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# Effects of fictive temperature and halogen doping on the boson peak in silica glass

N. Shimodaira,* K. Saito, N. Hiramitsu, S. Matsushita, and A. J. Ikushima
*Research Center for Advanced Photon Technology, Toyota Technological Institute, 2-12-1 Hisakata, Tempaku, Nagoya 468-8511, Japan*

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We have investigated the effect of structural disorder on the boson peak in the Raman scattering of silica glass. The structural disorder was controlled in two ways: fictive temperature ($T_f$) and concentration of doped halogen element (F or Cl). As results, it has been simply demonstrated from *nonreduced* Raman spectra that (1) the peak position and full width at half maximum of the boson peak linearly increase with increasing $T_f$ irrespective of the halogen concentrations, and in contrast, (2) the intensity is rather strongly dependent on the halogen concentrations than $T_f$. Since the result in (1) is much similar to the dependence on $T_f$ and fluorine concentration for the IR absorption around 2260 cm$^{-1}$, it has been concluded that the boson peak in silica glass is microscopically related to the average magnitude and distribution of Si-O-Si bond angles in glass network. The intensity enhancement in (2) has suggested two possibilities about the contribution of the doped halogen element to the boson peak: One is a direct contribution of F or Cl atoms due to diffusive motions falling within the range of the boson peak. The other is an indirect contribution introduced by the termination of Si-O-Si bridges to some sort of vibrational motions, which may be related to the boson peak.

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## I. INTRODUCTION

The Raman spectra of glasses always exhibit a characteristic low-frequency structure, which has so far been called the *boson peak*.[1,2] It has been believed that the boson peak is strongly correlated with structural disorder in glasses, and many reports on this topic in various glasses have been published.[3–8] In these reports samples with different degrees of structural disorder were prepared by thermal annealing, pressure application, chemical doping, neutron irradiation, and so on. In spite of the various efforts, microscopic origin of the boson peak has not been settled yet. The present paper reports on an investigation of the correlation between the structural disorder and the boson peak in silica glass.

The degrees of structural disorder in silica glass can be controlled in two ways: One is to change the fictive temperature $T_f$, which is determined as the temperature where the properties of glass are the same as those of the supercooled liquid.[9] $T_f$ does not always provide a complete characterization of the glass structure, because there is an example that glass samples having the same $T_f$, which is determined from one property, show differences in other properties.[10] This discrepancy comes from the situation that various properties are not necessarily always determined by the same relaxational processes.[11] However, when the sample reached really an equilibrium state at respective heat-treatment temperatures, $T_f$ determined as the heat-treatment temperature is a good indicator of the glass structure. In silica glass, an infrared (IR) absorption around 2260 cm$^{-1}$ and Raman scattering peak around 495 cm$^{-1}$ ($D_1$ peak) and 605 cm$^{-1}$ ($D_2$ peak) have been investigated in samples reaching the equilibrium states, and thus $T_f$ can be easily determined from these peaks.[12–15] Furthermore, various properties are strongly affected by the structural disorder. For example, the Rayleigh light scattering,[16,17] x-ray small-angle scattering,[18,19] Urbach edge,[20] and Si-O-Si bond angle distribution[14] have been found to change linearly with $T_f$. Therefore, it should be worthwhile for settling the microscopic model of the boson peak to investigate any quantitative correlation between the boson peak and $T_f$.

The other way to control the structural disorder employed in this study is to dope a halogen element such as F or Cl of different concentrations. The structural change induced by halogen doping is fundamentally different from that by changing $T_f$,[14] because Si-O-Si bonds in the glass network are cut by F or Cl, resulting in the formation of Si-F or Si-Cl bonds. Simultaneously, $T_f$ in the doped glass can be controlled by the above-mentioned way. Therefore, it is interesting to compare the two ways on the boson peak.

