Two-Directional Photoinduced Crystallization in $GeSe_2$ and $SiSe_2$ Glasses

S. Sugai

Department of Physics, Faculty of Science, Osaka University, Toyonaka 560, Japan

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Photoinduced crystallization is investigated by Raman scattering in $GeSe_2$ and $SiSe_2$ glasses. Crystallization into two different structures is observed according as the incident laser power is above or below the threshold. To interpret it a new stochastic random-network model composed of two types of molecules is proposed for the structure of chalcogenide glasses.

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Recently intensive experiments of Raman scattering have been done on semiconducting chalcogenide glasses, MX_2 (M = Ge or Si and X = S or Se).[1-9] The existence of a medium-range order has been stressed. The origin of a companion A_1 peak in the Raman spectra of GeS_2 and $GeSe_2$,[3] and the photoinduced crystallization in $GeSe_2$,[8,9] have been interpreted on the basis of the outrigger-raft model.[3]

The present experiment of the photoinduced structural change by means of Raman scattering discloses the existence of two-directional crystallization according to the intensity of the incident laser beam. The two microcrystalline phases are assigned to the low- and high-temperature structures of GeS_2 crystal. The appearance of two types of microcrystalline phases can hardly be explained by the outrigger-raft model,[3] because this model is constructed to preserve the crystal structure of $GeSe_2$, which is the same structure as the high-temperature phase of GeS_2, as much as possible. The present experiment is favorable for a stochastic random-network model composed of two types of molecules. This model is justified by a new assignment of the companion A_1 peak.[10,11]

Glassy samples were made by melt quenching into water. The Raman scattering is made in a backscattering configuration with the use of a 6328-Å He-Ne laser for $GeSe_2$ and 4579-Å Ar-ion laser for $SiSe_2$. The laser beam weakened by neutral-density filters was focused on the sample surface by the objective lens of a microscope. The same laser beam but with different intensity was used for the induction of crystallization and for the measurement of Raman scattering.

Figure 1 shows the Raman spectra in the sequence of photoinduced crystallization of $GeSe_2$. Spectrum (a) was obtained at incident laser power of 8 mW which corresponds to 0.4 kW/cm^2, if the focus is as sharp as the diffraction limit. At this input power the spectra are unchanged during the measurement of Raman scattering. Spectrum (d) was obtained at 8 mW after the exposure of a laser beam of 15 mW for 80 min. The start of crystallization is observable. Spectrum (e), which was obtained at 8 mW after the irradiation of 15 mW for 840 min, shows the increase of crystallization. The energies of sharp lines which appear at 210 cm^{-1} and below 150 cm^{-1} coincide with those in the crystal [spectrum (g)]. Spectrum (f) was obtained immediately after the scan (e) with the same power as used for the crystallization. The increase of the intensity of the sharp lines from the microcrystal state is observed in place of the decrease of the 200-

