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Energy landscape and photoinduced structural changes in chalcogenide glasses

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Abstract

It is shown that the magnitude of photostructural changes in chalcogenide glass is a function of the connectivity and fragility of the glass network. Glasses with a floppy network undergo larger photostructural changes, as shown by photorelaxation, photoexpansion and photodarkening measurements. The increasing magnitude of the changes correlates with a decrease in coordination number $\langle r \rangle$. The phenomenon is linked to the topography of the energy landscape and to the fragility of samples with different $\langle r \rangle$ values. Since a high density of minima on the landscape is generally associated with a floppy network and fragile glassformers, it is suggested that photoexcitation provides a means for the system to explore these minima and that, consequently, fragile systems exhibit far larger photostructural changes, as observed. On the other hand, strong systems with optimal rigidity undergo very little structural change upon irradiation. This is attributed to the low density of configurational states on the landscape. A parallel between individual bond breaking in the bond lattice model and individual photoexcitation of bonding electrons during irradiation is made to support the use of the landscape formalism in describing photostructural changes.

1. Introduction

Chalcogenide glasses represent a wide range of inorganic glasses that always contain one or more of the chalcogen elements: S, Se or Te, but no O. Owing to higher atomic mass, these glasses typically exhibit low phonon energies and have an optical window extending far into the infrared (IR). This property has made them good candidates for a number of applications, including thermal and medical imaging [1], bio-sensing [2] or telecommunications [3]. Another unique property of chalcogenide glasses is their remarkable photosensitivity to light sources with wavelengths corresponding to the glass bandgap. These photoinduced changes have been heavily studied in the last 30 years [4], in particular for applications such as optical memories [5] and laser writing [6]. However, the bulk of this research has focused on the

widely available As_2S_3 composition and a very limited number of studies have been directed at the compositional dependence of photostructural changes [7–9].

It is well known that physico-chemical properties of chalcogenides are strongly dependent on composition [10, 11] and that they appear to vary according to the average coordination number $\langle r \rangle$ of the Phillips and Thorpe rigidity theory [12, 13]. In particular, many properties exhibit an extremum at $\langle r \rangle = 2.4$ where rigid and floppy domains percolate throughout the glass network. One of these properties is the glassformer's fragility, defined according to the non-Arrhenius behaviour of the viscosity–temperature dependence of a system [10, 14]. The correlation between the fragility and $\langle r \rangle$ has been observed in several chalcogenide glassforming systems [15, 16].

The fragility of glassformers has also been associated with the topology of the energy landscape, which is used to quantify the myriad of structural configurations of a system [17–19]. This energy landscape reflects the number of possible configurations that a system of particles can adopt considering the set of restrictions imposed by bond distances and bond angles [14, 20]. Since fragility is strongly correlated to the average coordination number $\langle r \rangle$, the energy landscape topology is also correlated to the $\langle r \rangle$ value. The covalent nature of the network and the well-defined coordination of atoms in chalcogenide glasses provide a set of constraints that lend itself well to this type of theoretical treatment. Following this line of thought, the optimally constrained network of strong glasses then results in a smaller number of possible configurations that the system of particles can settle in at a given temperature. The corresponding energy landscape has a simpler topology [21].

In this study we investigate the compositional dependence of photostructural changes in chalcogenide glasses of various $\langle r \rangle$ values. The observed phenomenon is then described using the energy landscape formalism.

2. Background

2.1. The energy landscape formalism

A system of N particles can adopt a myriad of possible configurations that each requires a set of $3N$ coordinates to be fully characterized. Each energetically favourable configuration then corresponds to a minimum on an energy surface with $3N + 1$ dimensions often called the energy landscape or the potential energy hypersurface [17]. Each of these configurational states has a specific energy and can be visited by the system if (a) sufficient energy, $k_B T$, is available and (b) the particle mobility is large, i.e. the system is in the liquid state [21, 22]. In the glassy state, on the other hand, the system is stuck in one basin that corresponds to the unique structural configuration of a rigid laboratory glass. Nevertheless, it is possible for this glassy system to explore nearby states during annealing at temperatures near T_g . These configurational states or 'configurons' correspond to the basins or minima depicted in figure 1. In this picture, the energy hypersurface is represented schematically in two dimensions using an N -dimensional configuration coordinate Z^* . While this is a substantial oversimplification, it offers a convenient way to visualize the main features of the potential energy hypersurface [15, 18, 23].

