

The boson peak in melt-formed and damage-formed glasses: A defect signature?

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Abstract

We describe the preparation and characterization of a glassy form of the moderately good glassformer PbGeO_3 , by mechanical damage, and compare its properties with those of the normal melt-quenched glass and the crystal. The damage-formed glass exhibits a DSC thermogram strikingly similar to that of a hyperquenched glass, implying that it forms high on the energy landscape. The final glass transition endotherm occurs within 4 K ($0.006T_g$) of that of the melt-quenched glass, but crystallization occurs at a lower temperature, as if pre-nucleated. In particular, we have studied the low frequency vibrational dynamics of the alternatively prepared amorphous states in the boson peak region, and find the damage-formed glass boson peak to be almost identical in shape to, but more intense than, that of the normal melt-formed glass, as previously found for hyperquenched glasses. In view of the quite different preparation procedures, this similarity would seem to eliminate equilibrium liquid clusters as a source of the boson peak vibrations, but leaves plausible a connection to force constant fluctuations or to specific vitreous state defects.

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1. Introduction

The boson peak, which was first identified from Raman light scattering experiments [1–6], has been the source of much interest and controversy in the physics of glasses. Interest in the subject has been promoted largely by the recognition that excitations of boson peak energies are responsible for spectacular low temperature anomalies in glasses [7,8] (e.g., violations of the Debye T^3 law for low temperature heat capacity).

The boson peak is complex in character. While clearly identified as an excess in the vibrational density of states over that expected for a homogeneous elastic solid [4,5] its detailed character has been very difficult to establish, and interpretations are abundant [5,9–19,14,20,21]. The modes involved are acoustic but have been found to have both localized and extended mode character [22,23].

For some time it was thought that acoustic phonons could not propagate above the boson peak frequency because of strong scattering at the corresponding wavelength [23–25], but this has been proven generally incorrect by the observation (using inelastic X-ray scattering techniques) of distinct phonon-like excitations at wave vectors up to and well beyond, the first Brillouin zone boundary of the corresponding crystal [25–27]. Boson peaks are strongly enhanced in many glasses that have been formed by very rapid cooling [2,4,28–31] and their intensity, in normal

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glasses, slowly decreases on annealing [28,32]. In the case of the monatomic amorph, Ge, obtained by vapor deposition [33], the peak is much narrower than in the case of compound glasses [4]. It also decreases in intensity on annealing. In some cases [5] the decreases are found to correlate with differences in the intermediate range order, as shown by corresponding changes in the intensity of the first sharp diffraction peak of the structure factor.

In metallic glasses neither annealing nor quenching produces more than minor modifications of the vibrational density of states VDOS [34], though the changes observed, at boson peak frequencies, are always such as to decrease the boson peak strength as the potential energy of the glass decreases [30,34–36]. In fragile molecular liquids however, computer simulations indicate a different situation. Simulating the vibrational densities of states for different inherent structures of the fragile glassformer, *ortho*-terphenyl [37] in the Lewis–Wahnstrom model [38], Mossa et al. [37] found that quite large changes in the DOS could be observed. Furthermore, isosbestic points occurred in both constant volume and constant pressure studies [31,37]. Interestingly, the changes in ‘spectra’ were inverted for the two cases, the DOS at low frequencies (the boson peak modes), increasing with increasing fictive temperature only in the constant pressure case (which of course is the condition for most experimental studies).

The effect of pressure on the boson peak intensity of a relaxed glass is therefore a matter of interest. Indeed, it has been reported that the Gruneisen constant, hence the anharmonicity, of a glass is greatest at the boson peak [39]. This suggests, again [40,41], that these modes should be intimately involved in the structural relaxation of glasses. It is consistent with this idea that these modes should be associated with high energy, or defect, sites in the glass [42], and it is with an interest in this possibility that the present investigation has been undertaken. A defect model, involving two levels of different polarizabilities, was proposed long ago [43] to explain the boson peak, but then shown unsuitable [44], as is also known from thermodynamic studies [45]. However the objections do not apply to models with Gaussian defect distributions [46].

Most investigations of the boson peak in glasses have been made on glasses produced by cooling of the liquid, though in unusual cases like Ge and GeO₂, vapor deposition [33] and pressure-induced amorphization [47,48] preparative methods have been used. Glasses can be formed by many routes besides the latter [49,50], and one of the more interesting is the route of intense mechanical damage to the crystalline materials [51]. Since this latter is a mechanism that is directly related to the introduction of defect structures and high energy surface sites into the initially crystalline material, we reasoned that the study of the boson peak in glasses made in this way could be of diagnostic value.

Here we report on the production of glassy states of lead germanate PbGeO₃ by both liquid quenching and mechanical damage routes, and on their characterization by struc-

tural, thermal and low energy neutron scattering studies – with particular emphasis on the low frequency dynamics for the two cases. PbGeO₃ was chosen for its favorable X-ray and neutron scattering properties, and for the fact that it is both congruently melting and a moderate glass-former, making both glass and crystal states readily accessible.

We provide a brief background on athermal damage routes to the glassy state.