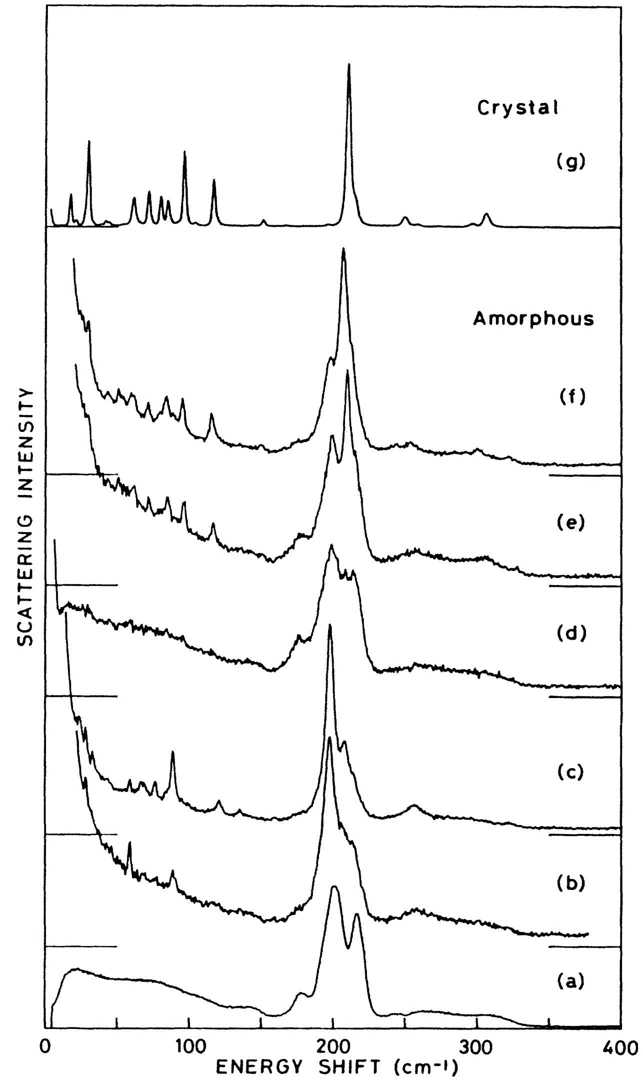

FIG. 1. The sequence of photoinduced crystallization of a-$GeSe_2$ into two different structures according to the laser intensity below (b),(c) and above (d)–(f) the threshold. The spectra (a) and (g) are typical ones in the glass and the crystal, respectively.

cm^{-1} A_1 line and the 172-cm^{-1} line.

The spectra (b) and (c) were measured at 12 mW just after the start of the irradiation (b) and after irradiation of 12 mW for 330 min (c). The intensity of the 198-cm^{-1} A_1 peak increases instead of the 210-cm^{-1} A_g peak. The linewidths of many peaks in spectrum (c) are almost the same as those in (f). But the set of peak energies, 28, 32, 42, 59, 67, 76, 88, 121, 135, 158, 198, 207, 256, and 321 cm^{-1}, is very different from that in spectrum (f), 29, 43, 51, 61, 71, 79, 84, 96, 116, 150, 199, 209, 248, 257, 305, and 327 cm^{-1} in which all but 51, 199, and 327 cm^{-1} are coincident with the peak energies in the crystal (g). The microcrystalline phase obtained by the low irradiation intensity is strongly supposed to be the low-temperature GeS_2 phase. It is known that in the case of GeS_2 glass the energy of the A_1 peak which corresponds to the 198-cm^{-1} peak in GeSe_2 is coincident with the energy of the strongest A' peak in the crystal of the low-temperature phase.[12] The modes at 59, 89, 198, and 257 cm^{-1} in spectrum (b), which are assigned to the E, F_2, A_1, and F_2 modes in a methane-like $\mathrm{GeSe}_{4/2}$ molecule, remain in (c). It is reasonable in the low-temperature phase, because only a single type of methanelike molecules is the constitutional element. The spectra (c) and (f) were almost unchanged after the sample was left in the dark at room temperature for one day.

There is a sharp threshold intensity between 0.6 and 0.8 $\mathrm{kW/cm}^2$. Haro *et al.*[9] have reported the existence of the threshold in the crystallization. Their measurement was limited to the spectral range from 150 to 250 cm^{-1} and then they did not measure the sharp lines below 150 cm^{-1}. They assigned the increase of the 200-cm^{-1} A_1 peak as a precursor effect of the crystallization to the normal crystal structure of GeSe_2. However, the present experiment clearly shows that this is another microcrystal structure. This will be discussed later in detail.

The threshold input intensity 0.7 $\mathrm{kW/cm}^2$ corresponds to 2×10^{21} photons/sec·cm^2. If we suppose that the penetration depth of the light is 300 μm,[3] the density of the incident photons is $10^{23}/\mathrm{cm}^3$. The density of GeSe_2 molecules is $10^{22}/\mathrm{cm}^3$. Therefore all GeSe_2 molecules are in the excited state, if the decay time of the excited state is longer than 100 msec.

At the beginning of the irradiation the spectra show complicated behavior with the change of the laser intensity. Figure 2 shows the time dependence of the intensity of Raman peaks at 199, 207, and 217 cm^{-1} with the irradiation of alternating laser power. The initial decrease of the intensity by the weak laser beam is due to photodarkening. The appearance of a flat or a decreasing region of the scattering intensity at the beginning of the irradiation of 26 mW indicates that accumulation of the excited molecules is necessary for the photoinduced crystallization.