In this representation, the crystalline phase is associated with the sharpest and deepest minima (figure 1). However, if crystallization is bypassed, the system will begin sampling other minima on the surface and proceed to find the deepest minima as the temperature is lowered. This process is usually kinetically arrested as the particle diffusivity becomes too large and causes the system to get trapped in a single minimum. In the idealized case of an infinitely slow cooling rate, the system would eventually reach the ideal glass configuration,

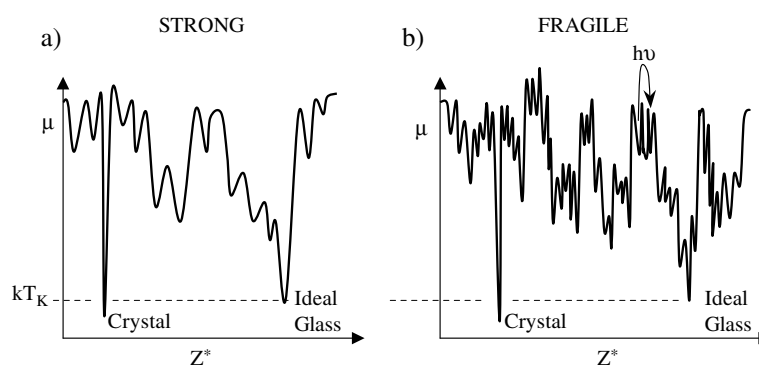


Figure 1. Two-dimensional representation of the potential energy hypersurface for (a) a strong glassformer and (b) a fragile glassformer. T_K is the Kauzmann temperature. The arrow denotes photoexcitation of a system into a neighbouring configurational state. Adapted from [18].

which corresponds to the lowest minima on the landscape and is associated with the zero excess entropy configuration obtained at the Kauzmann temperature, T_K .

Computer simulation on a Lennard-Jones system [20] has recently provided evidence that supports the relevance of the energy landscape formalism. Due to computation time limitations, only the top of the energy landscape could be probed, but it was shown that the topography of the landscape can be related to dynamic properties such as relaxation.

2.2. Energy landscapes and fragility

Figure 1 illustrates how the system must find deeper and deeper minima with decreasing temperature, but also shows that fewer of these minima are available towards the bottom of the landscape. This decrease in the number of accessible configurational microstates is associated with the drop in configurational entropy during cooling [22, 23]. Conversely, a glass trapped in one of the minima is suddenly allowed to visit a large number of minima when it passes above T_g and acquires diffusive mobility. This is associated with the jump in C_p , characteristic of the glass transition. It should also be noted that the number of microstates, W , available to the system depends on the topology of the energy landscape and that the topology is in turn a function of the glassformer's fragility. Specifically, fragile systems display a high density of minima, while strong systems have a notably lower density of microstates (figure 1) [14, 15, 18]. Consequently, for strong glassformers, the gain in entropy ($k_B \ln W$) at T_g is not so large, since W is relatively small and, in contrast, the gain in entropy and the jump in heat capacity at T_g are much larger for fragile systems. Tatsumisago *et al* have demonstrated this behaviour in the Ge–As–Se system [10].

It is usually more common to express the glassformer's fragility in terms of the viscosity–temperature profile of the liquid [14]. The networks of fragile systems collapse easily with increasing temperature and the viscosity rises suddenly with a non-Arrhenius profile. Conversely, strong liquids like SiO_2 retain their network character even at higher temperature and exhibit an Arrhenius viscosity–temperature profile. This kinetic behaviour can be directly linked to the energy landscape topology using the Adam Gibbs equation, $\tau = \tau_0 \exp C/T S_C$, and by recognizing the larger temperature dependence of S_C (configurational entropy) for fragile systems [14, 24] due to the greater number of minima. Following that line of thoughts, the fragile liquid's ability to access far more diverse configurational states would translate into structural collapse and lower viscosity. It is also shown that not only the density of minima but

also the height of the energy barrier between minima can affect the viscosity profile. Systems with high energy barriers would also exhibit an Arrhenius viscosity profile, despite a high density of minima on the energy surface. These systems are termed 'kinetically strong' [23].

