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Crystallization and nanometric heterogeneity in glass: *In situ* observation of the boson peak during crystallization

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In situ measurement of boson peak in several glasses was performed during the crystallization process to elucidate crystallization dynamics. In this study, it was experimentally illustrated that a drastic decrease in elasticity and damping of the boson peak occurred during the crystallization process when $T/T_g \sim 1.1-1.2$. A possible mechanism for the crystallization precursive stage is also discussed, which integrates our boson peak observation results, Hikima's description [J. Mol. Struct. **479**, 245 (1999)], Cabral's thermodynamic data [J. Non-Cryst. Solids **343**, 85 (2004)], and other works.

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I. INTRODUCTION

Glassy state is a thermodynamically nonequilibrium state and an external thermal stimulation will eventually lead to the more stable state, i.e., the crystalline state. Since it is expected that the formation of nonlinear optical crystals in the glass matrix enables us to create advanced photonic-device components, exploitation and development of new crystallizing oxide glasses have been extensively and vigorously performed.[1–4] However, during the transition from the glass to crystal phase, the process of the initial stage of crystallization is not fully understood. Although *in situ* high-temperature techniques, e.g., x-ray diffraction and magic angle spinning–NMR under heating conditions,[5–7] have been used for measurements in crystallization studies, they are insufficient to explain the transformation from the glass to crystal phase. Therefore, a new study providing an insight into crystallization is necessary to elucidate the crystallization dynamics.

In amorphous matter, an asymmetrical broad band is observed in the low-wavenumber region of inelastic light-scattering spectra and is termed as the boson peak. Although its origin is still controversial, an excess of density of state (DOS) of vibration originating in the nanometric heterogeneous region due to density fluctuation or the cohesive nanodomain with a certain characteristic dimension, R_c, i.e., correlation radius, is considered as one of the possible reasons for their origin.[8–14] Indeed, such a nanoheterogeneity in the glass has been proposed using the different approaches by several authors.[9,14–18] In addition, the relation between boson peak and microscopic glass structure and its relaxation mechanism have been investigated.[18–22] For instance, Takahashi *et al.*[22] verified the presence of inhomogeneous structure consisting of network-former and network-modifier enriched regions in glassy fresnoite, and they supported the structural models mentioned above on the basis of *in situ* observation of boson peak during the heating process. Based on these studies, it is expected that the boson peak observed in the crystallization process provides significant information about the transition state between the glassy and crystalline phases. Therefore, we performed *in situ* observations of boson peaks of crystallizing glasses while elevating the temperatures for the purpose of understanding the initial crystallization stage and its dynamics.

II. EXPERIMENTAL

In this study, we have three types of oxide glasses as samples, i.e., $33.3BaO-66.6SiO_2$ (BS), $15K_2O-15Nb_2O_5-70TeO_2$ (KNT), and $25K_2O-25Nb_2O_5-50GeO_2$ (KNG). Although these glasses consist of different glass-forming oxides, they indicate a strong tendency toward homogeneous nucleation.[23–26] This is quite suitable to observe the transition state between the glassy state and crystalline state because high nucleation density could be expected. In particular, because the thermodynamic parameters of BS glass have been reported, we can estimate the critical radius of nucleation (will be discussed later). The glass samples were prepared by a conventional melt-quenching technique. The glass-transition temperature, T_g, and crystallization on-set temperature, T_x, of the glass samples were estimated by differential thermal analysis (DTA). Heating rate was 20 °C/min. Depolarized inelastic light-scattering spectra (Stokes side) in the low-wavenumber region of the glass samples were measured using an Ar^+ gas laser operating at 514.5 nm and a system consisting of a triple-grating monochromator and liquid-nitrogen-cooled charge-coupled device detector (HORIBA-Jobin Yvon, T64000). Boson-peak measurement was performed while elevating the temperature from ~25 °C (RT) using a heat stage. (The heating rate was 20 °C/min.) The spectra obtained in the low-wavenumber region were normalized with respect to the Bose-Einstein factor. The normalized boson peak corresponds to the frequency-reduced DOS, i.e., $g(\omega)/\omega^2$. The reduced boson peak was analyzed by a log-normal function to evaluate the position of the maximum, ω_{BP}, and the full width at half maximum (FWHM).[21]

