Length scale dependence of high-pressure amorphization: the static amorphization of anorthite

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Abstract

High-pressure amorphization of anorthite has been observed by energy-dispersive X-ray diffraction of powdered samples held under static pressure in a diamond anvil cell. The onset of amorphization is accompanied by a significant reduction in the intensity of Bragg reflections at pressures between 10 and 14 GPa, and anorthite becomes completely X-ray amorphous between 14 and 20 GPa. These pressures are significantly lower than those suggested by earlier birefringence studies. The discrepancy can be reconciled in terms of a model of high-pressure amorphization in which partially amorphized anorthite can be regarded as a spatially heterogeneous anti-glass, with long-range order maintained but translational disorder dominating at shorter correlation lengths.

KEYWORDS: high-pressure amorphization, anorthite, anti-glass, metamictisation.

Introduction

DIAPLECTIC feldspar glasses have been recovered at many meteorite impact sites, and shock-compression has long been recognized as a route to the production of highly disordered non-crystalline material leading, for example, to the amorphization of plagioclase (e.g. Arndt *et al.*, 1982; Stöffler and Hornemann, 1972). More recently, Williams and Jeanloz (1989) demonstrated that room-temperature static compression of anorthite in the diamond anvil cell could also induce the breakdown of crystallinity and formation of a dense amorphous phase. Their experiments consisted of measurements of changes in infrared absorption of single crystals of anorthite conducted *in situ* at high-pressure. Alongside this, they made observations of changes in birefringence of the same samples, conducted at ambient pressure after the samples had been recovered from the diamond cell, in which they had been subjected to known peak pressures. Anorthites were studied at pressures between 1 bar and 33 GPa. The authors noted that the infrared absorption associated with *T*-O-*T* bends and stretches changed reversibly over this pressure range, and interpreted the changes as an increase in *T*-site coordination from four-fold to a more highly coordinated arrangement upon increasing pressure. They inferred amorphization from the changes in birefringence of the recovered samples, which became isotropic after compression above ~25 GPa. The latest results on the amorphization of anorthite come from *in situ* Raman spectroscopic experiments (Daniel *et al.*, 1995*a,b*), which suggest that vitrification proceeds above 11 GPa and is complete by 17 GPa. Daniel *et al.* (1995*a,b*) found that samples pressurized above 20 GPa transformed to an amorphous glass state irreversibly, while samples that were pressurized to lower peak pressures reverted to a disordered state with some lattice symmetry on decompression.

Such amorphization at modest pressures and ambient (or low) temperature has now been observed in a plethora of materials. Early X-ray and Raman spectroscopic work showed that *a*-quartz transforms to a dense amorphous phase on increasing pressure, and recent molecular dynamics simulations suggest that the high-pressure amorphization of SiO_2 phases involves a change in coordination of Si from four to six (Zhang and Ong, 1993; Binggeli *et al.*, 1994*a,b*) and a reduction in interstitial void space. These studies suggest that the transition from crystalline SiO_2 to a high-pressure glass is associated with an

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instability in Si-coordination between fourfold and sixfold sites. This distinguishes high-pressure amorphization from high-temperature melting, where the disordered phases are generally less dense than the crystalline ones. It is likely that the high-pressure amorphization of other tectosilicates such as anorthite may also be associated with an instability of the SiO_4 structural unit, as indeed the infrared results of Williams and Jeanloz (1989) would appear to confirm.

It is worth commenting at this stage on the high-pressure amorphization phenomena thus far observed in other silicate minerals. As well as the many investigations on SiO_2 polymorphs and the previous work on anorthite, there are reports of amorphization at pressure for micas (muscovite is reported to go amorphous by Faust and Knittle, 1994), pyroxenoids (Serghiou and Hammack, 1993, suggest wollastonite becomes amorphous at pressure), and olivine (Guyot and Reynard, 1992). The question arises as to whether the amorphization mechanisms inferred for tectosilicates also apply to these less-polymerized structures. Stacking faults and low-dimensional disorder may also play a part in the early stage amorphization of, in particular, the sheet and chain structures. Since most reports of amorphization simply refer to the production of X-ray amorphous material (i.e. material in which long-range correlation has broken down), it is not clear that the reports of pressure-induced amorphization in less-polymerized silicates necessarily imply a transition to a dense glass state akin to that seen in SiO_2.