2.3. Application to covalent system

Following the ideas of Phillips and Thorpe [12, 25], amorphous chalcogenides are often described in terms of the mean coordination theory, in which comparing the number of constraints (bond length and angle) with the number of degrees of freedom leads us to define rigid regions and floppy regions in the glass network. It can be shown that these two regions percolate at $\langle r \rangle = 2.4$ [12] and produce changes in the physical and chemical properties of the glass [11, 13]. This result is based on the idea that the number of floppy modes where the glass network can deform with no energy cost essentially vanishes at $\langle r \rangle = 2.4$.

The correlation between the average coordination number and fragility was demonstrated by Tatsumisago *et al* [10] on the Ge–As–Se system. It was shown that the Arrhenius viscosity profile, the heat capacity jump at T_g , and the activation energy for relaxation all show an extremum at $\langle r \rangle = 2.4$. Similar viscosity behaviours are observed in the Ge–Sb–Se [15] and Ge–Se [16] systems. Naumis justified this behaviour by correlating the number of floppy modes to the internal energy of the liquid and calculating the corresponding jump in specific heat between the glass and the melt [24]. Bohmer also emphasized the correlation between fragility and C_p jump, based on results from the Ge–As–Se system [26].

Naumis also applied the energy landscape formalism to covalent chalcogenide systems using the rigidity theory [27]. The number of floppy modes was correlated to the roughness of the landscape and was used to provide an estimate for the number of minimum energy basins. The results obtained correlate well with the features of the landscape theory developed by Angell [14, 18, 23].

2.4. Bond lattice model

The bond lattice model is another formalism that has been used successfully to describe the thermodynamic behaviour of glassformers [28]. It is based on describing the glassy network as a lattice of bonds that are independently excitable. Each bond breaking is associated with an excitation enthalpy and entropy, ΔH^* and ΔS^* . This model is of particular interest to us, since photoinduced changes can be regarded as a dynamic optical excitation of individual bonds in the network. This model should apply particularly well to the covalent network of chalcogenide glasses where each bond is well defined.

It is proposed that, in a fragile glass, a single bond breaking event is associated with a large entropy change, ΔS^* , which may be vibrational or structural in nature. This ΔS^* provides the entropy drive for the large heat capacity jump at T_g , typical of fragile systems. When ΔS^* has a mostly configurational character, its contribution can be linked to the density of configurational states on the energy landscape [29]. The bond lattice approach is then consistent with the landscape formalism discussed in section 2.2.

3. Experiment

Glasses from the Ge–Se and As–Se–S systems were chosen for this study. In particular, the Ge–Se system has been widely used to test the rigidity theory [15, 25] due to the similar size and electronegativity of the constituent atoms, which result in a 94% covalent network. Samples corresponding to $\langle r \rangle = 2.2, 2.3, 2.4$ and 2.5 were synthesized in high purity using a vacuum techniques and multiple purification steps. The synthesis conditions are described in more detail elsewhere [16].

Photostructural changes in the glass samples were studied using a pulsed Ti–Sapphire laser with 100 fs pulses and 82 MHz repetition rate. The wavelength was tuned to adapt to the difference in bandgap between samples in a way that each sample was irradiated at the same value of the absorption coefficient. It was then ensured that the quantum efficiency of the process was the same for all samples and that the variations observed between samples could be uniquely correlated to the glass composition [16, 30]. The variations in photostructural changes with $\langle r \rangle$ were of particular interest here.

The photoinduced structural changes were evaluated in three ways. First, the extent of photorelaxation was measured by modulated differential scanning calorimetry on a set of samples with a predetermined thermal history [16]. Second, the extent of photoexpansion was measured by profilometry on polished flat samples irradiated with various light intensities [30]. Third, photodarkening was measured by recording the shift in band edge using ultraviolet–visible (UV–vis) spectroscopy before and after irradiation.

It was revealed that irradiation of the GeSe₃ bulk glass ($\langle r \rangle = 2.5$) induced crystallization of the sample. Hence this sample could not be used reliably for this study.

4. Results

Several effects resulting from photostructural changes in the Ge–Se and As–Se–S systems are shown in figure 2. The result of irradiation can be observed in the form of photorelaxation, photodarkening, and photoexpansion. All of these changes appear to decrease with decreasing fragility and reach a minimum at the average coordination number corresponding to an optimally constrained network ($\langle r \rangle \approx 2.4$). Or, equivalently, the greater the floppiness of the network (and the fragility of the system), the greater the extent of photoinduced changes.

