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# Compositional dependence of $Se_2^-$ color center formation in silicate glasses

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ABSTRACT

We experimentally verified, within silicate glasses, the formation of $Se_2^-$ color centers that are responsible for a broad visible emission under optical excitation at UV wavelengths. In addition to Raman spectra, all the spectroscopic analyses on absorption, photoluminescence, and photoluminescence excitation unanimously confirm the formation of $Se_2^-$ color centers. However, the visible absorption due to $Se_2^-$ color centers disppeared upon increasing concentration of $Na_2O$, which implies that their formation would depend on the compositions of silicate glasses. The role of $Na_2O$ in the formation mechanism in relation to glass structure is then discussed in terms of various analyses on X-ray diffraction patterns, X-ray photoelectron spectroscopy, and Raman spectroscopy.

## 1. Introduction

Quantum dots (QDs) based on chalcogenide compounds can be easily formed within oxide glasses via conventional melt-quenching methods, and their optical properties have been investigated actively [1–3]. For example, QDs such as PbS and PbSe [3–5] show broad emissions at optical telecommunication window (1.2–1.7 μm). CdS (or CdSe) QDs, on the other hand, exhibit wide bandgap energy corresponding to visible wavelengths and have been extensively studied for applications such as solar cells, display, bio-imaging and light-emitting diodes [6–9]. It is also possible to control CdSe QD bandgap by incorporation into silicate glasses, and therefore CdS (or CdSe) QDs have been exploited [10–13]. ZnSe QDs can be incorporated within glasses via the sol–gel process and provide green emissions [6,14].

Visible emissions from chalcogen elements within glasses are also possible when proper color centers such as $S_2^-$ or $Se_2^-$ formed [15–17]. These emissions are electronic transitions between the molecular orbital states and do not have a direct relationship with QDs formation. Those visible emissions have been observed in halides or sodalite crystals at low temperatures where there is no evidence of QDs. Recently, Choi et al. [18] reported the formation and visible emissions from $Se_2^-$ color centers. They monitored broad visible emissions centered at around 550 nm at room temperature, varying ZnSe content. It appeared that the addition of ZnSe was responsible for the $Se_2^-$ color center formation [18]. In this study, we prepared silicate glasses to investigate the mechanism of $Se_2^-$ color center formation and its compositional dependency. X-ray diffraction, Raman, and X-ray photoelectron spectroscopies were used to investigate the role of glass structure in the formation of color centers.

## 2. Experimental

The nominal composition of silicate glass was $(90-x)SiO_2$–$xNa_2O$–5BaO–5ZnO ($x = 25$, 30, 35 and 40; in mol%), and 3 mol% ZnSe was additionally incorporated. Starting materials with high purity (>99.9%) were weighed and melted at 1350 °C for 1 h under ambient atmosphere using an alumina crucible. Glasses were prepared by quenching of the melts on a brass mold followed by annealing at 350 °C for 1 h. The glasses were cut into plates with a thickness of ~3 mm and optically polished. Absorption spectra were recorded with an UV/VIS/NIR spectrophotometer (Perkin-Elmer, Lambda 750). Photoluminescence (PL) spectra were measured by a fluorescence spectrometer (Perkin Elmer, LS55). The amorphous nature of the glasses was confirmed by an X-ray diffractometer (XRD; Rigaku, D/MAX-2500U) and field-emission transmission electron microscope (FE-TEM; JEOL, JEM-2100 F). A Raman spectrometer (HORIBA Jobin-Yvon Ltd., SPEX 1403) with a 514 nm excitation was employed to find the formation of $Se_2^-$ color centers as well as possible structural changes. An X-ray photoelectron spectrometer (XPS; Thermo Scientific, Multilab ESCA2000) was used to monitor the changes in the electronic state of oxygens. All measurements were performed at room temperature.

