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The Studies of Structural Aspects of the Cluster Formation in Silicate Glasses Doped with Cerium and Titanium Oxides by Small-Angle Neutron Scattering

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Abstract—The structural aspects of the formation of Ti–Ce–O nanoclusters in silicate glasses doped with oxides TiO₂ and CeO₂ have been studied by means of small-angle neutron scattering. It has been obtained that, in such glasses, complex oxide nanoclusters with sizes of 300–380 Å are formed; their average size increases and the fractal dimension is changed as the concentration of the initial oxides increases. Correlation between the structural characteristics of the nanoclusters and the optical properties of the doped silicate glasses is discussed.

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1. INTRODUCTION

One of topical problems of the modern condensed matter physics is searching for new optical materials with possibilities of fine tuning of their optical characteristics at the expense of varying the chemical composition. The promising materials are silicate glasses doped with oxides of transition and rare-earth elements [1]. The glasses doped with titanium and cerium oxides selectively absorb light in the visible spectral range (they have yellow–orange color), and they are characterized by high thermal stability and stability to hard ultraviolet radiation [1, 2]. This fact determines wide possibilities of using such materials as optical filters for laser engineering and for fabricating bulbs of automobile and signal lamps or jewel imitation [2, 3].

The optical studies of silicate glasses doped with oxides TiO₂/CeO₂ indicate a shift of the optical transmission edge (it changes the material color) with varying the relative concentration of the oxides [3, 4]; in this case, the summary absorption of these glasses is not a sum of partial contributions of absorption by cerium and titanium ions and their oxides. It is assumed that, during the synthesis, complex oxide Ce_xTi_yO_z clusters are formed; in the clusters, titanium is tetravalent, and cerium exists as Ce³⁺ and Ce⁴⁺ [3–5]. This feature provides a possibility of controlled

variation of the glass color, and such structures determine the glass thermal stability.

The physical properties and functional characteristics of the doped silicate glasses are determined by the chemical composition of a glass, electronic state of dopants, and structural features of Ti–Ce–O clusters. The experiments on the small-angle X-ray scattering [6] unambiguously indicate on the formation of Ti–Ce–O clusters with sizes to 2 nm. The method of small-angle neutron scattering makes it possible to expand the range of sizes of the structures under study and to study in more detail these structures with varying the relative concentration TiO₂/CeO₂. In this work, the small-angle neutron scattering is used to study the structure of silicate glasses with different relative concentrations of oxides TiO₂/CeO₂ with aim of elucidating the role of cluster in the formation of their optical properties.

2. SAMPLE PREPARATION AND EXPERIMENTAL TECHNIQUE

The silicate glasses were prepared from a melt of inorganic glass matrix of SiO₂–Al₂O₃–MgO–CaO–BaO–SrO–Na₂O–K₂O–Li₂O composition with addition of corresponding amounts of titanium and cerium oxides. The melt was prepared in a gas furnace