Here, the integration of new X-ray diffraction data with the earlier infrared and birefringence studies of Williams and Jeanloz (1989) as well as the Raman results of Daniel *et al.* (1995*a,b*) allows a reassessment of the nature of the pressure-induced amorphization of anorthite. Differences in measured amorphization pressure are reconciled in terms of a model in which amorphization proceeds heterogeneously throughout the lattice, and a comparison is drawn with similar differences in the experimental determination of the degree of amorphization of metamict phases.

Experimental methods

Highly-ordered anorthite from Val Pasmeda was used in this study. This specimen is identical to that studied at high-temperature by Redfern and Salje (1987). The sample was ground to a fine powder, mixed with powdered NaCl, and ~1 mg of the mixture was placed in an Inconel gasket in a lever arm diamond anvil cell. The NaCl acted as an internal standard and pressure calibrant. The gasket was pre-indented and drilled to form a 100 μm gasket hole. A non-dried 4:1 methanol:ethanol mixture was used as the pressure-transmitting medium. Pressures were determined from the observed volume of the NaCl standard, determined from the measured peak positions from the NaCl diffraction pattern, and using the equation of state of Decker (1971). The pressure-transmitting medium is known to be hydrostatic to greater than 11 GPa (Eggert *et al.*, 1992) and any non-hydrostaticity can be monitored additionally from the relative positions of the NaCl reflections. There was no indication of significant departure from hydrostaticity in the course of these experiments, but the higher-pressure data can only be assumed to be quasi-hydrostatic.

X-ray diffraction patterns were obtained at station 9.7 of the Daresbury synchrotron radiation source (Clark, 1992). The diffracted angle was set at 5.97°2θ (as determined from the diffraction pattern of NBS silicon standard 640b placed in the sample position). An attempt was made to monitor the kinetics of amorphization by taking diffraction patterns over successive ten minute intervals immediately following pressurization in the diamond cell, but successive isobaric diffraction patterns did not differ and it was concluded that any kinetic processes operated on a much shorter time scale. Collecting diffraction patterns over shorter time scales was not deemed worthwhile, however, since signal-to-noise deteriorated significantly at shorter collection times. The diffraction patterns presented here represent the total count accumulation over 30 min. The sample was pressurized over a time scale of 5 min between patterns.

Typical diffraction patterns collected on increasing and decreasing pressure are shown in Fig. 1, where the low-pressure diffraction pattern of anorthite (top) has been partially indexed. The position of the diamond anvil cell was unchanged in relation to the beam in the course of these experiments, and the intensity of the NaCl peaks, in particular the 200 reflection, was monitored to check that any loss of coherent scattering from the sample was genuine and not an artefact of cell misalignment.

Results and comparison with earlier work

It can be seen from Fig. 1 that there is a dramatic decrease in Bragg intensity from crystalline anorthite upon increasing pressure. Changes in the relative intensities of Bragg reflections are often observed during high-pressure energy dispersive diffraction of small amounts of sample in a diamond anvil cell: the small sample volume and fixed experimental arrangement (with only a fraction of the diffracting cone contributing to the signal) means that the intensity contributions to specific Bragg reflections may only be from as few as two or three crystallites. As the sample is pressurized, small movements of