Figure 1 shows the result of *in situ* measurements of inelastic light-scattering spectra in the low-wavenumber region for the studied glasses in the temperature range of RT to 900 °C. In all types of glasses, a broad asymmetrical band (i.e., boson peak) was clearly observed in the range below $\sim 150\ cm^{-1}$ and was well fitted using a log-normal curve (solid lines in Fig. 1). With increasing temperatures and par-

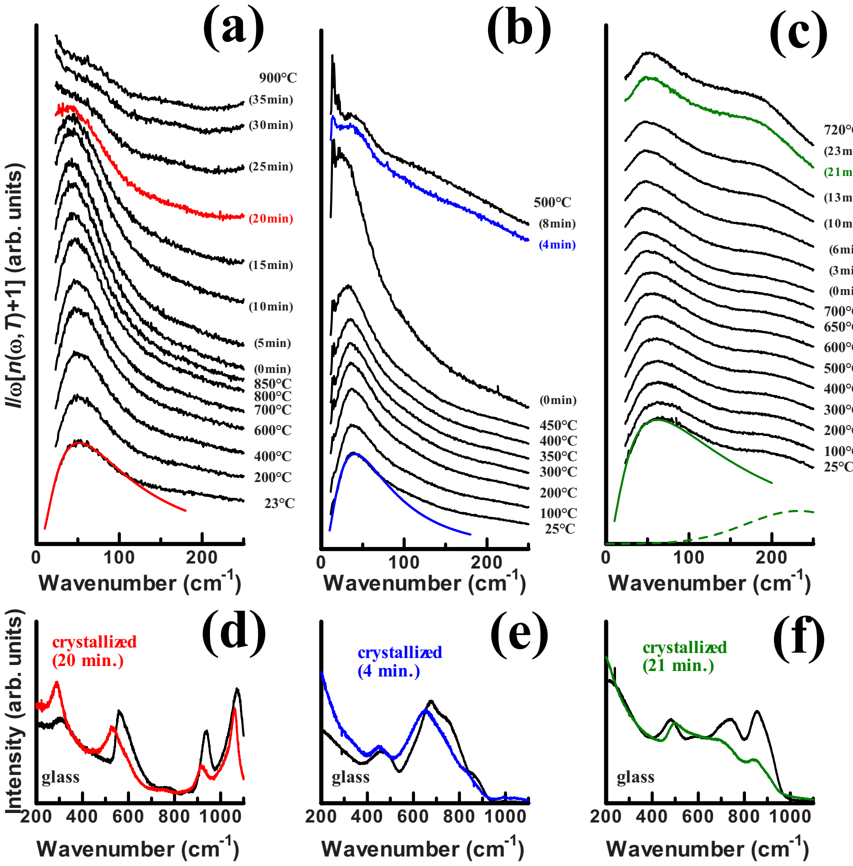

FIG. 1. (Color online) *In situ* measurement of inelastic light-scattering spectra in the low-wavenumber region in (a) BS, (b) KNT, and (c) KNG glasses during the heating process. The solid lines correspond to the fitting results of the boson peak. In the case of KNG glass, the obtained spectra of the low-wavenumber region (up to ~300 cm^{-1}) were analyzed using the sum of the boson peak and Gaussian curve [dashed curve in (c)] because the vibrational band, which is attributed to the Nb-O bond (Ref. 42), largely contributed to the spectra in the range around 200 cm^{-1}. Comparison of the crystallized phase spectra with that of (d) BS, (e) KNT, and (f) KNG glasses: the Raman spectra with colored lines in (d)–(f) correspond to the spectra of the early stage of crystallized phases in the studied glasses, suggesting that the glass samples still macroscopically maintained a glassy state before those samples.

ticularly around the T_x, (T_x=868, 504, and 682 °C for BS, KNT, and KNG glasses, respectively) the boson peak became much broader as the crystallization progressed, which was confirmed by the change in Raman spectra in the middle- and high-wavenumber regions [Figs. 1(d)–1(f)]. Chen *et al.*[14] pointed out that the so-called floppy mode, which appeared in the glass with $r<2.4$ (r: mean coordination number), contributes to the DOS of vibration in chalcogenide system glasses and implied that this effect should be taken into account in the boson-peak analysis. However, since the glasses in this study are oxide based and their values of r are expected to be higher,[27,28] the contribution of floppy mode to boson peak is probably negligible.