Vitrification by damage is one of the routes by which natural glasses are formed, often without loss of the crystalline morphologies. For instance, ‘metamict’ crystals are naturally occurring materials in which the well-formed crystals prove to have no internal structure beyond the short range order characteristic of the glassy states of the same substance [52–55]. The explanation is that their crystalline order has been destroyed by radiation damage from nearby sources providing heavy atom bombardment. Glassy states of certain chalcogenides can also be obtained by exposure to electromagnetic radiation of energy that exceeds that of the relevant covalent bond [50,56,57], though this vitrification mode is uncommon.

A cruder method of introducing structural damage is that of mechanical comminution, which has been known, since the work of Bogardus and Roy [51] in 1953, to vitrify certain crystalline materials. This has since been much used as a vitrification method for marginal glassformers, including metallic [58,59] and superionic [60] materials, but there have been few studies on normal glassformers made for the purpose of detailed comparison of physical properties with those of glasses produced by the normal melt-cooling route. An exception is the work of Yamamuro and co-workers [61] who studied the molecular glass tri- α -naphthyl benzene T α NB, the T_g of which is substantially above ambient. They found that an amorphous phase formed on sufficient grinding, and that it was obtained in a high enthalpy state as indicated by heat release on upscanning. However, their material crystallized before showing the glass transition despite being a quite strong glassformer from the liquid. In this respect their result is qualitatively distinct from the findings reported below, but much of the difference is due to the proximity of the normal T_g for T α NB to the grinding temperature. The findings for T α NB will be discussed further in a later section.

2. Experimental methods

2.1. Materials

Crystalline PbGeO₃ ($T_m = 799$ °C) was prepared from the pure oxides (99.99% GeO₂ from City Chemicals LLC, and 99.9% PbO from Alfa Products), by heating in air in a lidded platinum crucible at 900 °C to minimize vapor phase losses during melting, holding for 15 min to allow homogenization of the low viscosity liquid, and then slowly cooling to room temperature. Although Tomasi et al. [62] reported weight losses of only 0.5–1% after PbGeO₃ preparations at

1100 °C for 1 h, we observed a weight loss of 1.6%. We nevertheless obtained a glass transition temperature that agreed well (within 2 K) with the value the latter authors reported (see below). Vitreous samples were obtained by reheating some of the crystalline material to the liquid state, and then quenching between stainless steel plates.

For comminution studies, crystalline samples of about 2 g in mass were transferred to a Spex 8000D Dual Mixer/Ballmill equipped with stainless steel vials and stainless steel balls. A shaking frequency of 1060 reversals/min was applied for 100, 200 and 400 min. The latter was sufficient for complete amorphization as evidenced below. Although PbGeO_3 in bulk does not gain weight on long exposure to the atmosphere, the comminuted samples were stored in a desiccator and taken out only at the time of analysis.

To determine the extent of amorphization, powder X-ray diffraction studies of all the samples were performed on a Siemens D5000 X-ray diffractometer using the $\text{Cu-K}\alpha$ radiation having the wavelength 1.541 Å. For visualization of the sample after comminution for different periods, electron micrograph images were obtained using a scanning electron microscope (XL30 ESEM-FEG) and transmission electron microscope (JEOL JEM 2000FX TEM).

To determine the thermal properties of the amorphous products of comminution, and to compare them with those of the quenched and annealed glasses, we used differential scanning calorimetry (DSC) of powdered samples in hermetically-sealed aluminum pans scanned in TA Instruments Model 2920 DSC, (after carrying out preliminary qualitative studies using a Netsch STA449C fitted with a Netsch TASC 414/3A controller).

To measure the low frequency vibrational densities of states, neutron scattering experiments were performed on crystalline, melt-formed, and damage-formed samples, prepared using the methods described above. Although bulk (melt-formed) glassy samples (as well as crystalline samples) do not change mass detectably on standing in the laboratory atmosphere for periods of days, there is evidence from some of our preliminary neutron scattering measurements, supported by the results of prompt gamma activation analysis measurements [63], that finely divided comminuted samples adsorb significant amounts of water at room temperature, sufficient to affect the results at frequencies of interest in the present study. Accordingly, the damage-formed sample (comminuted for 400 min) was first vacuum-dried *in situ* at 500 K for ~60 min in order to drive off adsorbed water. The neutron experiments were carried out using the Disk Chopper Spectrometer at the NIST Center for Neutron Research [64].

Samples with masses of order 20 g (prepared by combining several batches made with the above methods) were placed in thin-walled cylindrical aluminum containers and measurements were made at room temperature using a pulsed beam of 5 Å neutrons. Counts were accumulated in 913 detectors placed 4 m from the sample and the energies of the scattered neutrons were determined from their

times of arrival, sorting events into 9 μs time channels. The energy resolution for elastic scattering, determined from measurements with the largely incoherent scatterer vanadium, was ~110 μeV full width at half maximum. The data were corrected for scattering from the empty container and reduced using the IDL-based program 'DAVE', developed at the NIST Center for Neutron Research and available at <http://www.ncnr.nist.gov/dave>.