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## 3. Results

Fig. 1 shows the UV/VIS absorption spectra of the silicate glasses with different $Na_2O$ concentrations. Characteristic absorption at ~365 nm due to $Se_2^-$ color centers within silicate glasses was observed [16–18]. $^2\Pi_g \rightarrow {}^2\Delta_u$ transition of $Se_2^-$ or photo-chemically formed $Se_2$ di-radicals from $Se_2^-$ is responsible for the absorption [16,17]. However, it is interesting to find that the intensities of the absorption peak decreased and disappeared as $Na_2O$ content increased up to 40 mol% while ZnSe content was fixed at 3 mol%. This decrease in absorption is also clear from changes in the color of glasses as shown in Fig. 1. The results indicate that the formation of $Se_2^-$ color centers became difficult with increasing $Na_2O$ content.

The compositional dependency of color center formation can also be found from the PL spectra in Fig. 2. The PL spectra were recorded while the specimens were excited at 266 nm using a cutoff filter at 490 nm to completely eliminate noise from the excitation source. Broad emissions centered at ~550 nm from $Se_2^-$ color centers were observed. The intensity decreased as $Na_2O$ content increased within the glasses. The inset figure shows the excitation PL (PLE) spectrum from x = 25 mol% specimen monitored at 550 nm while changing excitation wavelength. It should be noted that the PLE spectrum matches well to the absorption spectrum of $Se_2^-$ in a sodalite structure [16] and further supports that the $Se_2^-$ color centers are the origin of the emission. It should be mentioned that the emission intensity decrease is not linearly correlated to the decrease of absorption peak at ~365 nm. Difference in excitation wavelength at ~266 nm may be responsible for this which requires further spectroscopic study in detail.

Fig. 3 depicts the XRD and FE-TEM results which inspected the possible formation of crystalline phases within the silicate glasses. As shown in Fig. 3(a), no apparent crystalline peaks were found from our glasses containing 3 mol% ZnSe with varying $Na_2O$ content. FE-TEM was examined for x = 35 and 40 mol% at which composition the color of the glass vanished. Although crystalline peak has not been observed in XRD, Fig. 3(b) clearly show that nano-crystals (NCs) were formed within the glass at x = 35 mol%. Those NCs were attributed to Se nano-crystals based on the observed crystalline lattice parameter and XRD peak at high ZnSe concentration [18]. However, glass with x = 40 mol% showed no such an absorption peak due to the $Se_2^-$ color centers (Fig. 1), and at the same time revealed no NCs present inside, other than in some areas stained by the electron bombardment during TEM observations (Fig. 3(c)). These results imply that Se NCs and $Se_2^-$ color centers are formed up to x = 35 mol% with the same formation mechanism within the silicate glasses.

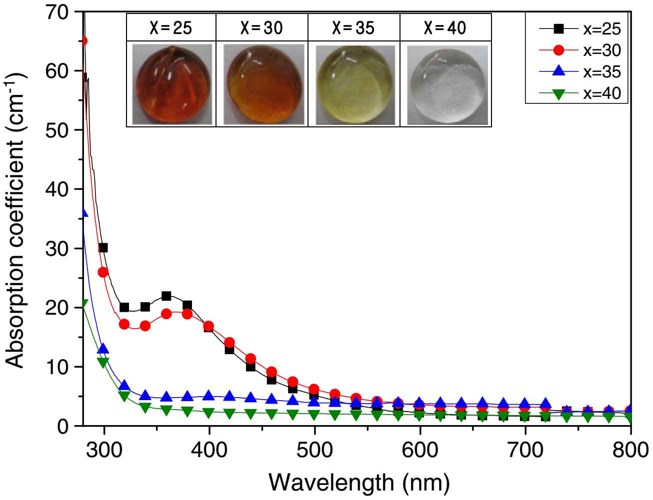

**Fig. 1.** UV/VIS absorption spectra of the silicate glasses with $Na_2O$ contents (x) of 25, 30, 35 and 40 mol% in $(90-x)SiO_2$–$xNa_2O$–5BaO–5ZnO. ZnSe was fixed at 3 mol%. The inset figure shows actual photographs of the samples varying $Na_2O$ contents.

