Effect of nanophase separation on crystallization process in Ge–Se glasses studied by Raman scattering

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Nanophase separation in glassy materials attract scientists' interests in the basic science of noncrystalline materials, and in current and evolving technologies as well. Recently, Boolchand and Bresser discussed the structural origin of broken chemical order in GeSe$_2$ glass by Raman scattering, $^{119}$Sn Mossbauer spectroscopy and temperature-modulated differential scanning calorimetry (MDSC) experiments performed on (Ge$_{0.99}$Sn$_{0.01}$)$_x$Se$_{1-x}$ glasses in the $0.30 < x < 0.36$ range [Phil. Mag. B 80 (2000)]. They pointed that the Ge–Ge bonds constitute part of a marginally rigid Ge$_2$(Se$_{1/2}$)$_6$-bearing nanophase that is formed separately from the Ge(Se$_{1/2}$)$_4$-tetrahedra-bearing backbone of the glasses. We have found several evidence of nanophase separation of the two structural units in the similar range of $0.30 \leq x \leq 0.37$ in Ge$_x$Se$_{1-x}$ glasses by investigating Raman spectra in a wide temperature range, 4–1200K. This paper reports our last results on how the nanophase separation influences the crystallization process induced by heating the glasses beyond the glass-transition temperature, $T_g$.

Raman scattering measurements were performed in an Ar gas atmosphere with a low power-density ($< 1W/cm^2$) and a long wavelength (730nm) excitation to avoid additional heating effect or light-induced structural changes. Temperature was controlled by an electric furnace to limit the fluctuation to less than 2K during we accumulated a spectrum. Glassy (or super-cooled liquid) spectral shapes in 150–300cm$^{-1}$ range are well fitted by a Ge–Ge bonds related bend, two Ge(Se$_{1/2}$)$_4$-tetrahedra bends and a Se–Se bonds related bend. We plot an intensity ratio, $I_{Ge-Ge}/I_{GeSe_4}$, of the Ge–Ge bend to the Ge(Se$_{1/2}$)$_4$-tetrahedra bends, which is normalized by its ratio at room temperature (RT) for each composition.

For $x \leq 0.35$, the intensity ratio of $I_{Ge-Ge}/I_{GeSe_4}$ starts to decrease with temperature much lower than the $T_g$ determined by a DSC measurement. In these glasses, the separated unit of Ge$_2$(Se$_{1/2}$)$_6$, which is marginally rigid, should be destabilized by the tetrahedra-bearing backbone of the glasses. Thus, the Ge$_2$(Se$_{1/2}$)$_6$ contained nanophase is easier than the backbone network to be deformed when we heat up glass, and thereafter, to be changed into a part of tetrahedra-bearing network through acquiring Se atoms nearby. Note that in GeSe$_2$ glass one Ge–Ge wrong bond companions two Se–Se wrong bonds. Such structural changes happen even well below $T_g$ and result a crystallization of GeSe$_2$. While for $x > 0.35$, the intensity ratio does not show a significant change below $T_g$. Furthermore, the glasses crystallize into GeSe and GeSe$_2$ crystalline phases (in a phase diagram of Ge-Se system, this two crystalline phases coexist in $x > 1/3$). A large nanophase, containing at least two units of Ge$_2$(Se$_{1/2}$)$_6$, certainly reduces the local stresses (a red shift of vibrational frequency of Ge–Ge bonds with $x$ apparently supports our conclusion). And the large nanophase in $x > 0.35$ enables an event of decomposing the ethane-like unit of Ge$_2$(Se$_{1/2}$)$_6$ into the GeSe and Ge(Se$_{1/2}$)$_4$ structural units to happen in the super-cooled liquid state that allows both the GeSe and GeSe$_2$ crystalline phases to appear simultaneously.