## II. EXPERIMENTS

### A. Experimental procedure

Raman experiments were performed with a NRS-2100(JASCO) using a 488-nm Ar line as excitation source with a laser power of 0.5 W. VH-depolarized spectra were measured with a triple monochromator over the range from 7 to 1000 cm$^{-1}$ at intervals of about 1 cm$^{-1}$. The spectral resolution was set to about 1 cm$^{-1}$. A pseudobackscattering configuration was chosen, where the incident angle of the laser was 30° and the scattering angle was 150°, because a backscattering configuration did not suit for measuring spectra in the range below 100 cm$^{-1}$ due to the strong reflected light. The detector was a 16-bit charge coupled device (CCD) cooled by liquid nitrogen.

All spectra were normalized by the intensity of the 800-cm$^{-1}$ peak ascribed to the Si-O-Si symmetric stretching vibration with Si motion.[21] Since all of them were obtained at room temperature, the change of the spectral shape could be directly evaluated without data reduction using the Bose factor.[22]

### B. Sample preparation

Six types of silica glass with different F concentrations between 0 and 7.2 mol % and three types with different Cl

TABLE I. Range of the fictive temperature in prepared samples.

| | Halogen concentration (mol %) | Range of the fictive temperature (K) |
|---|---|---|
| F: | 0 (Cl:0) | 1373–1623 |
| | 0.05 | 1223–1623 |
| | 0.6 | 1173–1523 |
| | 2.0 | 1073–1523 |
| | 4.0 | 923–1373 |
| | 7.2 | 823–1523 |
| Cl: | 0.07 | 1373 |
| | 0.14 | 1373 |
| | 0.3 | 1373 |
| | 0.7 | 1373 |
| | 1.8 | 1373 |

concentrations between 0 and 1.8 mol % were used. Metal impurities were less than $2\times10^{-6}$ mol % in all samples except a sample with 2.0 mol % F, where concentrations of Na, K, and Al were $1.0\times10^{-5}$, $1.7\times10^{-4}$, and $4.0\times10^{-4}$ mol %, respectively. OH concentrations in the samples with 0 and 0.05 mol % F were $1.8\times10^{-2}$ and $1\times10^{-3}$ mol %, respectively, whereas in other samples OH impurity could not been detected by IR absorption measurements. Samples were of $10\times10\times2$ mm in size.

Samples with different $T_f$ were prepared by thermal annealing in air. Since F or Cl accelerates the structural relaxation, samples with lower $T_f$'s could be prepared as the halogen concentration increases. Table I shows the range of $T_f$ in the samples prepared in this study. In order to prove that the samples reached really to equilibrium states at respective heat-treatment temperatures, the relaxational process during the annealing was monitored by measuring the IR peak absorption around 2260 $\mathrm{cm}^{-1}$ in quenched samples at room temperature.[12] Figure 1 shows examples of the relaxational process at 700 °C in samples with 4.0 and 7.2 mol % F.

$T_f$ was also checked by the intensity of the $D_1$ or $D_2$ peak in the VV+VH (random) Raman scattering. The $T_f$ dependence in samples with 0.6 mol % F is represented in Fig. 2(a). Difference spectra are shown in the lower parts in the figure. It was therefore explicitly verified that the intensities of the $D_1$ and $D_2$ peaks changed proportionally to $T_f$ [see Fig. 2(b)], as already reported.[13]

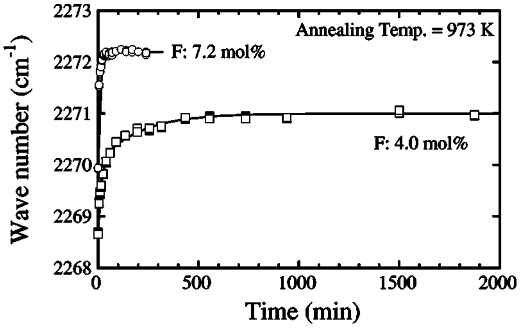

FIG. 1. Change of IR peak position around 2260 $\mathrm{cm}^{-1}$ during annealing processes.