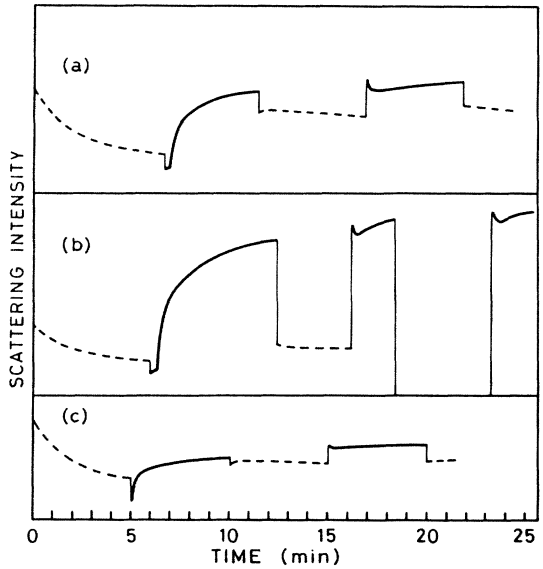

FIG. 2. Records of the scattering intensities from a-GeSe_2 at the energy shift of (a) 199 cm^{-1}, (b) 207 cm^{-1}, and (c) 217 cm^{-1} with alternating laser intensity of 5.2 mW (0.3 $\mathrm{kW/cm}^2$, dashed curves) and 26 mW (1.4 $\mathrm{kW/cm}^2$, solid curves).

Similar photoinduced crystallization is also observed in SiSe_2 glass. The Raman spectra are shown in Fig. 3. At the irradiation of a 4579-Å laser beam with above-threshold intensity, crystallization is observed as shown in spectrum (c). Below the threshold the increase of the 218-cm^{-1} peak relative to the 242-cm^{-1} peak is observed in the spectra (b). Many sharp lines as observed in GeSe_2 were not observed yet with this input power and irradiation time up to 5 h, but the relative increase of the 218-cm^{-1} peak is supposed to be a precursor effect of the crystallization to the low-temperature GeS_2 phase.

This kind of bidirectional photoinduced crystallization is interpreted with difficulty by the medium-range order such as the outrigger raft model in GeSe_2,[3] the extended-chain model,[4] or the cross-linked chain-cluster model[7] in SiSe_2. In the framework of the outrigger-raft model the photoinduced crystallization is caused by the increase of the domain size through movement or extinction of the domain boundary. Generally speaking the motion of the domain boundary is driven by very small force. Therefore the existence of the threshold intensity as observed in the present experiment is hardly explained. A model for the glass structure is proposed in the following by comparing with other chalcogenide glasses.

The Raman spectra in GeS_2, GeSe_2, SiS_2, and SiSe_2 glasses are shown in Fig. 4. For the benefit of comparison the energy scales for the sulfides are contracted by the factor $(M_{\mathrm{S}}/M_{\mathrm{Se}})^{1/2}$, where M_X is the atomic

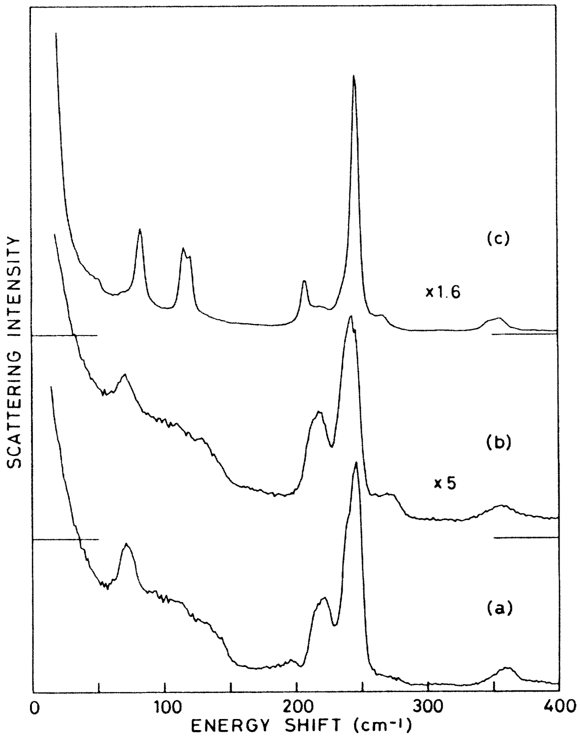

FIG. 3. The photoinduced crystallization of a-SiSe$_2$. Spectrum (a) is for the glass, which was measured at 3 mW (0.3 kW/cm^2). Spectra (b) and (c) were measured at 15 mW after irradiations of (b) 15 mW for 310 min and (c) 30 mW for 10 min.

