Microstructure of zirconia-based sol-gel glasses studied by SANS

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Abstract

Zirconia-based bulk glasses were prepared for the first time by sol-gel method. Such materials are very promising for application as photochromic devices, catalytic systems, chemical sensors, lasers and other nonlinear optics devices. Obtained transparent and semi-transparent materials were studied by small and ultra-small angle neutron scattering (SANS and USANS) methods. As evidenced by SANS, morphology of zirconia glasses is very sensitive to parameters of sol-gel synthesis, e.g. temperature and concentration of reactants. SANS data correlates rather well with surface porosity data. Increasing water concentration in reaction mixtures containing zirconium propylate leads to a significant increase in fractal cluster size, while decreasing the temperature results in an increase of the fractal dimension. The obtained results indicate that parameters of the microstructure and consequently physical properties of zirconia glasses can be effectively controlled by parameters of synthesis.

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Introduction

Transparent sol-gel glasses are widely used in photochromic devices, *e.g.* as chemical sensors or catalyzers, due to their low cost and good optical properties [1]. In order to overcome some application restrictions, an increasing interest is paid to zirconia [2] as a promising glass-forming component in the last decades. Synthesis of glassy materials using the sol-gel method brings some advantages in comparison with the conventional melting or sintering. Above all, it allows fine tuning of physical properties of glasses by controlling sol-gel synthesis parameters affecting structure of these materials at the nanoscale level.

Among other methods, small-angle neutron scattering (SANS) has been proved to be very effective for investigation of nanostructures in bulk of solid materials since 1970's (see *e.g.* [3–6]). In some cases, SANS

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data interpretation is not straightforward – in contrast to other complementary and cheaper techniques such as electron microscopy (SEM, TEM), gas adsorption/desorption (BET) *etc*. On the other hand, SANS has several inherent advantages including excellent statistics and easy sample preparation procedures. In this work, three SANS instruments were used for a microstructural study of zirconia-based sol-gel glasses in a wide size range (from nanometers to microns) aiming at determination of microstructure dependence on sol-gel synthesis conditions.

Synthesis of the samples

Solution of zirconium propylate (70 wt.% in n-propanol) was mixed with concentrated nitric acid (70 wt.%) and isopropanol (87.9 wt.%). Pure water was added as hydrolyzing agent in three molar ratios to Zr (1 : 10.58; 1 : 5.29; 1 : 2.65). Resulted mixtures were aged at either 20°C or 0°C. The obtained glassy samples are listed in Table 1. Detailed description of sample preparation procedure can be found elsewhere [7]. Images taken by Carl Zeiss N Vision 40 scanning electron microscope (SEM) instrument of the untreated samples with highest and lowest H_2O ratio in initial mixtures are shown in Figure 1.
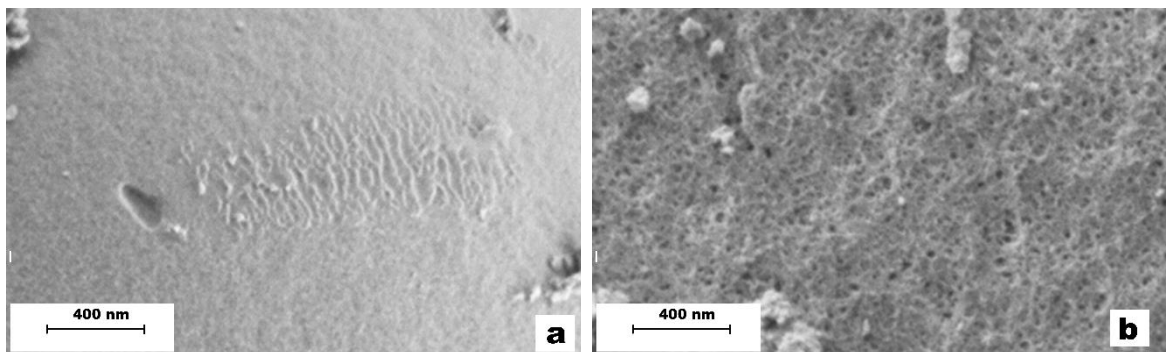

Fig. 1. SEM images of samples 4V(H_2O) – a, and 1V(H_2O) – b.

SANS analysis

SANS measurements were carried out at KWS-1, KWS-3 (FRM-II reactor, Garching, Germany) and MAUD (CANAM, NPI, Řež, Czech Republic) facilities. Joint use of these setups allows us to cover wide range of momentum transfers magnitude Q from $2 \cdot 10^{-4}$ Å^{-1} (MAUD) [8, 9] to 0.43 Å^{-1} (KWS-1) [10]. Resulting scattering curves (Fig. 2) show power law dependence $\sim Q^{-D}$ for low Q values. For samples with lower amount of water (1V/2V(H_2O)(-ice)), there is a notable increase in intensity in the region corresponding to the smallest pores (down to few nanometers), which are also visible in SEM images (Fig. 1). The power law behavior of

SANS curves with $D \neq 4$ at low Q can be explained by a fractal structure of the glasses [11, 12]. Therefore, low Q range of SANS data was fitted using fractal model.