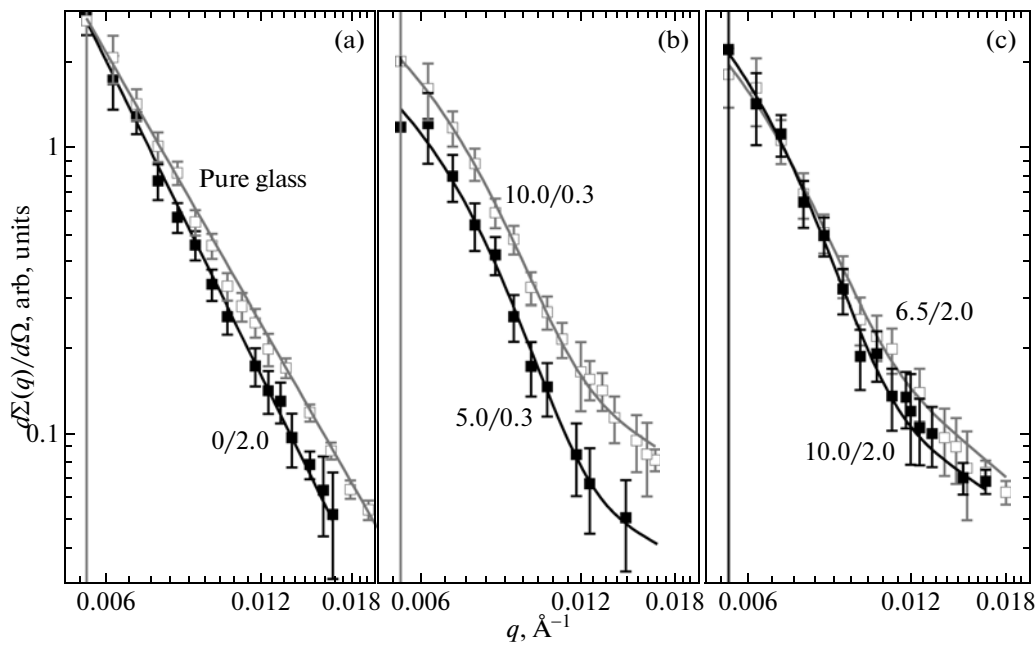


Fig. 1. Curves of small-angle neutron scattering (a) for pure silicate glass and the glass doped only with cerium oxide with the molar concentration 2.0 approximated by function (1) and (b, c) for the glasses doped with $\text{TiO}_2/\text{CeO}_2$ oxides with the relative molar concentrations (b) 5.0/0.3 and 10.0/0.3, (c) 6.5/2.0 and 10.0/2.0 approximated by function (2).

at a temperature of 1420–1450°C. For the experiment, we produced a set of glasses with the relative molar concentrations of oxides $\text{TiO}_2/\text{CeO}_2$ as follows: 0/2.0; 1.0/2.0; 5.0/2.0; 6.5/2.0; 10.0/2.0; 0/0.3; 5.0/0.3; and 10.0/0.3. This set involves the TiO_2 and CeO_2 concentration range to maximal values at which the glassy state of the samples still remains stable.

The small-angle neutron scattering experiments were performed on SANS-1 at the FRG-1 steady reactor (GKSS, Germany) [7]. Four positions of the detector corresponding to various distances from the sample allowed us to carry out the measurements in the q range from 0.005 to 0.25 \AA^{-1} . The neutron wavelength λ was 8.1 \AA , and the resolution was $\Delta q/q = 0.01$. For all spectra, the standard correction procedure for the background and the detector anisotropy was performed.

3. RESULTS AND DISCUSSION

Figure 1 shows the small-angle neutron scattering of the undoped and doped glasses with different relative concentrations of oxides $\text{TiO}_2/\text{CeO}_2$. The curve of small-angle neutron scattering of the undoped silicate glass (Fig. 1a) corresponds to scattering from a fractal structure, and it can be approximated by the function [8]

$$d\Sigma(q)/d\Omega = Aq^{-\alpha} + B, \quad (1)$$

where A and B are the scale coefficients; and α is the slope of the small-angle neutron scattering curve char-

acterizing the fractal dimension of scattering objects [8, 9]. The fractal dimension obtained from the experimental data is $\alpha = 2.99(5)$. The scattering objects can be pores formed during preparing the glasses. They do not contribute to the optical properties of the materials [5].

Doping of the glasses with titanium and cerium oxides appreciably change the shape of the small-angle neutron scattering curves (Figs. 1b and 1c): they take a reverse S-shape, and the degree of deviation from linearity increases with concentration of titanium dioxide. The curves were described using the model including the scattering from large objects (pores in glass, as in undoped glasses) and additional scattering from oxide Ce–Ti–O nanoclusters with smaller size (according to the Guinier formula). Then, the summary intensity of scattering can be represented as [8, 9]

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

where A , C , and D are the scale coefficients; R_g is the radius of gyration characterizing the average size of the oxide nanoclusters.

