Clustering of rare-earths and its effect on the precipitation of PbS quantum dots in glasses

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Glasses doped with PbS quantum dots (QDs) can absorb and emit light at wavelengths that can be controlled from ~0.7 ≤ λ ≤ ~2.0 μm by adjusting QDs' size from ~2 to ~10 nm. They have possible applications as solid-state saturable absorbers for mode-locked lasers and as fiber-optic amplifiers in optical communication. The average size of PbS QDs and their size distribution inside glasses can be tailored by carefully controlling the temperature and duration of thermal treatment. This process, however, normally results in an uncontrolled spatial distribution of QDs in the glass matrix. Ion-implantation and femto-second laser irradiation techniques were used to realize space-selective formation of QDs for micro- and nano-photonic devices.

We have reported that sizes of PbS QDs can be controlled by carefully optimizing the concentration of Er^{3+}, Tm^{3+} and La^{3+} ions in glasses. It was found that photoluminescence located at ~ 1500nm shifts to short wavelength side as Nd_2O_3 content increases. Scanning transmission electron microscopy (STEM) and energy dispersive x-ray spectroscopy (EDS) show that relatively high concentrations of heavy metals such as Pb^{2+}, Nd^{3+} inside QDs instead of glass matrix. For the investigation of growth kinetics, the diameters of PbS QDs in glasses containing different Nd_2O_3 were calculated from the center wavelengths of absorption bands. We found that the radius (r) is proportional to t^x when x varies between 0.203 to 0.217 and it is considerably smaller than the value predicted by Lifshitz-Slyozov-Wagner theory.

However, there is no fundamental analysis on the local environment and clustering of rare-earth ions in PbS QDs. Atom probe tomography (APT) method is used to analyze the distribution of RE^{3+} ions inside glass matrix and its effect on the precipitation of PbS QDs. We found Nd^{3+} clusters of approximately 2-4nm in diameter exist inside the glass (Fig. 1). Extended x-ray absorption fine structure (EXAFS) analysis in Fig. 2 showed that Nd^{3+} ions are surrounded by ~8 oxygen ions inside the QDs and there is no evidence of forming Nd-S bonds. Energy dispersive spectroscopy (EDS) and electron energy loss spectroscopy (EELS) analysis was used to analyze the role Nd^{3+}-O clusters on the formation of PbS QDs. EDS and EELS results showed that Nd^{3+} ions are preferentially concentrated inside the PbS QDs rather than in the glass matrix after heat-treatment. Therefore, we believe that those Nd^{3+}-O clusters work as nucleating sites for precipitation of PbS QDS.

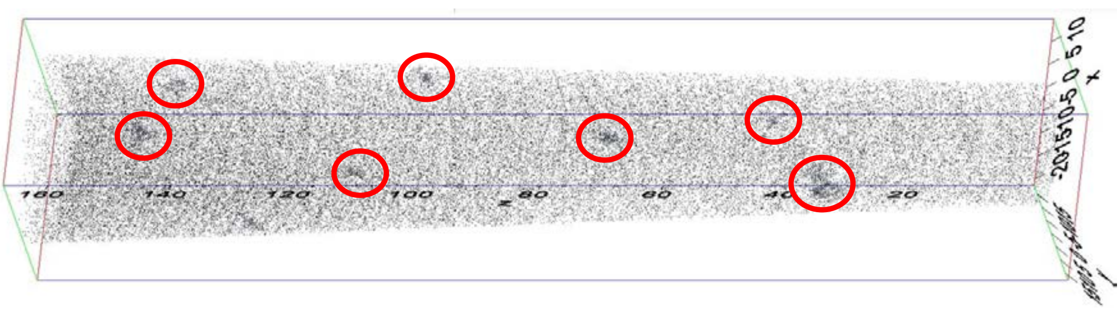
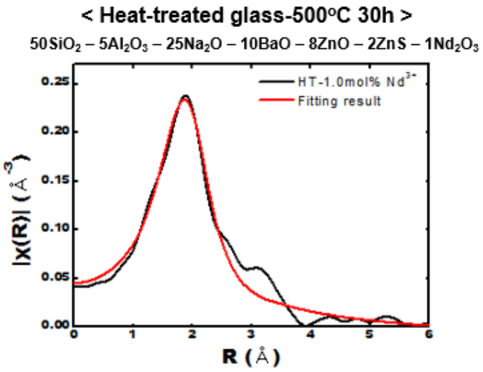


Figure 1: Atom distribution and concentration profile of Nd^{3+} ions



Nd-O pair	R(Å)	N	σ^2(Å²)	R-factor
	2.4166	7.6181	0.0225	0.0056

Figure 2. Local environment of Nd L_3-edge of the glass containing additional S^{2-} contents after heat-treatment at 500°C for 30h