3. Results

Electron microscope images, showing the progress of vitrification by damage at a constant rate for different periods of time, are shown in Fig. 1. We note that the average particle size at complete vitrification (400 min comminution) is well below 1 μm. The last image shows an individual particle at magnification 100000×, the particle diameter being ~0.1 μm. Any residual atomic ordering from untransformed material would be visible in enlarged versions of this image, but none were found.

The X-ray diffractograms of the second and last of these samples are seen in Fig. 2, where they are compared with those of the initial crystalline material and the melt-formed glass. After recrystallization by heating above T_g the X-ray diffractogram is found to be the same as that of the original crystal except for some minor changes in relative intensity.

Fig. 3 shows the DSC thermograms of melt-quenched and damage-formed glasses. Discussion of their characteristics is given later.

The neutron scattering spectra are shown in Figs. 4–6. In Fig. 4, we show the VDOS. Comparison is made of

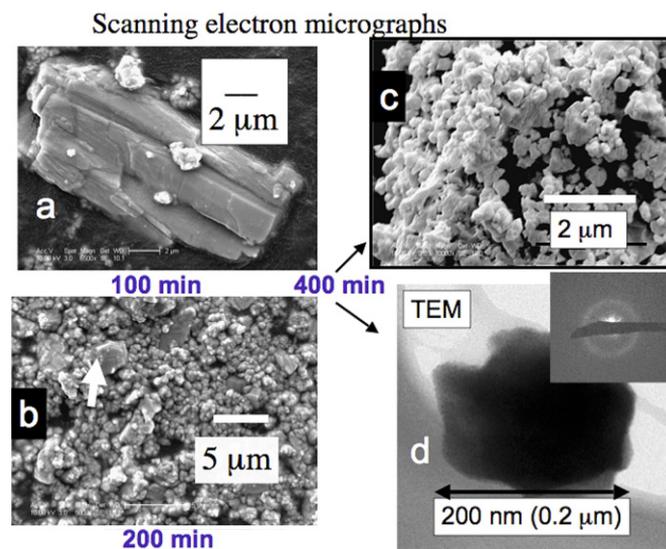


Fig. 1. Electron micrographs of initially crystalline samples of PbGeO_3 after comminution for different periods as indicated in the figure. Length scales are indicated by bars in each case. The arrow in the lower left panel indicates the sort of residual crystal that can give small residual Bragg peaks, and initiate crystallization on reheating. Panel d shows a transmission electron micrograph of a single small grain from the panel c sample, magnified 100000×. The insert shows the scattering halo for this sample and shows that it is fully amorphous.

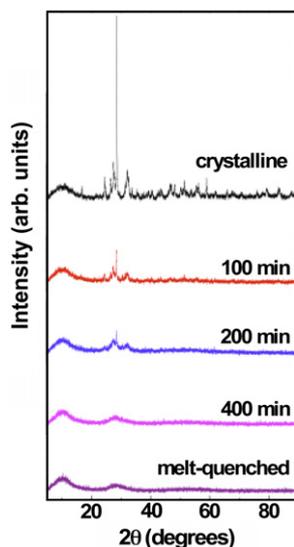


Fig. 2. X-ray diffractograms of PbGeO_3 in crystalline state (top, sharp lines) and three stages of comminution, measured in minutes of ball mill operation on 0.5 g samples of initially crystalline material, as marked. Comparison is made with the pattern for the melt-quenched glass (bottom). The feature at 10° , common to all samples, is an instrumental artifact.

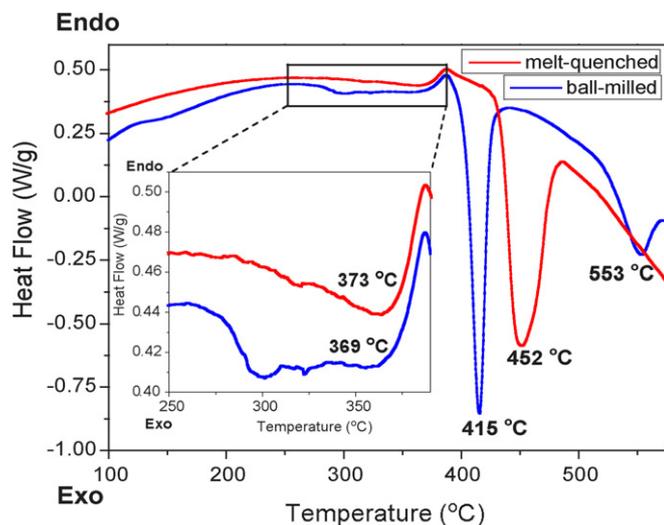


Fig. 3. Differential scanning calorimetry (DSC) thermograms of melt quenched glass (upper trace) and damage-formed glass. Note that the latter material exhibits a well defined glass transition temperature only a small interval (4 K or $0.006T_g$) below that of the melt-formed glass, but crystallizes at a lower temperature, as seen in previous studies [60,61].

crystal, melt-quenched glass, and 400 min comminuted crystal (i.e. damage-formed glass). Fig. 5 shows the latter data converted to the form usually used [4,65] for comparison with results of light scattering studies of the boson peak. Fig. 6 then breaks down the total scattering seen in Fig. 5 into contributions from different values of the wave vector transfer Q , as indicated in the legend.

