The studies of nanoparticles formed in silicate glasses doped by cerium and titanium oxides by means of small angle neutron scattering

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Abstract. The structure aspect of Ti-Ce-O nanoparticles, which is forming in silicate glasses doped by TiO\(_2\) and CeO\(_2\) oxides have been studied by means of a small angle neutron scattering. It was found, the complex oxide nanoparticles forms in these glasses in sizes range 30-38 nm and its average sizes depends on initial oxides concentration ratio. The correlation between nanoparticles structure features and silica glasses optical properties are discussed.

1. Introduction

At the present time one of the topical problems in optics is a search for nanosystems, which could efficiently absorb light in a given spectrum range [1]. The promising materials are silicate glasses doped by cerium and titanium oxides [1-3]. These glasses have yellow–orange color and its optical absorption edge can be shifted by varying the CeO\(_2\)/TiO\(_2\) concentrations ratio [2]. Such glasses are characterized by hard UV-radiation protection and thermal stability, and they are suitable for numerous technological applications, such as laser optics elements, light filters and gem imitation [3].

It was assumed [4], that these unique physical properties of these glasses can be result of complex oxide nanoparticles Ce-Ti-O forming. The nanoparticles structural characteristics define the fine color
tuning and UV radiation and temperature stability of such glasses. In those nanoparticles the titanium ions could be tetravalence, but the cerium ions can be both tetravalence and trivalence [3-5].

The physical and functional properties of these glasses depend on both the chemical composition of oxide system and the structure futures of Ti-Ce-O nanosystem constituents. The previous small angle X-ray scattering experiment [6] was detected the forming of nanoparticles in silicate glasses but its structural futures didn’t obtain. In the present work most attention is focused on the research of structure aspects of nanoparticles formation in glasses with different initial oxides concentration by means of small angle neutron scattering and finding of correlations between nanoparticles structural futures and optical properties of glasses.

2. Experimental

The present silicate glasses were obtained from the melting of inorganic glass matrix SiO$_2$-Al$_2$O$_3$-MgO-CaO-BaO-SrO-Na$_2$O-K$_2$O-Li$_2$O with the adding of titanium and cerium oxides with necessary concentrations by means of high temperature gas furnace. The collection of glasses with relative molar concentrations of TiO$_2$/CeO$_2$ oxides: 0.0/2.0; 1.0/2.0; 5.0/2.0; 6.5/2.0; 10.0/2.0; 0.0/0.3; 5.0/0.3 and 10.0/0.3 have been obtained.

The small-angle neutron scattering (SANS) experiments were carried out with the spectrometer SANS-1 [5] on the research reactor FRG-1 (HZG, Germany) [7]. The neutron wavelength in experiments was 8.1 Å with average resolution Δq/q = 1%. The four sample–detector distances to provide available in experiments q-range 0.005-25 nm$^{-1}$. The standard background and detector anisotropy corrections have been done.

3. Results and discussion

The SANS curves for pure silicon glass and glasses with different molar concentration ratio of CeO$_2$/TiO$_2$ oxides are shown in figure 1. The scattering curves from pure and titanium-free glasses are correspond with scattering from large objects and can be approximated by the simple power law [8]:

$$d\Sigma(q)/d\Omega = Aq^{-\alpha} + B,$$

where $A$ and $B$ are scaling prefactors, $\alpha$ - the curves slope coefficient, which characterized the fractional dimension of scattering objects [8]. The obtained value of the slope coefficient for pure glass is $\alpha = 2.99(5)$. The microscopic air bubbles and pores forming at glasses manufacturing can be such large scattering objects. Previously [5] it was observed, that these pores does not appreciably influence on optical properties of obtained silicate glasses.

