Formation of Silver Nanoparticles in $Li_2B_4O_7$-Ag_2O and $Li_2B_4O_7$-Gd_2O_3-Ag_2O Borate Glasses

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Nanocomposite materials, whose basis is consisted of metallic nanoparticles (MNPs) of noble metals (Au, Ag, Pt) in dielectric media, are the object of significant attention in recent years. This is caused by large influence of MNPs on linear and nonlinear susceptibilities of dielectric matrix [1], radiative recombination and giant surface enhanced Raman scattering.

Borate glasses, the basis of which is boron anhydride B_2O_3 with its tendency to polycondensation, can be prospective for MNPs formation. The borate glasses structurally consist of boroxole groups, which are joined by the bridge oxygen atoms that makes their structure enough open. These boroxole groups make the borate glass structure more open near the glass transition temperature T_g [2] that simplifies the process of MNPs formation.

The formation of metallic (silver) nanoparticles (AgNPs) in the near-surface layer of $98.0Li_2B_4O_7$–$2.0Ag_2O$ ($Li_2B_4O_7$:Ag) and $97.0Li_2B_4O_7$–$1.0Gd_2O_3$–$2.0Ag_2O$ ($Li_2B_4O_7$:Gd,Ag) glasses at the annealing in vacuum or in air has been reported. The proposed mechanism of AgNPs growth in the near-surface layer of $Li_2B_4O_7$:Gd,Ag glass during its annealing in air belongs to the "bottom-up" class. On the other hand, if the specimen is annealed in vacuum, the process of formation of neutral Ag^0 atoms on the surface substantially dominates over the reduction with the participation of gadolinium ions in bulk. As a result, the processes of AgNPs nucleation and formation run more intensively on the specimen surface. A conclusion is drawn that the annealing in vacuum does not necessarily require the presence of reducing ions, where as the formation of nanoparticles at the annealing in air is impossible without reducing agents. Structural defects play a crucial role in the AgNPs nucleation process. In the absorption spectra of glass samples $Li_2B_4O_7$:Ag, annealed in a vacuum, revealed an intense plasmon band characteristic for silver atoms. At the same time, for $Li_2B_4O_7$:Gd,Ag intensive similar plasmon bands detected in samples annealed in a vacuum and in air.

The radii AgNPs calculated by us on the basis of the plasmon band half-width $Li_2B_4O_7$:Gd,Ag glasses falls within the interval of 1.0–1.5 nm and well correlate with radii of 2.8–6.0 nm obtained for AgNPs in various glasses by other authors [3,4]. However, our previous AFM researches of AgNPs formed by annealing in the reducing atmosphere of H_2 [5] or in vacuum (in this work) on the surface of $Li_2B_4O_7$:Ag glass showed that the value of R falls within the limits from 7 to 25 nm, with a maximum near 15 nm. For samples $Li_2B_4O_7$:Gd,Ag, annealed in vacuum, the size of AgNPs on the surface was evaluated also by small-angle X-ray scattering. The average size of AgNPs was found to be $d \approx 26.0$ nm. Such a spread in the dimensions of AgNPs obtained using different methods in $Li_2B_4O_7$:Ag and $Li_2B_4O_7$:Gd,Ag glasses can be explained by the fact that different techniques of radius determination may give rise to nonidentical results.

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