4. Discussion

We first provide a thermodynamic rationale for the formation of glass directly from crystal by mechanical dam-

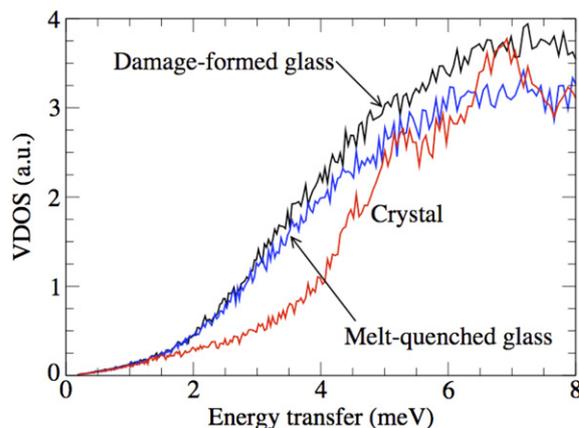


Fig. 4. Vibrational density of states for crystalline PbGeO_3 and for its melt-quenched and damage-formed glasses ($1 \text{ meV} = 8.1 \text{ cm}^{-1}$).

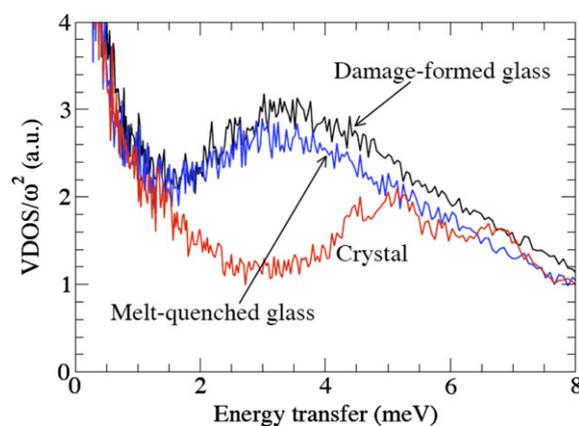


Fig. 5. Representation of the neutron scattering data of Fig. 4 needed to compare with results of light scattering measurements [65]. The glasses exhibit large excess scattering relative to the crystal in the low frequency range corresponding to the 20–40 cm^{-1} commonly associated with the boson peak in light scattering. When the VDOS has been quantitatively evaluated these curves can be extrapolated to 0 meV values determined by Debye theory from the velocity of sound [65] meaning that the low energy divergence seen in the figure is artifactual. Note that, at $\sim 5 \text{ meV}$, the crystal also has an excess scattering over the Debye expectation. This is often found to be the case with glassforming substances [36], and its implications are discussed in the text.

age, using Fig. 7 as a basis for explanation. The figure shows how the glass can form directly from crystal by mechanical damage by showing how the difference in free energy between crystal and glass at a temperature below T_g can be overcome by increasing the free energy of the crystal in two distinct ways during comminution. The first is by the reduction of crystal size with concomitant increase of surface free energy, while the second is by introduction of higher energy sites (defects of different types) into the internal structure of the crystal fragments. After a certain comminution time the crystal free energy exceeds that of the glass and a spontaneous conversion can occur.

We note that the size of the individual particles, most of which are clumped together according to Fig. 1 (panel c, upper right), is of the order of $0.2 \mu\text{m}$. An individual parti-

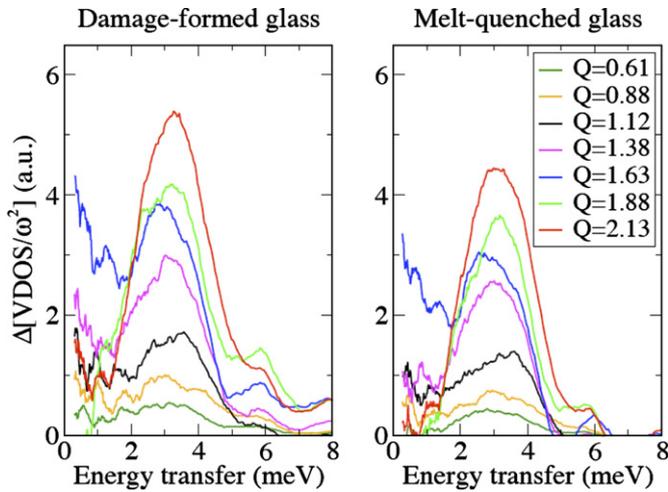


Fig. 6. Contributions to the VDOS of PbGeO₃ for different values of the wave vector transfer Q in \AA^{-1} , for melt-formed glass (RH panel) and 400 min comminuted glass (LH panel). There is little dispersion in the scattering, implying largely localized character of this boson peak. Note the interesting and significant differences in peak shape that occur between $Q = 1.88$ and 1.63\AA^{-1} , and again between 1.38 and 1.12\AA^{-1} , that are common to both damage-formed and melt-quenched glasses.