First, the effect of photorelaxation is shown in figure 2(a) for a series of samples with different connectivity. The entropy release measured by calorimetry is indicative of structural relaxation in the glass. It was shown that the samples with floppy networks exhibit very substantial structural changes within just several minutes of irradiation and eventually saturate after long irradiation times [5]. On the contrary, the glass corresponding to the rigidity percolation composition ($\langle r \rangle = 2.4$) shows almost no structural changes, even after extended irradiation. The data points shown in figure 2(a) correspond to the entropy relaxation value after saturation. In both systems, the photostructural relaxation is very pronounced in fragile systems and essentially vanishes in strong systems. In addition, the extent of the effect appears to vary almost linearly with average coordination number in the limited range of compositions studied here.

Second, the variation in photodarkening is depicted in figure 2(b) for a set of As–Se–S samples. The data correspond to the permanent red shift in the band-edge introduced after sub-bandgap irradiation for 2 h. While the measurements in figures 2(a) and (b) were performed on a different set of glass samples, the results appear to be surprisingly correlated. The photodarkening effect is usually associated with structural changes resulting in greater overlap of chalcogen lone pair orbitals which compose the top of the valence band or, alternatively, with the formation of defect states associated with stable charged defects such as valence alternation pairs. While the correlation between photorelaxation and photodarkening is unexpected, it is consistent with an increase in structural modifications in fragile/floppy systems.

Finally, sub-bandgap irradiation results in a third type of photostructural change, namely the photoexpansion effect reported in figures 2(c) and (d). The data in figure 2(c) correspond to the photoexpansion of a series of glass with different compositions exposed for a 2 h time span sufficient to reach saturation of the effect. Photoexposure results in a bump-shaped expansion [30] and the data points correspond to the maximum bump height. Figure 2(c)

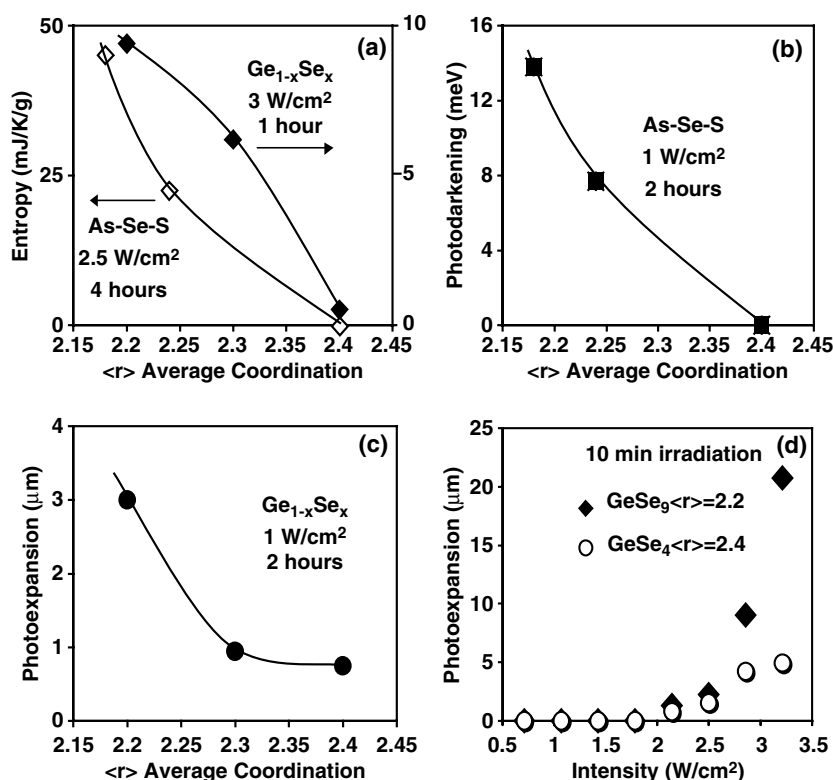


Figure 2. Photoinduced structural change in chalcogenide glasses with different network connectivity and fragility. (a) Photoinduced entropy relaxation measured by calorimetry. (b) Variation in photodarkening with average coordination number in the As–Se–S system. (c) Variation in the magnitude of photoexpansion with composition in the Ge–Se system. (d) Variation in photoexpansion with light intensity for a strong and fragile sample. Ge–Se data in (a) adapted from [16]. Data in (d) adapted from [30].

