest research reactor using the ‘PSD’ [6,7] and ‘MTEST’ [8] neutron powder diffractometers. Monochromatic wavelength of λ=1.07 Å was used, and the diffraction spectrum was measured in the scattering vector range Q= 0.95-9.8 $Å^{-1}$. The powder specimens of about 3-4 g were filled in cylindrical vanadium sample holder of 8 mm diameter, 50 mm height and 0.07 mm wall thickness. Since the specimens were prepared from natural boron being high neutron absorbent, accurate transmission measurements were performed. Transmission of the samples was between 80 and 82%.

Correction and normalization procedures utilized to obtain the structure factor *S(Q)* from the measured pattern was described in our previous work [9]. For data treatment to obtain the atomic pair correlation functions, both the traditional direct Fourier transformation technique and reverse Monte Carlo (RMC) simulation [10] were applied.

Sample characterization

Density of the produced samples was measured at 20 ºC by a picnometer calibrated at the same temperature. Values between 2.35 and 2.95 gcm^{-3} were found depending on composition. The hydrolytic stability of the specimens was measured by static method [see e.g. 2].

Despite of the great hydrolytic stability of the samples, the first few neutron diffraction experiments revealed their tendency to superficially adsorb H_2O. Atmospheric humidity caused a surface swelling of the air-kept samples, and the hydrolysed layer produced significant incoherent inelastic scattering, hindering the coherent scattering of the specimens (see figure 1/a). In order to dry the samples, heat treatment was applied at 120 °C for 4 hours under vacuum conditions, which proved to be completely sufficient to obtain neutron diffraction pattern adequate for data treatment. For illustration, neutron diffraction patterns of the



a/ b/

Figure 1. Neutron diffraction pattern of $65SiO_2*5B_2O_3*25Na_2O*5BaO$ (mole %) glass: ***a/*** *air-kept state with superficially absorbed H_2O (5 wt%)* ***b/*** *after heat treatment. The sample contains a small amount of crystalline phase.*

$65SiO_2*5B_2O_3*25Na_2O*5BaO$ specimen are shown in figure 1/a,b in air-kept state and after the applied heat treatment.

From the neutron diffraction pattern we have established that *BaO* is not sufficient to stabilize completely the amorphous structure (see figure 1/b), while ZrO_2 proved to be an effective glass stabilizer. All our ZrO_2 doped host glass samples were in pure amorphous-state, Bragg-peaks were not detected.

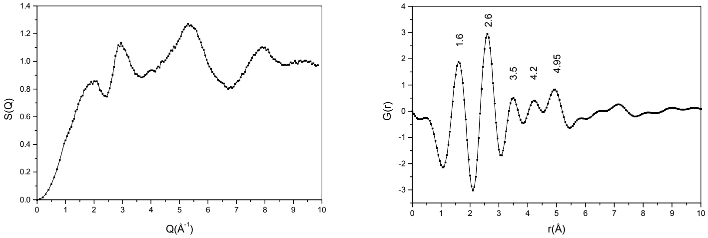
Addition of CeO_2 to the host matrix did lead to formation of crystallites, embedded in the glassy network. By increased addition of ZrO_2 content to the matrix, the glass network could be stabilized. The CeO_2 containing specimens proved to be completely amorphous with ZrO_2 amount above 3 mole%.

Data treatment and results

As a first step of data evaluation process the total reduced atomic distribution function, *G(r)* characterizing the average one-dimensional atomic pair correlations was calculated from *S(Q)* by sine Fourier transformation [see e.g. 9]:

$$G(r)=\tfrac{2}{\pi}\int_{0}^{Q_{\max}} Q\left[S(Q)-1\right]\sin Qr\,dQ\ , \tag{1}$$

where the integration limit Q_{max} was selected at the highest *Q* value where $S(Q)=1$ to minimize termination errors. For illustration, figure 2/a,b shows *S(Q)* and *G(r)* for the $60SiO_2*5B_2O_3*25Na_2O*5BaO*5ZrO_2$ glass. The information content of *G(r)* is very limited for this multi-component system being the weighted sum of the partial pair correlation functions. From *G(r),* anyhow*,* we can derive some information, namely: the *Si-O* and *B-O* first neighbour distributions overlap, resulting in the first peak at r=1.6 Å. The second peak at r=2.6 Å contains mainly the *O-O* first neighbours, as it is expected from the literature, and due to the sharp form of the peak we can suppose that most of the cation-oxygen first neighbours give contribution at this position. The position of these two peaks, denoting the *1st and 2nd* coordination spheres do not show significant changes as a function of Zr-content or/and Ce-content, meaning that the basic network configuration is preserved. Slight decrease of the *1st* peak intensity with increasing *Zr*-content may be observed, meaning the decreased number of first neighbour *Si-O* atomic pairs due to the presence of large Zr and/or Ce ion.



a/ b/

Figure 2. Glass $60SiO_2{*}5B_2O_3{*}25Na_2O{*}5BaO{*}5ZrO_2$ *(mole%): a/ Structure factor S(Q) and b/ total reduced distribution function G(r) calculated by Fourier- transformation.*

In order to get deeper insight into the atomic configuration, the reverse Monte Carlo (RMC) simulation technique was applied [10]. Our multicomponent glass system contains $k = 4, 5, 6$ different types of scattering centres, resulting in $k(k+1)/2 = 10, 15, 21$ partial pair correlation functions, $g_{ij}(r)$. Because of the very high number of $g_{ij}(r)$'s, the number of simulated parameters is enormously high, and the obtained results should be handled very carefully. For the RMC starting model a disordered atomic configuration was built up. The calculation consists of minimizing the squared difference between the experimental and calculated structural factors *S(Q)* by moving atoms randomly. The following definitions and basic relations are used in RMC calculations:

$$S(Q) = \frac{\sum_{i,j}^{k} c_i c_j b_i b_j S_{i,j}(Q)}{\left[\sum_{i,j}^{k} c_i b_j\right]^2} \tag{2}$$

$$S_{i,j}(Q) = 1 + \frac{4\pi\rho}{Q}\int_0^\infty r\left[g_{i,j}(r) - 1\right]\sin Qr\, dr\,, \tag{3}$$