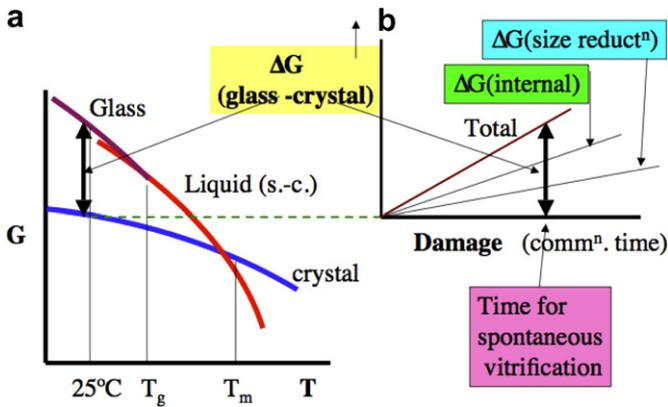


Fig. 7. Schematic showing manner in which mechanical damage can raise the free energy of a crystal until vitrification can occur spontaneously. LH panel shows free energy vs temperature illustrating the excess free energy of the glass at ambient temperature. Right hand panel shows how this free energy gap can be closed by increase of free energy during damage due to (a) decreasing sample particle size and (b) internal crystal damage by impact shock, until after sufficient damage production time, the glass has the lower free energy state and can form spontaneously.

cle of this size is shown in the lower right panel (panel d) at a magnification of $100\,000\times$, (assuming a 2 cm page image). The uniform halos in the electron diffraction pattern shown as an insert to this panel, establish that the particle is completely amorphous. By itself, a size reduction to $0.2 \mu\text{m}$ is not nearly sufficient to account for the free energy gap between ambient temperature glass and crystal, needed according to Fig. 7, so we suppose that most of the necessary gap reduction is brought about by internal damage to the microcrystal structure.

It is reasonable to suppose that defects introduced into incompletely vitrified crystals will cause scattering which

is a little better defined in character, i.e. more structured than that characteristic of the true glass, and that the difference could be seen most clearly in the low frequency VDOS if the damaged crystal state could be selected out for study. However, in practice, because of the random but ‘coarse grained’ manner in which the damage is introduced, the two states must coexist in the incompletely amorphized samples, and so be difficult to distinguish.

Irrespective of what the spectrum for damaged-but-still-crystalline material might be, Fig. 5 shows that, in the final collapse of this state to the glass, differences between the melt-formed and damage formed structures that can be seen in the low frequency vibrational dynamics, are all lost (at least, when the state of configurational excitement is taken into account). Based on previous experience [4,31], Fig. 3 tells us that we should find the boson peak to be somewhat more intense for the damage-formed glass, and this is substantiated by the data presented in the alternative forms of Figs. 4 and 5. However, the differences are small. We find it remarkable that glasses produced by such dramatically different routes can have such similar vibrational dynamics.

Let us consider the implications of our findings a little further. It seems that the defects introduced into the microcrystals during damage are capable of providing an almost continuous route from the crystal to the glassy state. Evidently, as in the case of a quartz crystal subject to radiation damage [66,67], there is a critical damage threshold beyond which a damaged microcrystal transforms cooperatively (spinodally collapses?) to a lower free energy amorphous state which, however, lies high up on the system’s configuration space energy landscape, as depicted in Fig. 8.

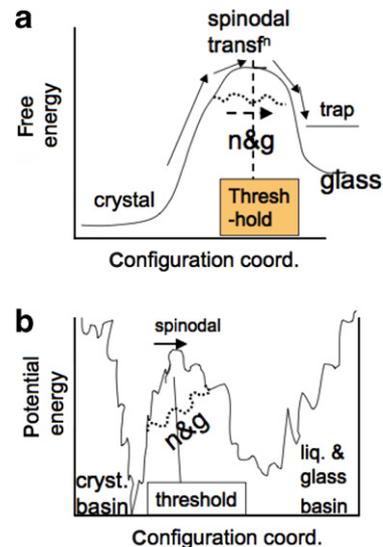


Fig. 8. Free energy (a), and potential energy ‘landscape’ (b), representations of the progress of a system from the crystalline free energy level to the excited glass free energy level during progressive mechanical damage. In both panels, ‘n&g’ indicates a state change occurring by a two step (nucleation and growth) process, as distinct from a one step ‘spinodal’ (nondiffusive) mechanism.

Enthalpically, it is close to the state of a hyperquenched glass, according to the data seen in Fig. 3.

A similar exothermic effect, during calorimetric upscan, was seen in the study of tri- α -naphthyl benzene by Tsukushi et al. [61]. However, in their case the damage-amorphized sample crystallized before the T_g of the normal glass was reached. The glass temperature in their case was less than 100 K above the temperature of damaging, so it is possible that crystal nucleation, which can occur at temperatures much lower than the observed crystallization onset, may have been occurring concomitantly with damage, such that the system was always nucleated. This would correspond to the system energy under communication being maintained at the ‘n&g’ level in Fig. 8 upper panel.

Comparison must be made here between the excess enthalpy of the damage-formed glass and the excess enthalpies of hyperquenched glasses of comparable T_g . For this comparison we turn to the calorimetric studies of Yue and co-workers on silicate glasses [68,69].