mass. In the crystal the low-temperature phase of GeS$_2$ is composed of corner-shared GeS$_{4/2}$ tetrahedra. GeSe$_2$ and the high-temperature phase of GeS$_2$ consist of a combination of corner-shared and edge-shared tetrahedra, and SiS$_2$ and SiSe$_2$ only edge-shared tetrahedra. In many experiments Raman peaks in the glassy state have been assigned on the analogy with those in the crystal. The peaks A in GeS$_2$ and GeSe$_2$ in Fig. 4 have been assigned to the breathing mode of $MX_{4/2}$ tetrahedra as shown in Fig. 5(a). In SiS$_2$ and SiSe$_2$ the peaks A have been assigned to the mode of Fig. 5(d) and the peaks B to the mode of Fig. 5(c).[7] In GeS$_2$ and GeSe$_2$ the peaks B which are called companion A_1 peaks are not observed in the crystals. The outrigger-raft model[3] was introduced to give the origin of these companion peaks. These peaks have been assigned in its model to the motion related to the Se—Se bonds which do not exist in the crystal.[3] Calculations of the phonon density of states by this model were done,[13,14] but they were unsuccessful in reproducing the companion peak directly.

Now let us return to the random-network model. Two types of molecules, methanelike tetrahedra, $MX_{4/2}$, and double-bonded molecules, $X_{2/2}MX_2MX_{2/2}$, are introduced as constitutional elements. The binding of these elements in the network is stochastically determined. It should be rememebered that in a material with a random structure Raman spectra represent only local vibrational modes. Modes which come from the medium- or long-range-order structures do not appear. The frequency of the mode (b) in Fig. 5 is expected to be higher than that of the mode (a), because the Se-Se distance of (b) is shorter than twice the ionic radius. Nemanich $et\ al.$[10] and Lucovsky, Wong, and Pollard[11] suggested the origin of the companion peak as the mode (b) in glassy GeSe$_2$. Now the mode (a) is assigned to the peak A and (b) to B in all four glasses independently of the structures in their crystals. The difference of the relative intensity between peaks A and B is due to the probability of the existence of double-bond molecules. The F_2 modes in the

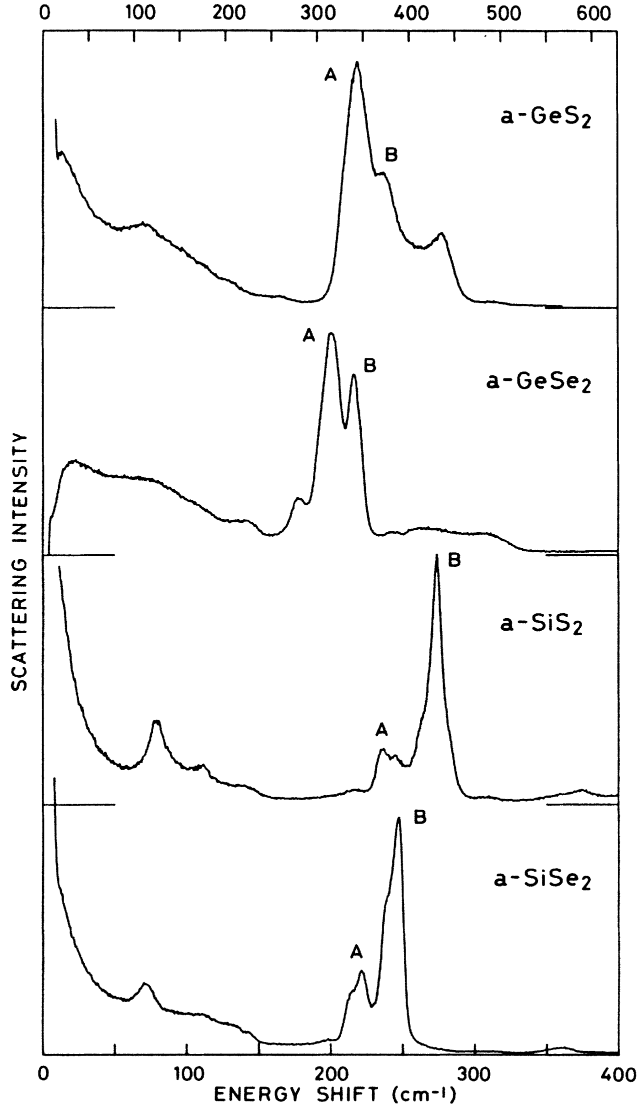

FIG. 4. The Raman spectra in a-GeS$_2$, GeSe$_2$, SiS$_2$, and SiSe$_2$. The lower energy scale is for selenides and the upper is for sulfides. The upper scale is contracted by $(M_S/M_{Se})^{1/2}$.