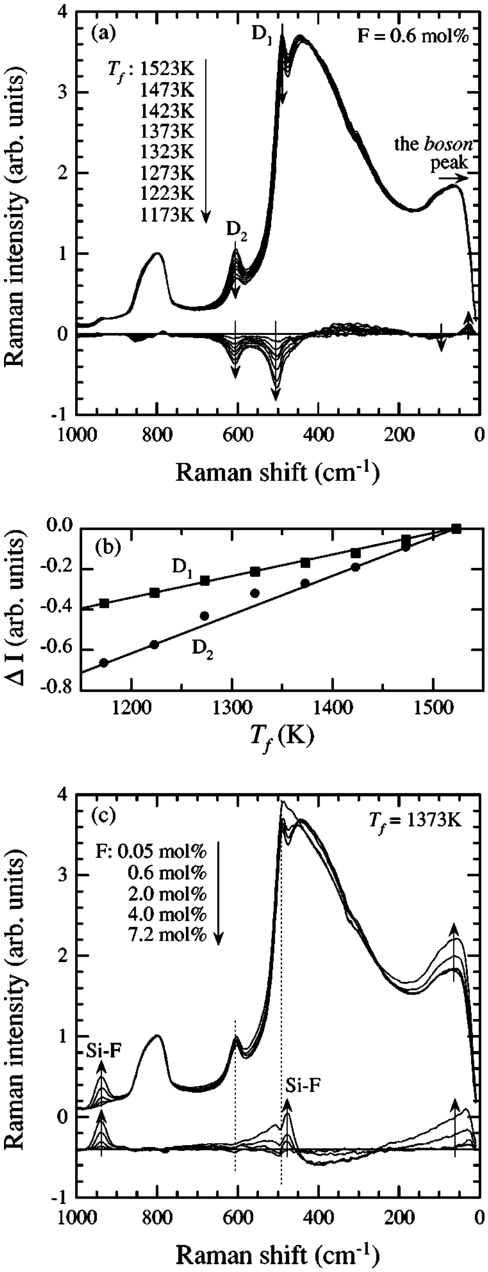

FIG. 2. (a) VV+VH Raman spectra of 0.6-mol % F-doped silica glasses with various $T_f$, (b) relative changes of the peak intensity, $\Delta I$, of $D_1$ and $D_2$ lines deduced from (a), and (c) VV+VH Raman spectra of samples with various F concentrations when $T_f$ is 1373 K. Difference spectra are shown in the lower parts in (a) and (b).

Figure 2(c) shows the F-concentration dependence in samples with $T_f$=1100 °C. The changes by changing the F concentration was consistent with our previous results:[23] when having the same $T_f$, the intensity of the $D_2$ peak is independent of the F concentration and the change of the $D_1$-peak intensity is also negligible. In addition, one can notice in Fig. 2(c) that the peaks at 945 and 480 $\mathrm{cm}^{-1}$ increase

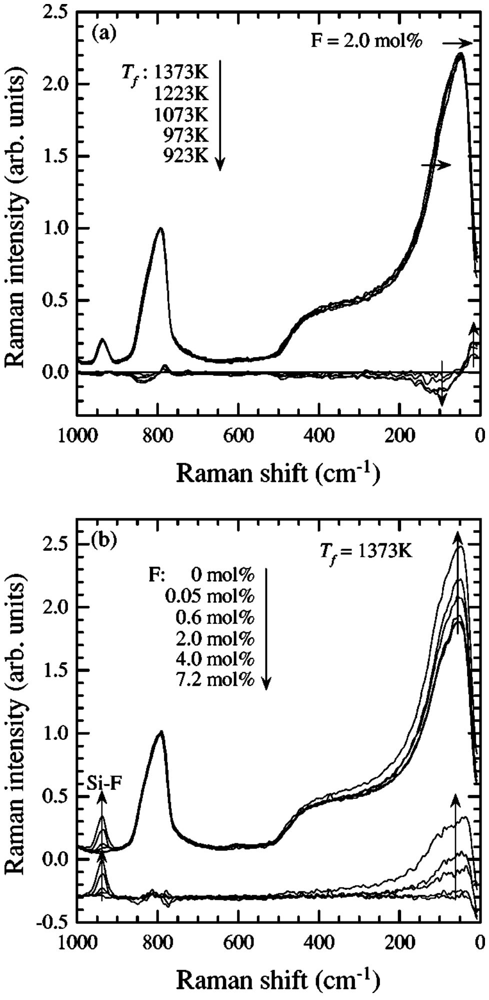

FIG. 3. (a) VH Raman spectra of 2.0-mol % F-doped silica glasses with various $T_f$ and (b) VH Raman spectra of samples with various F concentrations when $T_f$ is 1373 K. Difference spectra are shown in the lower parts.

proportionally to the F concentration, corresponding to the Si-F stretching and bending vibrational modes, respectively.