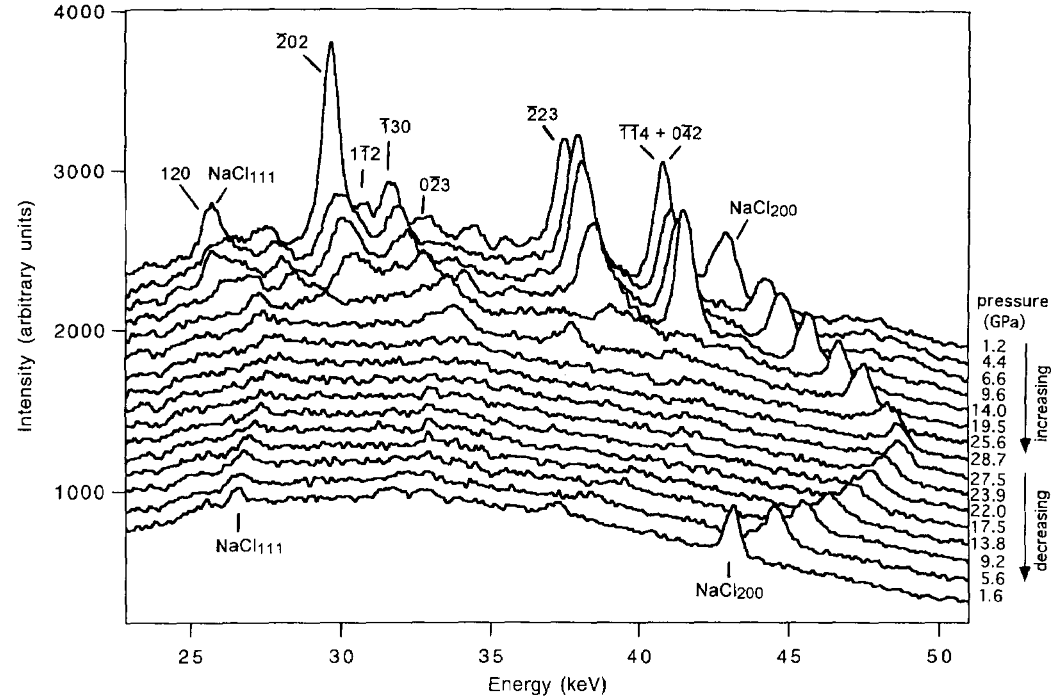

FIG. 1. Amorphization of $CaAl_2Si_2O_8$ anorthite as a function of pressure observed by high-pressure powder diffraction. The low-pressure starting material (top) has been partially indexed and NaCl peaks are indicated. Spectra have been offset vertically for clarity.

individual grains may move a crystallite into or out of the reflecting condition for a specific Bragg peak. The sudden reduction in intensity of the $\bar{2}02$ peak between the first and second spectra can be attributed to such small orientational changes occurring within the sample in the cell. The total loss of intensity across the entire anorthite diffraction pattern cannot, however, be attributed to similar small orientational adjustments. Such a loss of intensity occurs in these diffraction patterns at pressures between 9.6 and 14.0 GPa, with complete loss of coherent scattering indicated between 19.5 and 25.6 GPa. This loss of coherent scattering is interpreted as corresponding to high-pressure amorphization transition, and occurs in a similar pressure range to that observed by Daniel *et al.* (1995*a,b*) during their Raman experiments.

The pressure of amorphization indicated by these high-pressure diffraction experiments is around 14 to 20 GPa, substantially lower than the figure of 25 ± 3 GPa obtained by Williams and Jeanloz (1989) on the basis of their birefringence measurements. The diffraction data presented here are, however, in broad agreement with the results of Daniel *et al.* (1995*a,b*). This raises the question as to whether the birefringence measurements may be providing inherently different information about the structural state, compared with the diffraction experiments. The length scale over which the two processes probe the structure of material differ considerably. Birefringence measurements rely on coherence within the sample on the length scale of the wavelength of light, whereas the coherent X-ray scattering which gives rise to the diffraction signal attributed to non-vitreous material in Fig. 1 indicates correlated translational order within the sample on a length scale of some 500 to 1000 Å. One might at first expect that the breakdown of correlated order on transformation to a high-pressure amorphous phase would become apparent first of all at large length scales and progressively at shorter length scales. It would seem unusual, therefore, to observe the effects of transformation to a glass state first at a length scale of a few hundred Å (by X-ray diffraction) and then (by birefringence measurements) progressively at *higher* pressures on a length scale of a few hundred nm. Comparison of the birefringence data with the X-ray data does, however, suggest just this sequence of loss of correlated order.