In Yue et al.’s studies it was found that, in the case of the as-quenched glass, the initial relaxation (descent on the energy landscape) manifested itself calorimetrically as a weak exothermic displacement starting far below the T_g of the ‘standard glass transition’, see Fig. 9.

The fact that it commenced at such a low temperature means that the system was initially occupying a very shallow trap, which allows escape to be a fast process. Once this fast process had occurred in Yue et al.’s study, subsequent upscans showed a rather sharp onset of the relaxation exotherm, see Fig. 8.

This latter type of scan resembles that observed in the present work, Fig. 3, implying that the damage-formed glass is trapped at a level of the landscape above that of the normal glass but below that of a hyperquenched glass. Consistent with this notion, the intensity of the boson peak seen in Fig. 6 is greater than in the case of the normal glass, but not as great as that seen in hyperquenched glasses of Ref. [31].

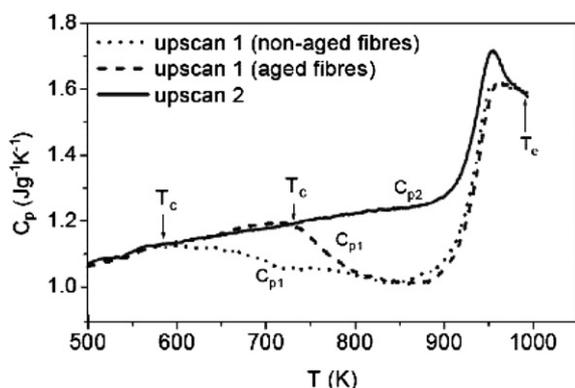


Fig. 9. DSC thermograms of hyperquenched and partly annealed hyperquenched samples, of a silicate glass [69], for which the boson peaks have previously been studied [31]. Note the similarity in shape of the aged sample before upscanning to that of our damage-formed glass in Fig. 2. (Adapted from Yue [69], by permission.)

Whether or not glasses with relatively more intense boson peaks can be formed by mechanical damage of systems with glass temperatures higher than that of the present system, is an interesting question which we will consider in future articles on this subject.

We can now address the question that motivated our study, by considering the implications of our findings for the elementary excitation, or vitreous defect, concept. After all, a system high up on an energy landscape is most simply interpreted, in real space terms, as a system containing a lot of energy-rich defects. When the threshold separating damaged crystal from glassy solid (see Fig. 8) is crossed, it means that a crystalline system containing defects identifiable by high resolution electron microscopy passes over to a state in which long range disorder prevents straightforward structural characterization. But at the temperature where this threshold-crossing event occurs (T (damaging) ≈ 298 K $\ll T_g$), the particle mobilities are extremely low. So, it is not easy to see how the system could suddenly rearrange to form the clusters that are attributed to the deeply supercooled liquid and incorporated in early explanations of the boson peak [6]. It is possible but not very likely that a major reconstruction of the system (to a state with a liquid-like distribution of force fluctuations [23]) occurs. Perhaps this distribution of force fluctuations is introduced in the crystal during damage, but it seems more likely that there occurs some more local collapse of the system of crystal defects to a system of topologically related vitreous state defects, with a Gaussian distribution of energies [46] (and characterized by long range disorder). In this case only a small gap in configuration space is crossed but, because of the free energy drop seen in Fig. 8(a), the process is irreversible, except by a nucleation and growth process. We note that the poor lattice energies characteristic of crystalline glassformers [53,70] pre-dispose them to become defective, and this may be the reason that the crystals themselves so often [36] show an excess DOS, though at somewhat higher frequencies, e.g., as in Fig. 5.

It is tempting to try to extract additional information on defect structures from the data in Fig. 6 where we see the total VDOS broken down into contributions from different scattering angles – corresponding to different distances in real space. In Fig. 6, we see that there are wave vector-dependent details common to both glass preparations. For instance, a shift to a different form of the boson peak occurs, in each case, between the same Q values, namely, 1.88–1.63 \AA^{-1} and, again, between 1.38 and 1.12 \AA^{-1} . However these features may be simply a consequence of de Gennes narrowing, associated with the presence of peaks in the structure factor. If annealing should produce diagnostic changes of these components of the peak, they may merit more attention.

5. Summary and concluding remark

The low frequency vibrational dynamics of glasses formed by progressive mechanical damage differ only

slightly from those of melt-formed glasses, and the difference lies in the same direction as found for quenched glasses (corresponding to the greater configurational enthalpy). The build-up of intensity in this low frequency domain by internal defect formation in crystals under damage is consistent with an interpretation of the boson peak in glasses as a manifestation of the glassy (Gaussian) analog of the crystal defect.

It should be relatively straightforward to investigate the transition, under increasing damage, from defective crystal to glass, in a computer simulation, though we know of no example that has been performed to date.