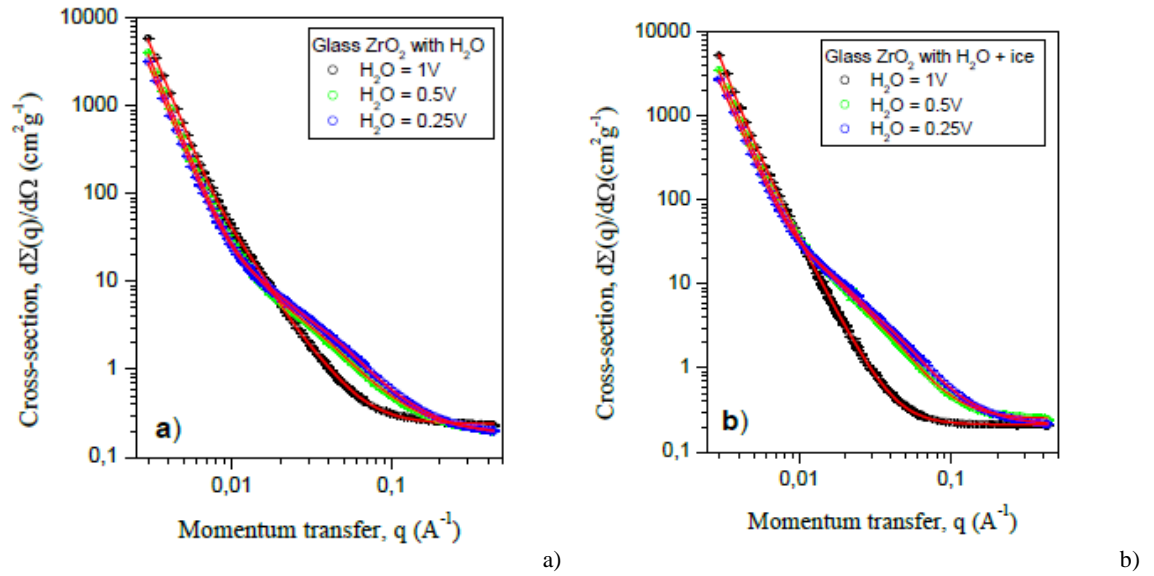a)   b)

Fig. 2. Scattering from samples synthesized at 20^0C (a) and 0^0C (b) obtained by KWS-1 and KWS-3 instruments.

For samples with lower water content (1V and 2V), SANS data were fitted using a combination of the mass-fractal model and a spherical particles model with narrow log-normal size distribution. SANS data for samples with higher water content (4V) did not show a presence of nanoporosity. Therefore those curves were fitted using just fractal models. Mean radii (R_s) and fractal dimensions (D_f, where $D_f=D$ for mass fractals) obtained from the fit are summarized in Table 1.

Table 1. Fitted parameters from SANS data

$H_2O : Zr$	14 mass % : 10.58 mol %		7.5 mass % : 5.29 mol %		4 mass % : 2.65 mol %	
Temperature of sol-gel processing	20°C	0°C	20°C	0°C	20°C	0°C
Sample name	4V(H_2O)	4V(H_2O)-ice	2V(H_2O)	2V(H_2O)-ice	1V(H_2O)	1V(H_2O)-ice
R_s, nm	-	-	12.0	9.9	9.2	9.5
D_f	2.73 ± 0.03	3.34 ± 0.03 ($D_s = 2.66$)	2.02 ± 0.03	2.74 ± 0.03	2.19 ± 0.03	2.39 ± 0.03

Decrease in the temperature of sol-gel process leads to an increase in fractal dimensions. In other words, the structure of corresponding samples is more compact [13]. Obtained values of $D_f > 2$ are typical for fractal aggregates produced under slow reaction conditions [14], so called reaction-limited cluster aggregation (RLCA). Scattering for the sample 4V(H_2O)-ice corresponds to surface fractal with the fractal dimension [11] $D_s = (6 - D) = (6 - 3.34) = 2.66$. Specific surface obtained by BET measurements is inversely depended on H_2O content (see Fig. 3) and it almost approaches zero for samples 4V. Such porosity behavior obtained by BET well correlates with SANS results, since nanopores observed using SANS in samples 1V and 2V contribute the most to the total porosity.
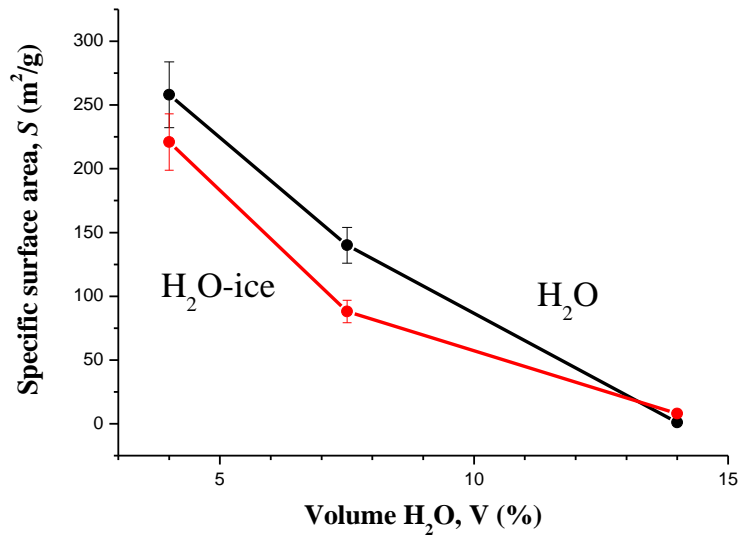

Figure 3. Specific surface of pores obtained by BET method.

Conclusions

Zirconia-based bulk glasses were prepared for the first time using sol-gel method. These materials possess high microstructure dependence on parameters of preparation procedure. The specific surface increases with decreasing water-to-zirconium ratio in initial mixtures due to formation of nanosized pores detected by SANS. This type of porosity is nearly absent in zirconia glasses prepared from reaction mixtures with higher water-to-zirconium ratio. Large inhomogeneities in studied glasses have fractal self-similar nature. The fractal dimension obtained from SANS increases with decrease of the synthesis temperature, *i.e.* microstructure of the glasses synthesized at lower temperature is more compact.

Acknowledgements

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