Small-angle scattering investigation of phase separation in glasses influenced by admixtures of TiO_2 , MoO_3 and WO_3

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Abstract: Two silicate glasses with different compositions have been investigated by combining conventional small-angle X-ray scattering with methods of contrast variation (anomalous dispersion, neutron scattering). It has been shown that in a base glass for glass ceramics TiO_2 additives which accelerate the process of phase separation are inhomogeneously distributed in the glass and cover the separating droplet phase. The influence of WO_3 and MoO_3 on the conditions of the phase separation in a soda-lime-silica glass mainly consists in a shift of the miscibility dome in the phase diagram up to higher temperatures.

Introduction

Phase separation is a phenomenon which strongly influences the optical and mechanical properties of glasses and glass ceramics. The kinetics of phase formation are determined by the temperature of the heat treatment and the composition as well. In recent years, the role of certain glass components acting as so-called nucleants has been studied intensively. However, most of the experimental techniques used for the investigation of nucleation and growth of particles of the separated phase do not permit an observation of the very beginning of the process, i.e. for particle dimensions between 1 nm and 10 nm. On the other hand, up to now there was a lack of experimental methods for studying the composition and the structural arrangement of different oxides within the particles and the surrounding region of the glass matrix. Small-angle scattering of synchrotron radiation and neutrons offers a field of new possibilities for solving this problem.

Small-angle X-ray scattering (SAXS) results can characterize structure heterogeneities in the size range between 1 nm and some hundreds of nm. In the case of sharp phase boundaries several structural parameters can be extracted from scattering data: mean particle size, volume fraction and particle number density. Furthermore, structure functions describing the particle size distribution and the distribution of the scattering length density in the scattering system can be obtained. In contrast to this conventional scattering technique contrast variation permits to investigate the spatial arrangement of distinct elements in the phase separating system owing to the fact that the scattering amplitude of an atom is decreased for X-ray energies near the absorption edge of the concerning element. This anomalous dispersion is the basis for the method of anomalous small-angle X-ray scattering (ASAXS) of synchrotron radiation. A second possibility for contrast variation is small-angle neutron scattering (SANS), because the scattering length densities for neutrons and X-rays differ from each other for the certain elements and phases.

The knowledge about the effect of TiO_2 , WO_3 and MoO_3 on the phase separation in silicate glasses of the type presented here is restricted to the fact that up to additions of some mole percent these oxides can promote both the nucleation rate and the growth velocity of the evolving new phase. The question whether this is caused by the formation of small crystallites which act as nucleation sites for the separating glass phase or by an influence on the thermodynamical conditions for the phase separation (phase diagram, interface tension) was not answered up to now. This is the topic our paper is dealing with.

Experimental

Typical structure parameters were obtained from the scattering curves $I(s)$ measured with pinhole collimation and $\tilde{I}(s)$ recorded with infinitely long slit collimation; $s = 4\pi/\lambda \cdot \sin\Theta/2$ is the amount of the scattering vector, λ is the wavelength. The mean squared deviation of the electron density

$$\langle(\Delta\rho)^2\rangle = 1/(4\pi^2) \int_0^\infty s \cdot \tilde{I}(s) ds \quad (1)$$

calculated from the absolute intensity in case of a two-phase system is determined by the volume fractions w and $(1-w)$ and the contrast $\Delta\rho$ between the electron densities of the two phases:

$$\langle(\Delta\rho)^2\rangle = w(1-w) (\Delta\rho)^2 \quad (2)$$

For spherical particles the so-called Guinier radius R_G can be obtained from $I(s)$ at small s -values:

$$I(s) = I(0) \exp\left[-1/5 R_G^2 s^2\right] \quad (3)$$

ASAXS intensities are recorded for different energies ε_i of the synchrotron radiation in order to take advantage of the anomalous dispersion of the atomic scattering amplitude f near the absorption edge:

$$f(\varepsilon) = f_0 + f'(\varepsilon) + if''(\varepsilon) \quad (4)$$

The term f'' is proportional to the absorption coefficient and it can be obtained directly from the XANES spectrum of the sample. The correction f' is calculated from f'' according to the Kramers-Kronig relation [1]. Taking into consideration that the electron density ρ is proportional to the atomic scattering amplitude f equation (4) demonstrates the possibility of a variation of the scattering contrast $\Delta\rho$ for certain atoms (resonant scatterers) in relation to the remaining scattering units in the system. Partial scattering functions are computed by a dispersion analysis from the ASAXS curves $I(s, \varepsilon_i)$ recorded at different energies ε_i near the absorption edge of the concerning element [2]:

$$I(s, \varepsilon_i) = I_0(s) + 2f'(\varepsilon_i) \cdot I_{OR} + \left[f'^2(\varepsilon_i) + f''^2(\varepsilon_i)\right] \cdot I_R(s) + c \cdot f''(\varepsilon_i) \cdot Flu(s), \quad (5)$$

where I_0 is the non-resonant term, I_{OR} is the cross term, I_R is the resonant term, c is a constant and Flu is the fluorescence. With ASAXS data for more than 4 energies ε_i the system of equations (5) is overdetermined and can be solved by a least squares method.