Using the approximation of the experimental data by Eq. (2), we have obtained the values of the radius of gyration of R_g and also the parameter α for oxide nanoclusters formed (table).

The size of Ce–Ti–O nanoclusters obtained are much larger than the size of clusters detected in [6]. It can be due to the fact that, in the range of values q

used, the small-angle neutron scattering method detects more complex objects including the above noted clusters of rare-earth ions [6] (in consequence of high sensitivity of neutrons as compared to X-ray radiation to the contribution of oxygen to the total structural factor of small-angle scattering [8]).

In the glasses doped only with cerium oxide (with relative concentrations $\text{TiO}_2/\text{CeO}_2$ 0.0/2.0 and 0.0/0.3), the above noted oxide clusters were not formed. It should be noted that, as the glasses are doped with oxide CeO_2 and with no TiO_2 , insignificant red shift of the absorption band occurs with increasing the cerium concentration. This shift is caused by the formation of Ce^{4+} ions. At the same time, cerium is predominantly in Ce^{3+} states at low concentrations [4, 5].

The dependence of the radius of gyration of the nanoclusters on the molar TiO_2 concentration at the constant concentration of cerium oxide $x(\text{CeO}_2) = 2.0$ is shown in Fig. 2. It can be described by a combination of linear functions with different slopes at low and high TiO_2 concentrations. As the molar TiO_2 concentration increases from 0.3 to 10.0, the radius of gyration R_g increases from 344(2) to 371(2) Å; in this case, the coefficient dR_g/dx is 4.3 Å at low concentrations of titanium oxide $x(\text{TiO}_2) < 2.0$, and it decreases to 2.2 Å at high TiO_2 concentrations. The parameter α decreases from 1.8 to 1.3 as the molar TiO_2 concentration increases from 0.3 to 10.0, and this fact demonstrates a change in the fractal dimension of scattering objects in the glass matrix during formation oxide aggregates. It is likely due to an increase in additional contribution to scattering from the object–matrix borders with the titanium oxide concentration because of increase in the relative number of nanoclusters formed.

Oxide nanoclusters form in the glasses with lower concentration of cerium oxide $x(\text{CeO}_2) = 0.3$ as well; in this case, the radius of gyration is slightly dependent on the TiO_2 concentration ($R_g \approx 330$ Å), and its value is markedly lower as compared to compositions with higher concentration $x(\text{CeO}_2) = 2.0$ (table). It can confirm the assumption that the aggregates can exactly be formed from titanium and cerium oxides with minimal participation of other components of the glasses [3].

Using the data of optical studies [3, 4] of silicate glasses with different molar concentrations of titanium and cerium oxides, we can build the dependence of the slope coefficient K for the optical transmission spectrum and the wavelength λ_{max} corresponding to the maximum value of K and characterizing the optical transmission threshold of the glasses on the radius of gyration of oxide nanoclusters in these glasses (Fig. 3). At $R_g < 350$ Å, the transmission curve slope coefficient K decreases significantly, while λ_{max} is almost unchanged ($\lambda_{\text{max}} \sim 390$ Å). At $R_g > 350$ Å, λ_{max}

Calculated values of the radius of gyration R_g for nanoclusters formed in silicate glass

| Molar ratio of initial oxides $\text{TiO}_2/\text{CeO}_2$ | Radius of gyration R_g , Å | Slope of the scattering curve α |
|---|------------------------------|--|
| 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 |
| 0.0/2.0 | — | 3.05 ± 0.08 |
| 0.0/0.3 | — | 3.09 ± 0.11 |

increases stepwise to ~ 470 Å, and it continues to increase with the average radius of nanoclusters. The slope coefficient K of the optical spectrum remains almost unchanged at $R_g > 360$ Å.