Is partially-amorphized anorthite an anti-glass?

There is one other class of materials where the breakdown of correlated crystalline order to form an amorphous phase proceeds first with the loss of X-ray intensity at Bragg reflections and then with the loss of birefringence. This phenomenon was observed in partially metamict zircons as long ago as 1955 (Holland and Gottfried, 1955).

In zircon, the transformation to amorphous state occurs through radiation self-damage resulting from the decay of uranium, thorium and their daughter elements within the zircon lattice. Holland and Gottfried (1955) measured the properties of a suite of gem zircons which had received a range of radiation dosages (defined in terms of the total number of α disintegrations per mg.). They noted the change in intensity of the 112 reflection of crystalline zircon (I_{112}) as a function of metamictization, as well as the change in birefringence, although they made no direct comparison of the two in their paper. Using their data, however, such a comparison can now be drawn, and the normalized values of peak Bragg intensity are shown as a function of α-dosage in Fig. 2 alongside the normalized values of birefringence. Data have been taken from Figs. 3 and 6 of Holland and Gottfried (1955). It becomes clear that measurements of amorphization of zircon by X-ray diffraction and by birefringence studies would yield conflicting values for a critical value of α-dosage. The α-dosage required to reduce I_{112} to one tenth of its initial value is half that required to reduce Δn to the same fraction of its initial value. Comparing these results with those for the amorphization of anorthite at high-pressure a certain similarity emerges. This may provide an explanatory framework to reconcile the apparently conflicting values for critical pressure of amorphization determined from, on the one hand, the X-ray results here and on the other, the birefringence results of Williams and Jeanloz (1989).

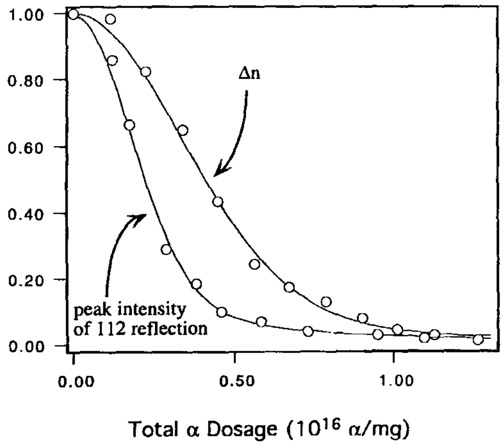

FIG. 2. The behaviour of the normalised peak intensity of the 112 reflection and the normalized birefringence, Δn, of zircon as a function of α-dosage during metamictization (data from Figures 3 and 6 of Holland and Gottfried, 1955). Zircons which appear almost completely amorphous by X-ray diffraction may still show appreciable anisotropy when viewed under crossed polars, and the transformation from crystalline to metamict state is indicated at different α-dosages by the two techniques.

The process of metamictization results in a so-called 'anti-glass' material, where the translational symmetry of the lattice is preserved over long length-scales within a grain, but the translational order is destroyed at more local length-scales. Figure 3 gives a schematic illustration of how this occurs. Damage from U-recoil upon α-decay creates local metamict regions, which after time and a certain α-dosage coalesce, leaving isolated pockets of ordered crystalline material which remain undamaged. These crystalline islands are, however, still in alignment with one another and the long-range periodicity of the original crystal is maintained between these regions. Thus the translational and orientational symmetry is retained between small pockets of material which remain 'in register' with one another despite intervening metamict disorder. This means that these regions can maintain coherence, and this coherence will be apparent when the partially disordered phase is probed by radiation of a suitable wavelength. The criterion is that the interaction length of the radiation must be long enough to span the gaps between the crystalline 'in-register' regions. If the coherence length of the radiation is substantially shorter, however, the material will appear essentially disordered, possibly showing some short-range order, but the longer-range correlation will not be apparent. Such a material, where the long-range correlation is maintained but the lattice order is destroyed at shorter length scales, is termed an *anti-glass*. The interaction length of the radiation is determined both by its wavelength and by the physical process by which it interacts with the solid. The loss of coherent scattering by short-wavelength high-energy X-rays becomes significant when the distance between the remaining crystalline pockets exceeds a certain value, but observations of birefringence, hinging on the interaction between the sample and longer-wavelength visible light, are still sensitive to the remaining correlation in the anti-glass at greater degrees of metamictization, because the interaction length of light is longer and the distance between the remaining crystalline pockets can therefore be greater.