The small angle neutron scattering curves from silicate glasses doped by CeO$_2$/TiO$_2$ oxides are significant differ when for pure glasses (figure 1b-c). For SANS data treatment the complex model with consideration of the scattering from large objects and additional scattering from formed small Ti-Ce-O nanoparticles [6] have been used. In order to obtain the values of the gyration radius $R_g$ corresponded with average size of the formed oxides nanoparticles, the experimental data were fitted by a function [8]:

$$d\Sigma(q)/d\Omega = Aq^{-\alpha} + C \exp\left(-\frac{1}{3}q^2R_g^2\right) + D,$$

where $A$, $C$ and $D$ – scaled prefactors coefficients and $R_g$- gyration radius of forming nanoparticles. The obtained values of $R_g$ and curves slope coefficients $\alpha$ are listed in Table 1.
Figure 1. The small angle neutron scattering curves for pure and doped silicate glasses with relative molar concentration CeO$_2$/TiO$_2$ 2.0/0 (a), 0.3/5.0 and 0.3/10 (b), 2.0/6.5 and 2.0/10.0 (c). The solid lines are experimental data fit by equation (1) (for curves at a part) and (2) (for curves at b and c parts).

Table 1. The gyration radius and curve slope coefficients for silicate glasses.

| The molar ratio of initial oxides TiO$_2$/CeO$_2$ | Gyration radius $R_g$, Å | The curves slope coefficient $\alpha$ |
|-----------------------------------------------|--------------------------|----------------------------------|
| 0.3/2.0                                      | 344±2                    | 1.79±0.11                        |
| 1.0/2.0                                      | 347±2                    | 1.91±0.03                        |
| 5.0/2.0                                      | 360±4                    | 1.63±0.02                        |
| 6.5/2.0                                      | 364±4                    | 1.6±0.1                          |
| 10.0/2.0                                     | 371±4                    | 1.28±0.02                        |
| 5.0/0.3                                      | 331±5                    | 1.06±0.16                        |
| 10.0/0.3                                     | 329±4                    | 1.16±0.09                        |
| 0/2.0                                        | -                        | 3.05±0.08                        |
| 0/0.3                                        | -                        | 3.09±0.11                        |

The nanoparticles formation in the glasses doped by cerium oxides only did not observed. The previous optical measurements [4, 5] did not find some significant changes in optical properties of glasses doped without TiO$_2$ inclusions.
Figure 2. The gyration radius $R_g$ as function of relative molar concentration of TiO$_2$ at fixed $x$(CeO$_2$)=2.0

The oxides nanoparticles gyration radius us function of the relative TiO$_2$ molar concentration at fixed cerium oxide concentration $x$(CeO$_2$) = 2.0 are shown in Figure 2. The obtained data can be described by a combination of two linear functions: for low and for high TiO$_2$ concentrations regions. At low molar concentration of titanium oxide range from 0.3 to 2.0 gyration radius $R_g$ of formed nanoparticles increases with coefficient $dR_g/dx \approx 4.3(1)$, while in high concentration range of TiO$_2$ this coefficient decreased to 2.2(2).

The previous obtained [3, 4] optical transmission coefficient $K$ and corresponding wavelength $\lambda_{\text{max}}$ of silicate glasses as a function of Ti-Ce-O nanoparticles gyration radius are shown at figure 3. For smaller nanoparticles with $R_g<350$ Å the significant decreasing of transmission coefficient $K$ was found but the border $\lambda_{\text{max}} \sim 390$ Å characterized of glasses color is unchanged. For larger nanoparticles with $R_g>350$ Å the shaper increasing of $\lambda_{\text{max}}$ to 470 Å was found (figure 3).

We can propose the model of complex oxide nanoparticles forming based on the present SANS data and color centers nature studies [5, 6]. At small molar concentrations ratio of initial CeO$_2$/TiO$_2$ oxides the nanoparticles are formed of predominately from oxygen, trivalent cerium ions Ce$^{3+}$ and tetravalent titanium Ti$^{4+}$ [5]. At relative concentration increasing a valence state of cerium ions changes to tetravalence Ce$^{4+}$ [5, 6] and this fact are reason to formation of another nanoparticles type, which characterized by larger average size and differ mechanism of optical properties forming.
Conclusions

The results of our studies shown that in silicate glasses doped by cerium and titanium oxides the complex oxide Ti-Ce-O nanoparticles formed. The variation of TiO$_2$ relative concentration in low molar concentration range is reason the average size of formed nanoparticles increases as $dR_g/dx \approx 4.3(1)$, but at high TiO$_2$ doping concentration this coefficient approximately twofold decreased. This fact can be explain by model with two different type nanoparticles forming in glasses at different initial oxides ratio and corresponding with different valence state of cerium, and as result the noticeable influencing on glasses optical properties are observed.

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