## III. RESULTS

### A. VH-polarized Raman spectra

VH spectra were measured to investigate the behaviors of the boson peak, because the main broad band at about 430 $\text{cm}^{-1}$, which overlaps the bottom of high-frequency side of the boson peak in the VV or VV+VH spectra, almost disappears in the VH configuration. For example, Figs. 3(a) and 3(b), respectively, show the $T_f$ dependence with a sample of 2.0 mol % F and the F-concentration dependence with a sample of $T_f$=1100 °C. Difference spectra are shown in the lower parts. Apparently, some features of the boson peak can be clearly observed in Fig. 3: the peak position seems to be sensitive to $T_f$. The intensity markedly depends on the F concentration.

### B. $T_f$ dependence

In order to look quantitatively at the asymmetric shape of the boson peak, the VH spectra were fitted in the 10–200-$\text{cm}^{-1}$ frequency range with a log-normal curve as

$$I(\omega) = I_{BP}\exp\left(-\frac{(\ln\omega-\ln\omega_{BP})^2}{\sigma^2}\right),$$

where $I_{BP}$ is the peak intensity, $\omega_{BP}$ is the peak position, and $\sigma$ is related to the full width at half maximum, FWHM $=\omega_{BP}\{\exp(\sigma\sqrt{\ln 2})-\exp(-\sigma\sqrt{\ln 2})\}$. Because the log-normal curve has already been proposed for attempting a cluster model,[24] it fitted well in all the spectra (see the residuals in Fig. 4), and 99% confidence intervals of the fitted parameters were calculated ±0.012 for $I_{BP}$, ±0.5 $\text{cm}^{-1}$ for $\omega_{BP}$, and ±3.2 $\text{cm}^{-1}$ for FWHM, on average.

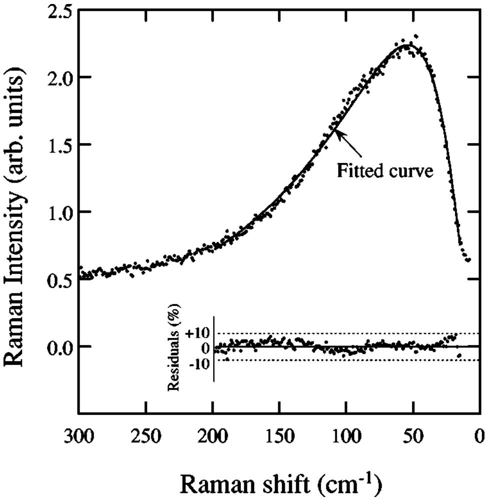

FIG. 4. Measured VH Raman spectra (dot) with a fitted curve (line) using a log-normal function in the frequency range 10–200 $\text{cm}^{-1}$. The residuals of the fit in % are shown in the lower parts.

Figure 5(a) shows the change of the intensity ($I_{BP}$) in the samples with different F concentrations as a function of $T_f$. The intensity is markedly enhanced by the F concentration while it tends to decline slightly with decreasing $T_f$. On the other hand, it is noted that both the position ($\omega_{BP}$) and the FWHM are simply linear to $T_f$ irrespective of F concentration, as shown in Fig. 5(b). The tendency of the peak shift to a lower frequency with decreasing $T_f$ coincides with the previous report.[4]

### C. Halogen concentration dependence

The effect of the doped halogen concentration on the peak intensity is shown in Fig. 6. It was found that Cl doping much more enhances the intensity than F doping, while apparently it does not affect the position and the FWHM.

## IV. DISCUSSION

In the present experiment, the authors made it clear that both the position and FWHM of the boson peak in silica glass linearly correlate with $T_f$ irrespective of halogen concentration. In contrast, the intensity is strongly enhanced by the halogen concentration.