shows that the fragile system undergoes the greater magnitude change, about three times larger than the strong system. The extent of photoexpansion measured as a function of laser intensity is shown in figure 2(d) for the two most differing compositions. The resulting photoexpansion after 10 min irradiation shows that the fragile glass undergoes a consistently larger photostructural change than the strong glass at any intensity. It should be pointed out that there is no inconsistency in observing entropy relaxation and expansion in the same sample. The two effects are competing contributions, as described in [30], and photoexpansion prevails at longer time or higher intensity. The important point is that the magnitude of the changes seems to be correlated to the $\langle r \rangle$ value and is minimal in strong systems.

The three types of photostructural changes investigated here are therefore consistent in showing that fragile/floppy systems undergo larger photoinduced structural change than strong/rigid systems.

5. Discussion

It can be noticed that the photoinduced entropy release depicted in figure 2(a) parallels the trend in thermal relaxation commonly observed in chalcogenide glasses of decreasing fragility.

However, photostructural changes are known to be athermal phenomena that are not induced by laser heating [31, 32]. The mechanism of this optical phenomenon is indeed fundamentally different, and was thus termed photorelaxation [16, 30, 33]. Still, the similarity in trend between the two phenomena can be traced to the same origin, namely the fragility and consequently the topography of the energy landscape.

As discussed in section 2.2, fragile systems exhibit a larger change in configurational entropy for a given change in potential energy due to the greater density of minima on the landscape. This conforms to the thermodynamic definition of fragility, which states that a fragile liquid loses entropy at a faster rate than a strong liquid for a given decrease in temperature [34]. The consequence of this trend when the system freezes is a sharper departure from equilibrium for fragile systems. This translates into a greater build up of excess entropy for fragile glassformers cooled below T_g and, consequently, a greater propensity for structural relaxation [16].

In the case of photoinduced entropy variations, the mechanism for configurational changes involves photoexcitations of electron–hole pairs, which allow structural rearrangements prior to recombination. The substantial changes observed in fragile glass suggest that the photoexcitation process allows the system to explore surrounding minima on the energy surface. The density of minima being far larger for fragile systems, the corresponding structural changes are also larger. This trend is confirmed by the photomodification results of figure 2, which show much larger structural alterations in the fragile systems. In terms of network rigidity, this suggests that the floppy network can easily rearrange between photoexcitation and recombination, while the rigid networks are far more resilient to such changes and mostly remain unchanged throughout the process. The energy landscape of such strong, optimized networks has few minima, and the probability of a configurational change is therefore smaller.

It was also shown that the photoinduced entropy variation can actually be either positive or negative, depending on the initial fictive temperature of the sample [30]. A relaxed glass corresponding to a state at the bottom of the energy landscape gains entropy upon irradiation, while a quenched glass trapped in the upper part of the landscape releases entropy upon irradiation. The former corresponds to photorelaxation where the system is allowed to trickle down the landscape and the latter corresponds to the entropy gain of a relaxed glass photoexcited into a higher energy level where more states are available for exploration. In other words, the glassy system initially trapped in one minimum is dynamically photoexcited into surrounding minima, but the direction of the change is dictated by the thermal energy that is available and the initial configurational energy of the glass. Hence the irradiation process can be regarded as either a means for the system to acquire degrees of freedom (and explore the landscape at a level where it is normally frozen) or a means to acquire potential energy and rise in the landscape. In any case, these two contributions are opposite and result in an equilibrium between photoexcitation and thermal relaxation, illustrated by the plateaus observed after extended irradiation [30]. This idea is supported by the observation that the value of the plateau is a direct function of temperature (see figure 5 in [16]).

Generally, the irradiation process is seen as a dynamic sum of local excitations or defect creations. Two main types of mechanism have been suggested for photostructural changes in chalcogenides: the first involves bond twisting of chalcogen atoms [35–37] and the second involves the generation of charge defects called valence alternation pairs which can subsequently relax into new structural configurations [38–40]. The two models are illustrated in figure 3.