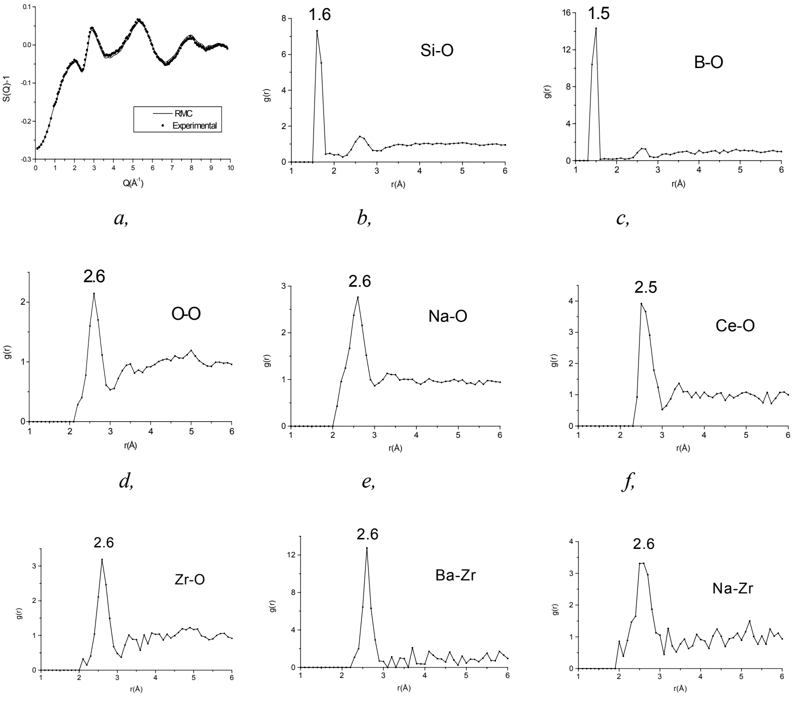
$$g_{i,j}(r) = 1 + \frac{1}{2\pi^2 r\rho}\int_0^\infty Q\left[S_{i,j}(Q) - 1\right]\sin Qr\, dQ\,, \tag{4}$$

where ρ is the number density, c_i, c_j the molar fractions of components and b_i, b_j the coherent neutron scattering amplitudes. $S_{ij}(Q)$ are the partial structure factors whose sine Fourier transforms are $g_{ij}(r)$. For simplicity, we denote the $g_{ij}(r)$ functions as *g(r)* in the forthcoming description.

The convergence of the RMC calculation was good and the final calculated *S(Q)* matched very well the experimental structure factors, as it is illustrated in figure 3/a for the $90\%\{60SiO_2{*}25Na_2O{*}5BaO{*}5B_2O_3{*}5ZrO_2\}+10\%CeO_2$ sample.

We could successfully calculate most of the *g(r')'s*, and the atomic distances of the glass network was calculated. The partial atomic correlation functions *g(r)* are very similar for all samples, therefore here we present the obtained results only for the $90\%\{60SiO_2*25Na_2O*5BaO*5B_2O_3*5ZrO_2\}+10\%CeO_2$ glass, representing all investigated samples. The *Si-O and B-O* pair correlation functions contributing to the *1st* coordination shell of *G(r)* are shown in figure 3/b,c. For the first neighbour *Si-O* and *B-O* distances 1.6 Å and 1.5 Å were revealed, respectively. The *O-O, Na-O, Ce-O, Zr-O, Ba-Zr and Na-Zr g(r)'s* contributing to the *2nd* coordination sphere of *G(r)* are collected in figures 3/d-i.

More detailed analyses of the g(r)'s, regarding coordination numbers, bond angles, distributions at the 3rd coordination sphere are in progress.



a, *b,* *c,*

d, *e,* *f,*

g, *h,* *i,*

Figure 3. Glass $90\%\{60SiO_2*5B_2O_3*25Na_2O*5BaO*5ZrO_2\}+10\%CeO_2$: a/ Structure factor S(Q)-1, experimental (dots) and RMC simulation (solid line); b/Si-O, c/B-O, d /O-O, e/ Na-O, f/Ce-O, g/Zr-O, h/Ba-Zr, i/Na-Zr partial pair correlation functions g(r), as obtained by RMC simulation.

Conclusions

We have performed neutron diffraction study on a newly synthesized sodium-borosilicate glass added with CeO_2 and ZrO_2, with the aim to model isolating host media for storage of radioactive waste materials. The following main findings have been revealed:

- The air-kept samples did show tendency to superficially adsorb H_2O. Heat treatment at 120 °C for 4 hours under vacuum conditions proved to be completely sufficient to dry the specimens.
- Addition of BaO proved to be not sufficient to stabilize completely the glassy structure, while ZrO_2 proved to be an effective glass stabilizer.
- Addition of CeO_2 to the host matrix did lead to formation of crystallites, embedded in the glassy network. With addition of ZrO_2 , however, the glass network could be stabilized.
- From RMC simulation of the neutron diffraction data we have obtained the partial atomic pair correlation functions for these multi-component glasses.

It was established that the short-range structure of the CeO_2 doped samples preserves the basic network configuration of the matrix glasses, making them suitable for radioactive waste material storage.

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