Disclaimer

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References

- [1] R.J. Nemanich, *Phys. Rev. B* 16 (1977) 1655.
- [2] H. Kawamura, K. Fukumasu, Y. Hamada, *Solid State Commun.* 43 (1982) 229.
- [3] A. Boukenter, E. Duval, T. Achibat, *J. Condens. Matter* 2 (1990) 10227.
- [4] V.K. Malinovsky, A.P. Sokolov, *Solid State Commun.* 57 (1986) 757.
- [5] V.K. Malinovsky, V.N. Novikov, P.P. Parshin, A.P. Sokolov, M.G. Zemlyanov, *Europhys. Lett.* 11 (1990) 43.
- [6] A. Boukenter, B. Champagnon, E. Duval, J.L. Rousset, H.M. Rosenberg, *Philos. Mag. B – Phys. Condens. Matter Statist. Mech. Electron. Opt. Magn. Prop.* 59 (1989) 125.
- [7] R.C. Zeller, R.O. Pohl, *Phys. Rev. B* 4 (1971) 2029.
- [8] P.W. Anderson, B.I. Halperin, C.M. Varma, *Philos. Mag.* 25 (1972) 1.
- [9] L. Borjesson, A.K. Hassan, J. Swensen, L.M. Torell, A. Fontana, *Phys. Rev. Lett.* 70 (1993) 1275.
- [10] A. Wischnewski, D. Engberg, U. Buchenau, L. Borjesson, A.J. Dianoux, A.P. Sokolov, L.M. Torell, *Phys. Rev. B* 58 (1998) 9087.
- [11] S.N. Taraskin, Y.L. Loh, G. Natarajan, S.R. Elliott, *Phys. Rev. Lett.* 86 (2001) 1255.
- [12] U. Buchenau, N. Nucker, A.J. Dianoux, D. Krause, *Physica A* 201 (1993) 372.
- [13] A.P. Sokolov, U. Buchenau, W. Steffen, B. Frick, A. Wischnewski, *Phys. Rev. B* 52 (1995) R9815.
- [14] S.R. Elliott, *Europhys. Lett.* 19 (1992) 201.
- [15] W. Gotze, M.R. Mayr, *Phys. Rev. E* 61 (2000) 587.
- [16] M.I. Klinger, A.M. Kosevich, *Phys. Lett. A* 295 (2002) 311.
- [17] S.P. Das, *Phys. Rev. E* 59 (1999) 3870.
- [18] H. Tanaka, *J. Phys. Soc. Jpn.* 70 (2002) 1178.
- [19] S.R. Elliott, in: S.R. Elliott (Ed.), *Encyclopedia of Materials: Science and Technology*, vol. 4, Pergamon, 2001, p. 171.
- [20] A.K. Hassan, L. Borgesson, L.M. Torell, *J. Non-Cryst. Solids* 172 (1994) 154.
- [21] M. Kruger, A. Kisliuk, A. Sokolov, M. Soltwisch, D. Quittman, *J. Phys. – Condens. Matter* 5 (1993) B127.
- [22] A.I. Chumakov, I. Sergueev, U. van Burck, W. Schirmacher, T. Asthalter, R. Ruffer, O. Leupold, W. Petry, *Phys. Rev. Lett.* 92 (2004).
- [23] A.P. Sokolov, *J. Phys. – Condens. Matter* 11 (1999) A213.
- [24] S.N. Taraskin, S.R. Elliott, *Philos. Mag. B – Phys. Condens. Matter Statist. Mech. Electron. Opt. Magn. Prop.* 79 (1999) 1747.
- [25] G. Ruocco, F. Sette, *J. Phys. – Condens. Matter* 13 (2001) 9141.
- [26] C. Masciovecchio, G. Ruocco, F. Sette, M. Krisch, R. Verbeni, U. Bergmann, M. Soltwisch, *Phys. Rev. Lett.* 76 (1996) 3356.
- [27] C. Masciovecchio, A. Mermet, G. Ruocco, F. Sette, *Phys. Rev. Lett.* 85 (2000) 1266.
- [28] S.L. Isakov, S.N. Ishmaev, V.K. Malinovsky, V.N. Novikov, P.P. Parshin, S.N. Popov, A.P. Sokolov, M.G. Zemlyanov, *Physica A* 201 (1993) 386.
- [29] J.B. Suck, H. Rudin, H. Bretscher, P. Grutter, H.J. Guntherodt, *Z. Phys. Chem. Neue Fol.* 157 (1988) 817.
- [30] J.-B. Suck, in: *Dynamics of Disordered Materials*, in: D. Richter, A.J. Dianoux, W. Petry, J. Teixeira (Eds.), *Springer Proceedings in Physics*, vol. 37, Springer, Heidelberg, 1989, p. 182.
- [31] C.A. Angell, Y.Z. Yue, L.M. Wang, J.R.D. Copley, S. Borick, S. Mossa, *J. Phys. – Condens. Matter* 15 (2003) S1051.
- [32] E. Duval, L. Saviot, L. David, S. Etienne, J.F. Jal, *Europhys. Lett.* 63 (2003) 778.
- [33] J.S. Lannin, N. Maley, S.T. Kshirsagar, *Solid State Commun.* 53 (1985) 939.
- [34] J.-B. Suck, *Adv. Solid State Phys.* 42 (2002) 393.
- [35] T. Otomo, M. Arai, J.B. Suck, S.M. Bennington, *J. Non-Cryst. Solids* 312 (2002) 599.
- [36] A. Meyer, J. Wuttke, W. Petry, R. Bormann, G. Coddens, O.G. Randl, H. Schober, *Phys. Rev. B* 53 (1996) 12107.
- [37] S. Mossa, E. La Nave, H.E. Stanley, C. Donati, F. Sciortino, P. Tartaglia, *Phys. Rev. E* 65 (2002) 041205.
- [38] L.J. Lewis, G. Wahnstrom, *Phys. Rev. E* 50 (1994) 3865.
- [39] Y. Yamaguchi, T. Nakayama, T. Yagi, *Physica B* 263&264 (1999) 258.
- [40] D. Quitmann, M. Soltwisch, G. Ruocco, *J. Non-Cryst. Solids* 203 (1996) 12.
- [41] G.N. Greaves, F. Meneau, O. Majerus, D.G. Jones, *J. Taylor, Science* 308 (2005) 1299.
- [42] C.A. Angell, *Philos. Trans. R. Soc. London Ser. A – Math. Phys. Eng. Sci.* 363 (2005) 415.
- [43] N. Theodorakopoulos, J. Jäckle, *Phys. Rev. B* 14 (1976) 2637.
- [44] V.Z. Gochiyaev, A.P. Sokolov, *Sov. Phys. Solid State* 31 (1989) 557.
- [45] C.A. Angell, K.J. Rao, *J. Chem. Phys.* 57 (1972) 470.
- [46] D.V. Matyushov, C.A. Angell, *J. Chem. Phys.* 123 (2005) 034506.
- [47] K.H. Smith, E. Shero, A. Chizmeshya, G.H. Wolf, *J. Chem. Phys.* 102 (1995) 6851.
- [48] D.J. Durben, G.H. Wolf, *Phys. Rev. B* 43 (1991) 2355.
- [49] C.A. Angell, *Science* 267 (1995) 1924.
- [50] M. Frumar, A.P. Firth, A.E. Owen, *J. Non-Cryst. Solids* 193 (1995) 447.
- [51] A.E. Bogardus, R.S. Roy, *J. Am. Ceram. Soc.* 48 (1965) 205.
- [52] M. Zhang, E.K.H. Salje, I. Farnan, A. Graeme-Barber, P. Daniel, R.C. Ewing, A.M. Clark, H. Leroux, *J. Phys. – Condens. Matter* 12 (2000) 1915.
- [53] J. Wong, C.A. Angell, *Glass: Structure by Spectroscopy*, Marcel Dekker, 1976 (Chapter 9.4).
- [54] J. Lian, J. Chen, L.M. Wang, R.C. Ewing, J.M. Farmer, L.A. Boatner, K.B. Helean, *Phys. Rev. B* 68 (2003) 134107.