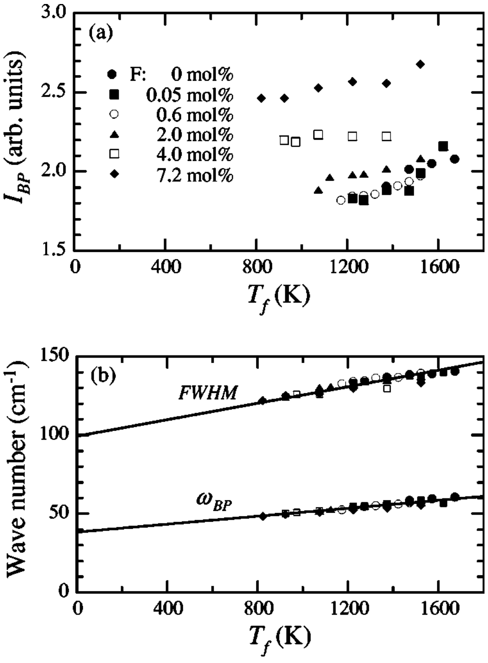

FIG. 5. (a) Intensity ($I_{BP}$), (b) position ($\omega_{BP}$), and FWHM of the boson peak as a function of $T_f$, calculated from the fitted curve. 99% confidence intervals of the fitted parameters were calculated ±0.012 for $I_{BP}$, ±0.5 cm$^{-1}$ for $\omega_{BP}$, and ±3.2 cm$^{-1}$ for FWHM, on average. The solid lines in (b) are guides to the eye.

The $T_f$ dependence for the boson peak is much similar to that for the IR absorption at around 2260 cm$^{-1}$, attributed to an overtone of the stretching vibrational mode of Si-O-Si bridges. Its position, being strongly proportional to $T_f$,[12] is reflected by the variations of the average of Si-O-Si bond angles in silica glass network: the smaller wave number corresponds to the smaller average bond angle.[25] In our previous study,[14] it was additionally shown in the $T_f$ dependence that its width, indicating the distribution of the bond angles, or basically the degree of "structural disorder" in silica glass, linearly decreases with decreasing $T_f$.

We further pointed out the F-concentration dependence of the IR absorption that when the sample $T_f$ is the same, the width does not change so much while the position marginally shifts. As shown in Fig. 2(c), the intensities of the $D_1$ and $D_2$ peaks, thought to be associated with the four- and three-membered Si-O ring structures,[26] respectively, almost correspond with each other. These results can be interpreted as follows: although the Si-O-Si bridges are partly terminated by the formation of Si-F or Si-Cl bonds, the remaining Si-O-Si network structures, characterized by the average and distribution of the Si-O-Si bond angles and the proportion of the small ring structures, are comparable as far as they have the same $T_f$.

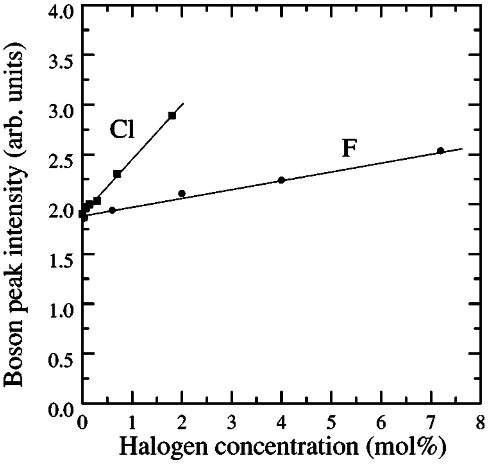

FIG. 6. Halogen concentration dependence of the boson peak intensity. The solid lines are guides to the eye.

Accordingly, it may be allowed to conclude that the position and FWHM of the boson peak in silica glass are microscopically related to the average magnitude and distribution of the Si-O-Si bond angles in the networks, irrelevant to the network termination by halogen elements. It is very interesting that the boson peak behaves in the same manner as an optical vibrational mode.