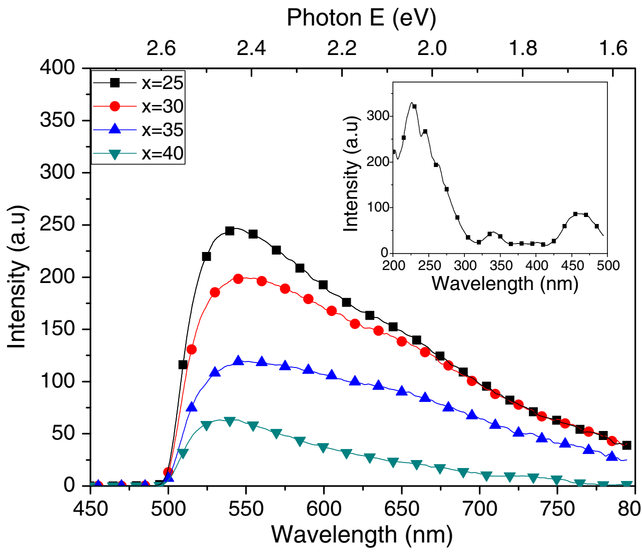

**Fig. 2.** PL spectra of the silicate glasses with $Na_2O$ contents (x) of 25, 30, 35 and 40 mol% while ZnSe was fixed at 3 mol%. The excitation wavelength was 266 nm. The inset figure shows the PLE spectrum of a sample with x = 25 mol% while monitoring at 550 nm.

## 4. Discussions

As shown in the figures, $Na_2O$ played a crucial role in the formation of $Se_2^-$ color centers as well as Se NCs within silicate glass. Possible formation of ZnSe QDs can be also considered, but the formation of ZnSe QDs was unlikely as there was no evidence found from XRD and TEM analyses. It should be noted that the absorption peak in Fig. 1 did not show any shift when the glass with x = 25 mol% was heat treated above its glass transition temperature (~460 °C), i.e., 580 to 620 °C for 20 h, supporting that the origin of the absorption peak is hardly related to the possible quantum dots formed inside the glass.

The role of $Na_2O$ and the existence of ZnSe QDs within the present silicate glass can be directly observed by Raman spectra. As exhibited in Fig. 4, characteristic strong Stokes shifted peaks at ~323 $cm^{-1}$ and its overtones at ~644, 965, 1287 $cm^{-1}$ due to $Se_2^-$ [16,19] were detected from the glass with x = 25 mol%, and their intensities decreased as $Na_2O$ content increased. A decrease in the intensities of Raman bands suggests that it becomes difficult to form $Se_2^-$ color centers as $Na_2O$ replaces $SiO_2$ in glasses. The result coincides with the decrease in the absorption and PL intensities. A small Raman peak at ~260 $cm^{-1}$ due to the vibration mode of the Se–Se chain [16,19] also appeared and decreased with increasing $Na_2O$ concentration. The presence of the Se–Se chain within the glass network proposes the possibility of Se NC formation. Thus, it seems plausible to conclude that the formation mechanism of $Se_2^-$ color centers and relevant Se NCs become difficult due to the modification of the network through $Na_2O$ addition. The decrease of Raman peaks at ~1100 $cm^{-1}$ along with the increase at ~950 $cm^{-1}$ is due to the structural change of sodium silicate glasses with an $Na_2O$ increase as Raman peaks at ~1100 and ~950 $cm^{-1}$ are attributed to the symmetric stretch of $[SiO_4]$ tetrahedra with one NBO and two NBOs, respectively [20]. It should be noted that characteristic transverse optical (TO) and longitudinal optical (LO) phonon modes at ~205 and 250 $cm^{-1}$ [21,22] due to ZnSe QDs have not been observed eliminating ZnSe QDs formation.

It is well-known that $Na_2O$ breaks Si–O–Si bonds between $[SiO_4]$ tetrahedral units producing non-bridging oxygens (NBOs), and these NBOs can be easily detected with XPS [23]. Fig. 5 shows the separation of an $XPS{:}O_{1s}$ band in glasses with different $Na_2O$ content. The inset figure shows an example of deconvultion for a glass with x = 40 mol%.