In Figs. 2(a) and 2(b), we show the variation in ω_{BP} as a function of reduced temperature (T/T_g) and time around T_x, respectively, in the studied glasses (closed symbols connected with solid lines). One can see a similar response of ω_{BP} to the temperature irrespective of the constituents of glasses; ω_{BP} gradually shifted to lower wave numbers and dropped suddenly in the vicinity of T_g. ω_{BP} eventually reached a minimum at $T/T_g\sim1.1-1.2$ ($\approx T_x$), i.e., 900, 500, and 720 °C in BS, KNT, and KNG glasses, respectively (hereafter, these temperature are denoted as T_{min}). When the temperature was maintained at T_{min}, the glasses showed a shift of ω_{BP} to higher wave numbers after ~4–20 min [Fig. 2(b)].

III. DISCUSSION

The frequency of the boson peak ω_{BP} is closely related to the sound velocity in a glass, i.e.,

$$\omega_{\mathrm{BP}} \approx \frac{v_t}{cR_c}, \tag{1}$$

where R_c is the correlation radius, v_t is the transverse sound velocity, and c is the light velocity.[29,30] Since $v_t^2=G/d$ (G: shear modulus; d: density), the square of ω_{BP} is approximately equivalent to the shear modulus of the heating process, i.e., $\omega_{\mathrm{BP}}^2\propto G$.[22] According to Rouxel,[31] at $T/T_g\geq1$, the elastic modulus dropped suddenly in the vicinity of T_g because of a decrease in the viscosity of the glass phase caused by the transition from the glass state to the supercooled-liquid (SCL) state. On the other hand, according to Soga,[32] elasticity increases with increase in volume fraction of the crystalline phase (i.e., the decrease in specific volume) in silicate glasses. The most likely reason for this is the decrease in the specific volume.[22,33] KNT and KNG glasses, which crystallize the $K_2(Nb_{1/3}Te_{2/3})_2O_{4.8}$ and $K_{3.8}Nb_5Ge_3O_{20.4}$ phases, respectively, showed a large increase in sound velocity after crystallization.[26,34] Fukawa *et al.*[35] also reported that the increase in sound velocity, which corresponds to an increase in the elastic modulus due to crystallization, was observed with increasing temperature in the Brillouin scattering spectra of a Li_2O-B_2O_3 glass system. Although the total G is increased by the crystallization, the G of glassy phase should be small as elevating temperature since the boson peak comes from the glassy (or SCL) phase. However, the ω_{BP} exhibited the ascent at $T/T_g\sim1.1-1.2$. It is suggested that "apparent" shear modulus in the glassy phase increases with the increase in volume fraction of crystalline phase, and consequently the boson-peak shift reflects

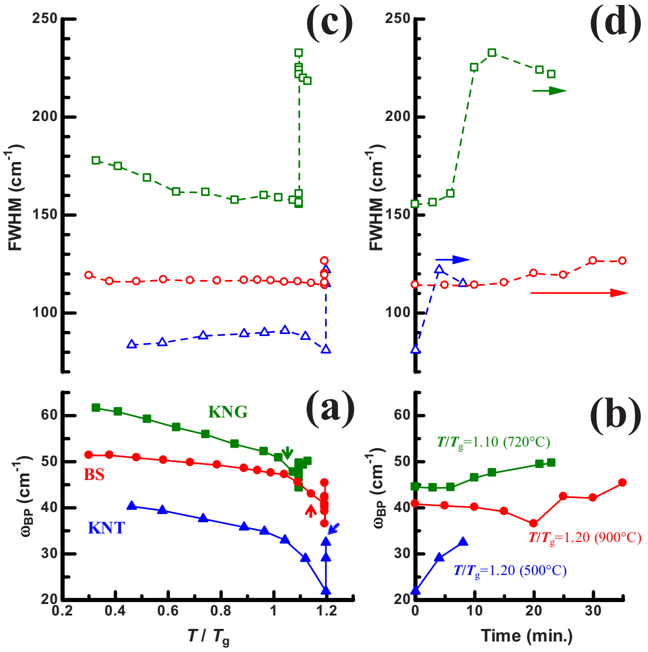

FIG. 2. (Color online) (a) The Variation in ω_{BP} (closed symbols) as a function of reduced temperature, T/T_g, (b) the variation in ω_{BP} at T_{min}, (c) the FWHM of boson peaks (open symbols) as a function of T/T_g, and (d) the FWHM at T_{min} in the studied glasses. The values of T_g in BS, KNT, and KNG glasses were estimated to be 710, 373, and 633 °C, respectively, by DTA. Small arrows correspond to the T_x/T_g (T_x: crystallization on-set temperature) of glasses, which were estimated to be 868, 504, and 682 °C for BS, KNT, and KNG glasses, respectively. Large arrows indicate the beginning of crystallization, which is confirmed by a change in the shape of the Raman spectra [Figs. 1(d)–1(f)].