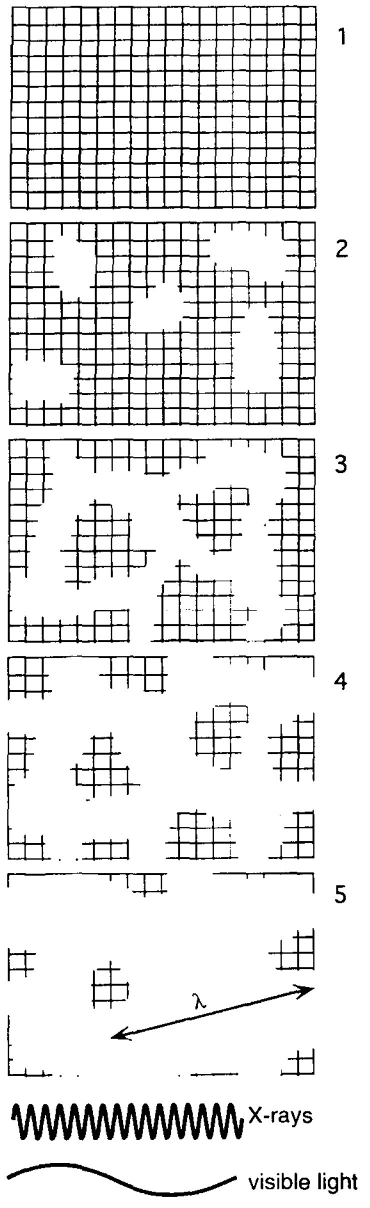

FIG. 3. The process of formation of an anti-glass by metamictization. Initial recoil damage of the pristine crystal (1 and 2) becomes progressively pervasive (3 through 5) and in the final anti-glass state small crystalline regions remain with long-range translational symmetry retained. Interaction with radiation on long length scales (of the order of λ) will reveal this remnant long-range order, but shorter-length scale interaction will give a picture of a more disordered material.

If the process of low-temperature high-pressure amorphization proceeds via a similar anti-glass route, with the production of a two-phase crystalline/amorphous mixture in which the crystalline regions remain 'in register' in partially amorphized material, then the loss of coherent X-ray diffraction would be expected to occur at an earlier stage (and lower pressures) than the loss of birefringence. There is plenty of evidence that low-temperature high-pressure amorphization is a spatially heterogeneous process, both in anorthite and in other tectosilicates. Williams and Jeanloz (1989) noted that their sample developed isotropic bands before becoming fully amorphous. Furthermore, in a transmission electron microscopy study of the amorphization of α-quartz and α-berlinite, Cordier *et al.* (1993) reported the irreversible formation of amorphous lamellae (interpreted as shear lamellae) within a crystalline matrix prior to complete amorphization. Thus, it seems feasible that the lower pressures of amorphization of anorthite determined by X-ray diffraction here (between 14 and 20 GPa), as compared to the value of 25 ± 3 GPa reported by Williams and Jeanloz (1989), may be attributed to this spatial heterogeneity and the possible anti-glass nature of the partially amorphized material. These data provide the first experimental evidence that partially amorphized anorthite may be regarded as an anti-glass. Confirmation of this model for amorphization awaits a detailed microstructural analysis of partially amorphized anorthite. These data do, however, suggest that high-pressure amorphization observed by X-ray diffraction in any material simply indicates the pressure above which the coherence length of crystallinity in the sample becomes less than that of the incident X-rays: different experimental methods will furnish the experimentalist with different amorphization pressures. If this is the case, the exact definition of what is termed a high-pressure 'amorphous' phase demands re-examination, proper interpretation, and a multi-technique approach.

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