Results and Discussion

Samples of the initially homogeneous glass 11 Na₂O - 13 CaO - 76 SiO₂ (mole %) were heat treated at 600 °C. Because the composition lies within the miscibility gap of the phase diagram the glass separates into an almost pure SiO₂ droplet phase and a 11 Na₂O - 13 CaO - 73 SiO₂ matrix phase [3]. The expected volume fraction of the droplets w_K can be estimated from the known phase compositions (see Fig. 2):

$$w_K = (x_0 - x_M) \cdot d_0 / [(x_K - x_M) \cdot d_K], \quad (6)$$

where x is the mole fraction of SiO₂ in the corresponding phase: $x_0 = 0.76$, $x_M = 0.73$, $x_K = 0.99$; $d_0 = 2.5 \text{ g cm}^{-3}$, $d_K = 2.2 \text{ g cm}^{-3}$ are the densities of the glass and the droplet, respectively. According to (2) $\langle(\Delta\rho)^2\rangle = 7.2 \cdot 10^{44} \text{ cm}^{-6}$ is estimated for the equilibrium stage of the phase separation at $T = 600 \text{ °C}$. This value is shown as a dashed line in Fig. 1. It has been confirmed by the SAXS data of the base glass.

Small additions of 0.5 mole % MoO₃ or WO₃ to the glass increased the saturation value of $\langle(\Delta\rho)^2\rangle$ for long treatment times at 600 °C in relation to the undoped glass. This behaviour is demonstrated in Fig. 1 where the SAXS data were evaluated according to (1).

Fig.1.: Mean squared electron density fluctuation of the phase separating soda-lime-silica glass doped with different additives, $T = 600\text{ }^{\circ}\text{C}$

Fig.2: Phase diagram of the soda-lime-silica glass
solid line: without admixtures
dashed line: with 0.5 mole % WO_3 , MoO_3

The observed increase of $\langle(\Delta\rho)^2\rangle$ up to 180 % can not be explained by the existence of a third phase which mainly consists of WO_3 or MoO_3 . This was proved for both the model of a third distinct phase of the added oxides and the model of SiO_2 particles covered by the doping material applying the formula for $\langle(\Delta\rho)^2\rangle$ in case of a three-phase scattering system [4]. The enrichment of the added oxides in the SiO_2 phase can be excluded on account of the very low solubility. Therefore, the SAXS results should be caused by a shift of the miscibility dome in the phase diagram up to higher temperatures for about 60 K as has been demonstrated by the dashed line in Fig.2. That means, that the small admixtures of WO_3 or MoO_3 influence the phase separation only by changing the phase diagram.

The base glass for glass ceramics $11.0\text{ MgO}-31.0\text{ Al}_2\text{O}_3-47.1\text{ SiO}_2-6.9\text{ ZrO}_2-1.8\text{ TiO}_2+2.2\text{ (LiF, SnO}_2, \text{Fe}_2\text{O}_3, \text{Na}_2\text{O, K}_2\text{O; weight\%)} heat treated at 820\text{ }^{\circ}\text{C}$ for different times was investigated by ASAXS at the K absorption edge of Ti (see Fig. 3). Previous SAXS results revealed that in the early stage spherical particles formed by a glass-in-glass phase separation grow according to a diffusion-limited growth mechanism. In the later stage of phase separation Ostwald ripening takes place. The particles are enriched with MgO and Al_2O_3 . They are surrounded by diffusion zones which are characterized by a depletion of the oxides that dominate the droplet composition.

In order to investigate the spatial arrangement of the TiO_2 units which are stimulating the phase separation process, according to (5) the dispersion analysis of the ASAXS data was carried out. The result for the sample $820\text{ }^{\circ}\text{C} / 4\text{ h}$ is shown in Fig.4. The resonant scattering term $I_R(s)$ represents the scattering information of the TiO_2 units, whereas I_0 is the scattering from the remaining structure elements formed by non-resonant atoms. Comparing the Guinier radii R_G obtained with (1) from the resonant and non-resonant scattering terms it has to be concluded that the structure elements enriched with TiO_2 form larger geometrical structures in relation to the phase separated particles (Table 1). Therefore, the TiO_2 units must be distributed inhomogeneously within the phase separated glass.

Table 1: Comparison of the Guinier radii R_G for the resonant and non-resonant scattering term

time of treatment		2h	4h	8h	13.5h
R_G [nm]	non-resonant	1.7	5.4	15.8	18.2
	resonant	3.3	7.3	20.0	22.8

Fig.4: Dispersion analysis for sample 820 °C / 4h

Fig.3: Development of the scattering intensity $I(s)$ during the heat treatment at 820 °C
solid line: SAXS
dashed line: SANS

This assumption is supported by additional SANS experiments where the contrast is varied because of the negative scattering length of titanium. The Guinier radii obtainable from the SANS curves, which are compared with the corresponding SAXS data in Fig.3, exhibit even smaller particle dimensions than those extracted from the non-resonant SAXS scattering term of the ASAXS data (Table 1). The SANS curves exhibit a stronger effect of the diffusion zone which is demonstrated by a decrease of the scattering intensity at small s -values. Furthermore, the examination of ASAXS curves at different energies gave the result that the particles seem to be smaller for X-ray energies ϵ near the Ti-K absorption edge than for energies far beneath from the edge.

Taking into account the decrease of the scattering amplitude for ASAXS near the Ti absorption edge and considering the negative scattering length of Ti for SANS an explanation for the experimental outcomes is that the particles consist of a TiO_2 depleted core and a cover enriched with TiO_2 . This model is consistent with a smaller particle radius in case of experiments where the scattering amplitude of TiO_2 is decreased (ASAXS, SANS). This may be caused either by a surface activity of TiO_2 or by a segregation process of the TiO_2 units towards the interface during the beginning crystallization of the separated particles.

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