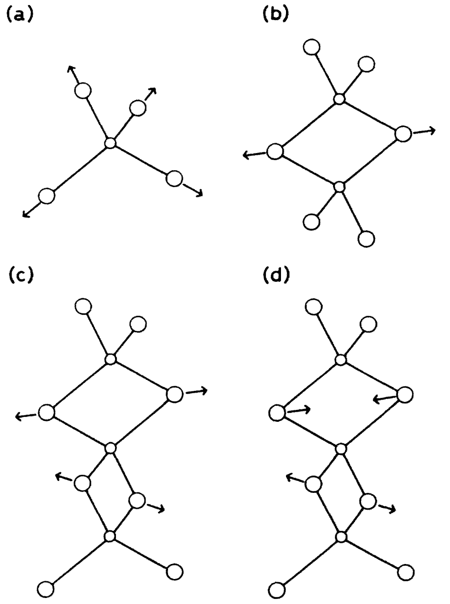

FIG. 5. The normal vibrational modes for the molecules which are constitutional elements of chalcogenide glasses.

tetrahedral units are both infrared and Raman active. In glassy $SiSe_2$ the peak at 360 cm^{-1} is assigned to the summation of one of the F_2 modes and the mode of Si displacement perpendicular to the chain axis in the double-bonded units. The absorption due to the F_2 mode is observed as a shoulder in the absorption spectra.[15] In the crystal the modes (a) and (b) are no longer independent. The strongest A_g mode in the crystal $GeSe_2$ is the coherent vibration of the local modes (a) and (b). The specific behavior of the compositional dependence in the intensity of the companion A_1 peak relative to the A_1 peak in Ge_xSe_{1-x}[2] naturally explained in the present model. It will be presented separately.

The two-directional photoinduced crystallization is interpreted as follows. The irradiation of intense light above the threshold causes the crystallization with the same structure as the crystal, but weak light below the threshold increases methanelike molecules and constructs microcrystals with the same structure as the low-temperature phase of GeS_2. At the intense irradiation all the peaks which are observed in the crystal appear simultaneously. This implies that the long-range order composed of two types of molecules is essential for the Raman spectra in the high-temperature GeS_2 phase. The threshold intensity possibly corresponds to the photon density which excites all molecules in the irradiated volume.

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[1] G. Lucovsky, F. L. Galeener, R. C. Keezer, R. H. Geils, and H. A. Six, Phys. Rev. B **10**, 5134 (1974).

[2] P. Tronc, M. Bensoussan, A. Brenac, and C. Sebenne, Phys. Rev. B **8**, 5947 (1973).

[3] P. M. Bridenbaugh, G. P. Espinosa, J. E. Griffiths, J. C. Phillips, and J. P. Remeika, Phys. Rev. B **20**, 4140 (1979).

[4] M. Tenhover, M. A. Hazle, and R. K. Grasselli, Phys. Rev. Lett. **51**, 404 (1983).

[5] M. Tenhover, M. A. Hazle, R. K. Grasselli, and C. W. Tompson, Phys. Rev. B **28**, 4608 (1983).

[6] M. Tenhover, M. A. Hazle, and R. K. Grasselli, Phys. Rev. B **28**, 5897 (1983).

[7] J. E. Griffiths, M. Malyj, G. P. Espinosa, and J. P. Remeika, Phys. Rev. B **30**, 6978 (1984).

[8] J. E. Griffiths, G. P. Espinosa, J. P. Remeika, and J. C. Phillips, Phys. Rev. B **25**, 1272 (1982).

[9] E. Haro, Z. S. Xu, J.-F. Morhange, M. Balkanski, G. P. Espinosa, and J. C. Phillips, Phys. Rev. B **32**, 969 (1985).

[10] R. J. Nemanich, F. L. Galeener, J. C. Mikkelsen, Jr., G. A. N. Connell, G. Etherington, A. C. Wright, and R. N. Sinclair, Physica (Amsterdam) **117&118B+C**, 959 (1983).

[11] G. Lucovsky, C. K. Wong, and W. B. Pollard, J. Non-Cryst. Solids **59&60**, 839 (1983).

[12] K. Arai, J. Non-Cryst. Solids **59&60**, 1059 (1983).

[13] K. Murase, T. Fukunaga, Y. Tanaka, K. Yakushiji, and I. Yunoki, Physica (Amsterdam) **117&118B+C**, 962 (1983).

[14] J. A. Aronovitz, J. R. Banavar, M. A. Marcus, and J. C. Phillips, Phys. Rev. B **28**, 4454 (1983).

[15] M. Tenhover, R. S. Henderson, D. Lukco, M. A. Hazle, and R. K. Grasselli, Solid State Commun. **51**, 455 (1984).