the apparent increase in G in accordance with $\omega_{\mathrm{BP}}^2 \propto G$. Therefore, the immediate depression (in the vicinity of T_g) and subsequent ascent ($T/T_g \sim 1.1-1.2$) of ω_{BP} are attributed to the decrease and increase in the shear modulus (G), corresponding to the transition states of glass-SCL and SCL-crystal, respectively. Moreover, according to Sokolov *et al.*,[29] SCL has T_c/T_g values of $\sim 1.1-1.2$ (T_c: critical temperature in the mode-coupling theory). This study reveals that the elasticity reaches a minimum and the initial crystallization stage occurs at $\sim 1.2T_g (=T_{\mathrm{min}})$. Thus, it is considered that the early stage of crystallization is closely related to the α-relaxation process.

FWHM of boson peaks as a function of temperature is shown in Fig. 2(c) (open symbols connected with dashed lines). A remarkable feature of FWHM in the studied glasses was observed. Although FWHM of boson peaks did not show any significant change as the temperature was increased, an increase in FWHMs was confirmed with the passage of time at $T/T_g \sim 1.1-1.2$ along with the ascent of ω_{BP} [Fig. 2(d)]. Assuming a damped oscillation model, FWHM of the vibration peak corresponds to the damping factor,[20] indicating that under damping conditions, FWHM of the vibration band would be broad. Therefore, it is considered that the damping of boson peaks takes place in the crystallization process at $T/T_g \sim 1.1-1.2$. Brodin *et al.*[20] described that the parameter of boson-peak damping increased above T_g with increasing temperature and subsequently reached a maximum around T_c. In addition, it was found that the temperature at which overdamping of the boson peak occurs almost corresponds to the T_c for o-terphenyl, m-tricresyl phosphate and glycerol.[29] Thus, in this study, the variation in both ω_{BP} and FWHM of boson peaks suggests that the glass phase becomes more liquidlike at temperatures approaching T_c and subsequently the initial crystallization process begins. Furthermore, according to Hikima *et al.*,[36] α-process is interpreted as a rearrangement of the molecules within the cluster (the cluster means the region of somewhat ordered arrangement of molecules) in the SCL state. Taking into account their description, it is strongly suggested that crystallization (nucleation/crystal growth) is triggered by α-relaxation in the specific region of SCL, that is, the molecularly denser (or cohesive nanodomain) region.

Nucleation is considered to be caused by a thermally induced local density fluctuation. On the other hand, the nanometric heterogeneity in the amorphous phase occurs due to the density fluctuation and such regions are randomly distributed. The local situation pertaining to the formation of embryos/nuclei is quite similar to the case of the denser region in amorphous phase. In other words, the site within the denser (cohesive nanodomain) region seems to be favorable for nucleation. This implies that the precursors of nuclei originate in the local-density-fluctuation sites, which are already present in the quenching period of glass melt, indicating that the size of the nuclei evolved by thermal stimulation of the glass phase is more or less comparable to the correlation radius, R_c. Therefore, we attempted to evaluate the R_c and critical radius of nuclei, r^*, based on the boson-peak results and thermodynamic parameters. Then, we compared R_c with r^* in the case of BS glass. R_c of BS glass was estimated using ω_{BP} and v_t on the basis of Eq. (1).[37] On the other hand, according to nucleation theory, r^* is expressed as follows:

$$r^* = \frac{-2\gamma}{\Delta G_v}, \tag{2}$$

where ΔG_v and γ correspond to the free energy per unit volume and crystal-liquid surface energy per unit area, respectively. Cabral *et al.*[25] reported that the γ in BS glass is $0.130\ \mathrm{J/m^2}$. In addition, at the temperature that gave a maximum nucleation rate (T_{max}), ΔG_v could be $\sim 2.2 \times 10^8\ \mathrm{J/m^3}$ based on the relation between ΔG_v and the reduced temperature (from Fig. 6 in Ref. 25). The calculated R_c and r^* values were ~ 17 and ~ 12 Å, respectively; therefore, $R_c \approx r^*$. This implies that the nuclei evolve within the denser/cohesive domain region due to the nanometric heterogeneity in glass phase. In other words, denser regions with the R_c, which are larger than the r^*, can transform into crystal nuclei near the temperature at which the constituent atoms are able to migrate in the SCL state, i.e., $\geq T_g$. In fact, James[38] found that glasses exhibiting homogeneous nucleation had a value of $T_{\mathrm{max}}/T_g \sim 1.0-1.1$. Although this temperature is somewhat lower than $\sim 1.2T_g$ ($\sim T_c$), it is expected that the α-relaxation process occurs in this temperature range, which is sufficient for the nucleus evolution within the denser regions, because it is speculated that the nucleus can be formed only by rearrangement in these regions (that is, the ingredients of the nucleus are already prepared), whereas an atomic diffusion or a more liquidlike situation (i.e., $\sim T_c$) is necessary for crystal growth of the nuclei.

IV. CONCLUDING REMARKS

The present work can be summarized in a possible scheme for the precursive stage of crystallization in a glass illustrated with the help of Fig. 3.

(a) In the as-quenched glass, although the constituent atoms are distributed without periodic ordering, the molecularly denser and thinner regions are already present.

(b) As the temperature increases to $T/T_g \sim 1.0-1.1$, at which an early stage of α-relaxation occurs, the glass state changes into the SCL state along with a rapid decrease in ω_{BP} (i.e., elastic modulus), which enables the atoms to move in the SCL, and subsequently, the denser regions with a large size ($\geq r^*$) begin to “untie.”

(c) The denser regions transform into nuclei.

(d) Thereafter, at $T/T_g \sim 1.1-1.2$, the constituent atoms acquire a high fluidity, and the nuclei capture the surrounding atoms and eventually crystal growth starts.

In the aluminosilicate and $\mathrm{Bi_4Ti_3O_{12}}$ glasses, it is proposed that the R_c in the glassy state nearly corresponds to that of crystallites formed in the annealed glasses, which was estimated by high-resolution transmission electron microscopy[39] and atomic force microscopy.[40] These experimental results also suggest that the denser regions, which originated from density fluctuation, are precursors of nuclei in the SCL phase. Moreover, it is proved by molecular dynamics that the nanometric heterogeneous state develops into SCL during a cooling period.[41] Based on this finding and our proposed scenario, we predict that nucleation sites in the glass matrix are already settled at the moment the glass melt is quenched through $\sim T_g$. Although further investigations are necessary to clarify this issue, based on our experimental facts and the reports mentioned above, our proposed model is deemed to be a possible mechanism for the crystallization precursive stage.

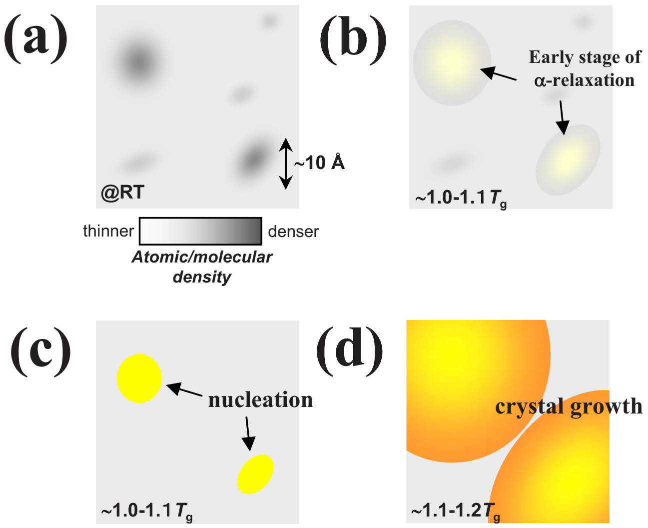

FIG. 3. (Color online) A possible scenario for the precursive stage of crystallization in glass proposed in this study (see text). Gray scale indicates the density of atomic/molecular density in glassy/supercooled liquid phase.

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