As suggested in section 2.4, this aspect of the photostructural process can be linked to the bond lattice model, since both involve individual bond excitations. In turn, the good correlation between the bond lattice excitation profile and the landscape energy profile shown

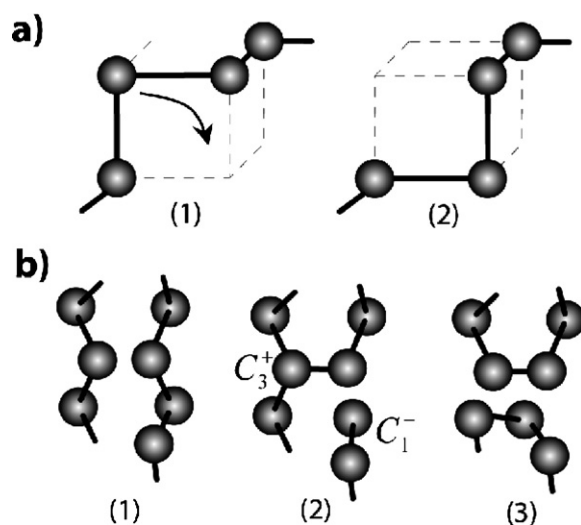


Figure 3. (a) Bond twisting of a chalcogen atom after photoexcitation of a localized lone pair state from the top of the valence band. Irradiation with sub-bandgap light generates a population of localized excitons. Bond twisting can occur if the exciton lifetime is longer than a molecular vibration. (Adapted from [35].) (b) Formation and recombination of a valence alternation pair. These charge defects are low-energy centres that can persist in the glass for long times or recombine into new local configurations. (Adapted from [40].)

in [29] suggests that it is reasonable to connect the landscape formalism to a process involving individual bond excitation and, in particular, to the photostructural process. As mentioned in section 2.4, the bond excitations considered in these models generate structural defects and are associated with an entropy change, ΔS^* . Also, the defect formation can be related to the energy landscape by considering that each collection of defects corresponds to a configurational minimum on the landscape [29]. Fragile glassformers have a large ΔS^* , which results in a greater thermodynamic drive, therefore excitation is far more likely and the density of minima is high at a given temperature. On the other hand, strong systems have low ΔS^* and fewer bonds are excited even at higher temperature, consequently the landscape has fewer minima. As a result, strong glassformers such as SiO_2 retain their network even in the liquid phase. In the case of irradiation, the photoinduced defects are associated with the same ΔS^* . Hence, during photoinduced softening of the glass [31, 41] the creation of these defects is highly probable if ΔS^* is large and, as a consequence, the observed photostructural changes come out far larger in fragile glasses.

Overall, it is suggested that the dynamic excitation of defects and the thermodynamic nature of these defects can help to explain macroscopic changes in irradiated glasses. A link between bond defect formation and dynamic properties of glassforming systems was recently emphasized by Angell [42].

6. Conclusion

Chalcogenide glasses are useful systems for testing the effect of network connectivity because of the possibility of tuning the bond density by varying the glass stoichiometry. In this study, we showed that the nature of the network affects the magnitude of photostructural changes in glasses irradiated with sub-bandgap light. Several approaches that are regularly

used for describing glass networks and their associated properties were presented in an effort to explain the phenomenon. The connection between network floppiness, fragility and density of configurational states on the energy landscape was used to describe the effect of photoexcitation in the glass. Strong glassformers that correspond to an optimally connected network with no residual strain show minimal changes during the photoexcitation process. This effect is associated with the low density of configurational minima that the system is optically allowed to sample. On the other hand, fragile systems, which are characterized by a high density of floppy modes, show a large structural change during irradiation. This is associated with the high density of configurational states that are made accessible during the photoexcitation process. The photoinduced formation of individual defects is paralleled by the individual bond breaking invoked in the bond lattice model that is used to describe glassy dynamics.