- [55] W.C. Ewing, A.M.L. Wang, S. Wang, *Rev. Mineral. Geochem.* 39 (2000) 319.
- [56] A.V. Kolobov, V.A. Bershtein, S.R. Elliott, *J. Non-Cryst. Solids* 150 (1992) 116.
- [57] A.V. Kolobov, S.R. Elliott, *J. Non-Cryst. Solids* 189 (1995) 297.
- [58] A.E. Ermakov, E.E. Yurchikov, V.A. Bariniov, *Fiz. Met. Metalloved.* 52 (1981) 1181;
R.B. Schwartz, *Appl. Phys. Lett.* 49 (1986) 146.
- [59] U. Herr, *Nonequilib. Mater.* 103 (1995) 113.
- [60] T. Ohtomo, F. Mizuno, A. Hayashi, K. Tadanaga, M. Tatsumisago, *Solid State Ionics* 176 (2005) 2349.
- [61] I. Tsukushi, O. Yamamuro, T. Ohta, T. Matsuo, H. Nakano, Y. Shirota, *J. Phys. – Condens. Matter* 8 (1996) 245.
- [62] C. Tomasi, M. Scavini, A. Speghini, M. Bettinelli, M.P. Riccardi, *J. Therm. Anal. Calorim.* 70 (2002) 151.
- [63] R.L. Paul, R.M. Lindstrom, *J. Radioanal. Nucl. Chem.* 243 (2000) 181.
- [64] J.R.D. Copley, J.C. Cook, *Chem. Phys.* 292 (2003) 477.
- [65] D. Engberg, A. Wischnewski, U. Buchenau, L. Borjesson, A.J. Dianoux, A.P. Sokolov, L.M. Torell, *Phys. Rev. B* 59 (1999) 4053.
- [66] J.S. Lukesh, *Phys. Rev.* 97 (1955) 345.
- [67] I. Simon, *J. Am. Ceram. Soc.* 40 (1957) 150.
- [68] Y.Z. Yue, S.L. Jensen, J.D. Christiansen, *Appl. Phys. Lett.* 81 (2002) 2983.
- [69] Y.Z. Yue, *J. Non-Cryst. Solids* 348 (2004) 72.
- [70] C.A. Angell, J.L. Green, in: M. Pikal, R. Constantino (Eds.), *Lyophilization of Biopharmaceuticals*, AAPS press, 2005, p. 367.