Thus, based on the presented results of small-angle neutron scattering and the data on studies of the color centers in the glasses [3], we can propose the model of formation of complex oxide nanoclusters in these objects. At low relative concentrations of oxides $\text{TiO}_2/\text{CeO}_2$, they form predominantly of oxygen, trivalent cerium ions Ce^{3+} , and tetravalent titanium ions Ti^{4+} [3]. As the relative concentration of $\text{TiO}_2/\text{CeO}_2$ increases, the valence state of the cerium ion is changed to Ce^{4+} [3, 10], and it provides the formation of other type of nanoclusters with larger average size (Fig. 2) and changes of optical glasses (Fig. 3).

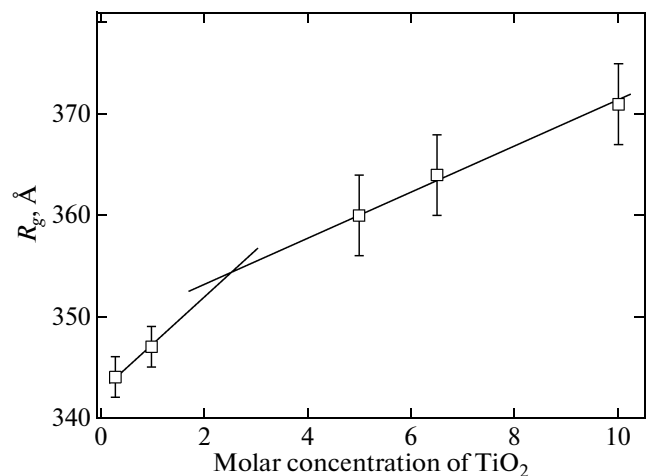


Fig. 2. Dependence of the radius of gyration R_g of oxide nanoclusters on the molar TiO_2 concentration for the constant level of doping $x(\text{CeO}_2) = 2.0$.

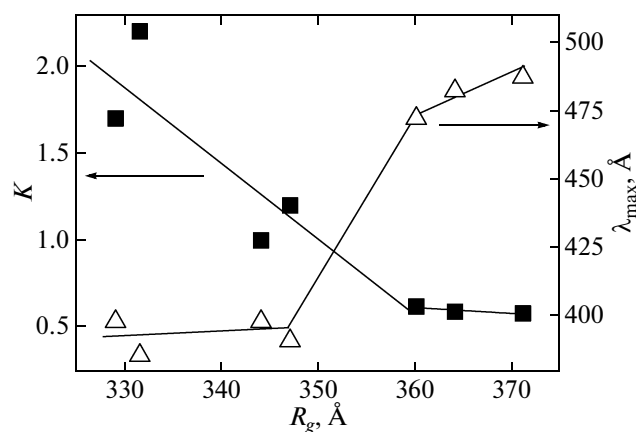


Fig. 3. Dependence of the slope of the optical transmission spectrum K and corresponding wavelength λ_{\max} (according to [3]) on the radius of gyration of R_g of nanoclusters.

It is likely that the stoichiometry of $\text{Ce}_x\text{Ti}_y\text{O}_z$ structures is changed with the $\text{TiO}_2/\text{CeO}_2$ ratio; however, to make more adequate conclusion on the composition, a further study is necessary.

4. CONCLUSIONS

The results of this study show that oxide 330–380-Å-sized nanoclusters form in silicate glasses doped simultaneously with cerium and titanium oxides. In the glasses with low concentrations $x(\text{CeO}_2) = 0.3$, the average size of nanoclusters formed is slightly dependent on the TiO_2 content. In the glasses with high concentrations $x(\text{CeO}_2) = 0.2$, their average size increases nonuniformly. The concentration dependence of the nanocluster size is characterized by the coefficient $dR_g/dx = 4.3 \text{ \AA}$ at $x(\text{TiO}_2) < 2.0$ that decreases to 2.2 \AA at high TiO_2 concentrations. We found the correlation between the average size of these nanoclusters and the optical properties of the silicate glasses that can be due to the variation in the valence of cerium ions and the stoichiometric composition of the glasses.

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