References

- [1] Bureau B, Zhang X H, Smectala F, Adam J L, Troles J, Ma H L, Boussard-Plédel C, Lucas J, Lucas P, Le Coq D, Riley M R and Simmons J H 2004 *J. Non-Cryst. Solids* **345** 276
- [2] Lucas P, Le Coq D, Juncker C, Collier J, Boesewetter D E, Boussard-Plédel C, Bureau B and Riley M R 2005 *Appl. Spectrosc.* **59** 1
- [3] Asobe M, Kanamori T and Kubodera K 1993 *IEEE J. Quantum Electron.* **29** 2325
- [4] Kolobov A V and Tanaka K 2001 *Handbook of Advanced Electronic and Photonic Materials and Devices* vol 5, ed H S Nalwa (New York: Academic) p 47
- [5] Kolobov A V and Tominaga J 2003 *J. Mater. Sci. Mater. Electron.* **14** 677
- [6] Zakery A, Ruan Y, Rode A V, Samoc M and Luther-Davis B 2003 *J. Opt. Soc. Am. B* **20** 1844
- [7] Vateva E, Skordeva E and Arsova D 1993 *Phil. Mag. B* **67** 225
- [8] Zakery A, Ewen P J S and Owen A E 1996 *J. Non-Cryst. Solids* **198–200** 769
- [9] Ewen P J S, Zakery A, Firth A P and Owen A E 1987 *J. Non-Cryst. Solids* **97** 1127
- [10] Tatsumisago M, Halfpap B L, Green J L, Lindsay S M and Angell C A 1990 *Phys. Rev. Lett.* **64** 1549
- [11] Senapati U and Varshneya A K 1995 *J. Non-Cryst. Solids* **185** 289
- [12] Thorpe M F 1983 *J. Non-Cryst. Solids* **57** 355
- [13] He H and Thorpe M F 1985 *Phys. Rev. Lett.* **54** 2107
- [14] Angell C A 1991 *J. Non-Cryst. Solids* **131–133** 13
- [15] Senapati U and Varshneya A K 1996 *J. Non-Cryst. Solids* **197** 210–8
- [16] Lucas P, Doraiswamy A and King E A 2003 *J. Non-Cryst. Solids* **332** 35
- [17] Angell C A 1998 *Nature* **393** 521
- [18] Angell C A 1988 *J. Phys. Chem. Solids* **49** 863
- [19] Angell C A, Green J L, Ito K, Lucas P and Richard B E 1999 *J. Therm. Anal. Cal.* **57** 717
- [20] Sastry S, Debenedetti P G and Stillinger F H 1998 *Nature* **393** 554
- [21] Angell C A 2000 *Insulating and Semiconducting Glasses* vol 17, ed P Boolchand (Singapore: World Scientific) p 1
- [22] Angell C A, Ngai K L, McKenna G B, McMillan P F and Martin S W 2000 *J. Appl. Phys.* **88** 3113
- [23] Bohmer R and Angel C A 1994 *Disorder Effects on Relaxational Processes* ed R Richer and A Blumen (Berlin: Springer) p 11
- [24] Naumis G G 2000 *Phys. Rev. B* **61** R9205
- [25] Phillips J C 1979 *J. Non-Cryst. Solids* **34** 153
- [26] Bohmer R 1998 *Phase Transit.* **65** 211
- [27] Naumis G G 2005 *Phys. Rev. E* **71** 026114
- [28] Angell C A and Rao K J 1972 *J. Chem. Phys.* **57** 470
- [29] Angell C A, Richards B E and Velikov V 1999 *J. Phys.: Condens. Matter* **11** A75
- [30] Lucas P, King E A, Doraiswamy A and Jivaganont P 2005 *Phys. Rev. B* **71** 104207
- [31] Hisakuni H and Tanaka K 1995 *Science* **270** 974
- [32] Schardt C R, Lucas P, Doraiswamy A, Jivaganont P and Simmons J H 2005 *J. Non-Cryst. Solids* **351** 1653
- [33] Lucas P and King E A 2006 *J. Appl. Phys.* at press
- [34] Martinez L M and Angell C A 2001 *Nature* **410** 663
- [35] Tanaka K 1983 *J. Non-Cryst. Solids* **59/60** 925
- [36] Krecmer P, Moulin A M, Stephenson R J, Rayment T, Welland M E and Elliott S R 1997 *Science* **277** 1799

-
- [37] Tanaka K 2000 *J. Non-Cryst. Solids* **266** 889
 - [38] Kastner M, Adler D and Fritzsche H 1976 *Phys. Rev. Lett.* **37** 1504
 - [39] Street R A 1977 *Solid State Commun.* **24** 363
 - [40] Fritzsche H 1993 *Phil. Mag. B* **68** 561
 - [41] Salimonia A, Galstian T V and Villeneuve A 2000 *Phys. Rev. Lett.* **19** 4112
 - [42] Angell C A 2004 *J. Phys.: Condens. Matter* **16** S5153