On the contrary, it is possible that the intensity of the boson peak is related directly to the doped halogen element or indirectly to the termination of Si-O-Si networks. As shown the difference spectra in Fig. 2(c) or 3(b), they keep the similarity in characteristic asymmetric shape below ~200 cm$^{-1}$ with changing the F concentration. The kind of halogen element does not affect the position and width at the same $T_f$. Thus, it appears certain that the intensity is not apparently enhanced by overlapping a *new* optical mode attributed to the Si-F or Si-Cl bond at such low frequencies.

In Raman scattering (RS) the Bose factor reduced spectrum is proportional both to the vibrational density of states, $g(\omega)$, and the Raman coupling coefficient $C(\omega)$.[22] Even if all the spectra in this study are reduced, the tendency in the spectral shape by changing halogen concentration as well as $T_f$ does not change because they were measured at the same room temperature. At this point, however, it cannot be distinctly determined which, $g(\omega)$ or $C(\omega)$, contributes to the intensity enhancement accompanied by halogen doping.

The difficulty of separation between $g(\omega)$ and $C(\omega)$ for RS has so far produced a few interpretations concerning the origin of the boson peak in silica glass. For example, a model of the phonon localization by disorder in glass structure,[27,28] a cluster model,[24,29,30] and so on have been introduced from the frequency dependence on the reduced spectral shape relative to the Debye prediction. Some have attempted to directly evaluate $g(\omega)$ from the inelastic neutron scattering (INS),[31,32] and others further to deduce $C(\omega)$ by comparing INS with RS.[33,34] Among them, the possibility of optical modes ascribed to collective rotational motions of several $SiO_4$ tetrahedra has been suggested as the origin of the boson peak from INS,[31] hyper-Raman scattering,[35] and theoretical calculations.[36] From many points of view it has still been under debate.

At this moment, two possibilities can be considered about the intensity enhancement in the boson peak by halogen doping. One is a direct contribution of F or Cl atoms due to diffusive motions falling within the range of the boson peak. The other is an indirect contribution by the termination of Si-O-Si bridges to some sort of vibrational motions related to $SiO_4$ tetrahedra as described above. The latter hypothesis is consistent with the increase of the far-IR absorption corresponding to the boson peak with increasing OH concentration.[37] Further investigations with INS, specific heat at low temperature, etc., will make clearer this point.

## V. CONCLUSIONS

We have presented the effects of $T_f$ and halogen doping on the boson peak in silica glass. It has been simply demonstrated from *nonreduced* Raman spectra that both the peak position and FWHM linearly correlate with $T_f$ irrespective of halogen concentrations and that the intensity is rather strongly dependent on the halogen concentrations. From other peak behaviors of the IR absorption and the $D_1$ and $D_2$ in the Raman scattering, we have concluded that the position and FWHM of the boson peak in silica glass are microscopically related to the average magnitude and distribution of the Si-O-Si bond angles. The intensity enhancement has suggested two possibilities about the contribution of the doped halogen element to the boson peak: One is a direct contribution of F or Cl atoms due to diffusive motions falling within the range of the boson peak. The other is an indirect contribution introduced by the termination of Si-O-Si bridges to some sort of vibrational motions, which may be related to the boson peak.

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*On leave from Research Center, Asahi Glass Co. Ltd., 1150 Hazawa-cho, Kanagawa-ku, Yokohama 221-8755, Japan.

[1] See, for example, J. Jackle, in *Amorphous Solids, Topics in Current Physics*, Vol. 24, edited by W. A. Phillips (Springer-Verlag, Berlin, 1981), Chap. 8.

[2] Current literature can be seen in *Proceedings of the 4th International Meeting on "Relaxations in Complex Systems*," edited by K. L. Ngai, G. Floudas, A. K. Rizos, and E. Riande [J. Non-Cryst. Solids 307–310, 73–160 (2002)].

[3] V. K. Malinovsky and A. P. Sokolov, Solid State Commun. **57**, 757 (1986).

[4] C. Chemarin, B. Champagnon, and G. Panczer, J. Non-Cryst. Solids **216**, 111 (1997).

[5] C. McIntosh, J. Toulouse, and P. Tick, J. Non-Cryst. Solids **222**, 335 (1997).

[6] S. Sugai and A. Onodera, Phys. Rev. Lett. **77**, 4210 (1996).

[7] Y. Imamura, M. Arai, M. Nakamura, T. Otomo, N. Kitamura, S. M. Bennington, A. C. Hannon, and U. Buchenau, J. Non-Cryst. Solids **293**, 389 (2001).

[8] F. Terki, C. Levelut, M. Boissier, and J. Pelous, Phys. Rev. B **53**, 2411 (1996).

[9] S. R. Elliot, in *Physics of Amorphous Materials*, 2nd ed. (Longman Scienctific & Technical, New York, 1990), p. 32.

[10] See, for example, H. N. Ritland, J. Am. Ceram. Soc. **39**, 403 (1956).

[11] See, for example, P. B. Macedo and A. Napolitano, J. Res. Natl. Bur. Stand., Sect. A **71**, 231 (1967).

[12] A. Agarwal, K. M. Davis, and M. Tomozawa, J. Non-Cryst. Solids **185**, 191 (1995).

[13] A. E. Geissberger and F. L. Galeener, Phys. Rev. B **28**, 3266 (1983).

[14] K. Saito and A. J. Ikushima, J. Appl. Phys. **91**, 4886 (2002).

[15] H. Kakiuchida, K. Saito, and A. J. Ikushima, J. Appl. Phys. **93**, 777 (2002).

[16] K. Saito, A. J. Ikushima, T. Ito, and A. Itoh, J. Appl. Phys. **81**, 7129 (1997).

[17] H. Kakiuchida, K. Saito, and A. J. Ikushima, Proc. SPIE **4905**, 355 (2002).

[18] T. Watanabe, K. Saito, and A. J. Ikushima, J. Appl. Phys. **94**, 4824 (2003).

[19] T. Watanabe, K. Saito, and A. J. Ikushima, J. Appl. Phys. **95**, 2432 (2004).

[20] K. Saito and A. J. Ikushima, Phys. Rev. B **62**, 8584 (2000).

[21] F. L. Galeener, Phys. Rev. B **19**, 4292 (1979).

[22] R. Shuker and R. W. Gammon, Phys. Rev. Lett. **25**, 222 (1970).

[23] N. Shimodaira, K. Saito, and A. J. Ikushima, J. Appl. Phys. **91**, 3522 (2002).

[24] I. Pocsik and M. Koos, Solid State Commun. **74**, 1253 (1990).

[25] R. A. B. Devine, J. Non-Cryst. Solids **152**, 50 (1993).

[26] F. L. Galeener, J. Non-Cryst. Solids **49**, 53 (1982).

[27] A. J. Martin and W. Brenig, Phys. Status Solidi B **64**, 163 (1974).

[28] S. R. Elliot, Europhys. Lett. **19**, 201 (1992).

[29] E. Duval, A. Boukenter, and T. Achibat, J. Phys.: Condens. Matter **2**, 10227 (1990).

[30] V. K. Malinovski, V. N. Novikov, and A. P. Sokolov, Phys. Lett. A **153**, 63 (1991).

[31] U. Buchenau, M. Prager, N. Nucker, and A. J. Dianoux, N. Ahmad, and W. A. Phillips, Phys. Rev. B **34**, 5665 (1986).

[32] A. Arai, Y. Inamura, T. Otomo, N. Kitamura, S. M. Bennington, and A. C. Hannon, Physica B **263–264**, 268 (1999).

[33] T. Achibat, A. Boukenter, and E. Duval, J. Chem. Phys. **99**, 2046 (1993).

[34] A. P. Sokolov, U. Buchenau, W. Steffen, B. Frick, and A. Wischnewski, Phys. Rev. B **52**, R9815 (1995).

[35] B. Hehlen, E. Courtens, R. Vacher, A. Yamanaka, M. Kataoka, and K. Inoue, Phys. Rev. Lett. **84**, 5355 (2000).

[36] T. Nakayama, J. Phys. Soc. Jpn. **68**, 3540 (1999).

[37] T. Ohsaka and S. Oshikawa, Phys. Rev. B **57**, 4995 (1998).