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Pressure-induced transformations of β -BaZr₂F₁₀ and its relationship to glassy BaZr₂F₁₀

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Abstract. X-ray and Raman measurements show that β -BaZr₂F₁₀ becomes disordered at pressures greater than 3.7 GPa at ambient temperature. This transformation occurs via a largely displacive mechanism because the disordering is reversible. Comparisons of glassy BaZr₂F₁₀ and the high-pressure states of β -BaZr₂F₁₀ provide structural insight into the medium-range order of ionic glasses. Specifically, we believe that layers of tightly packed pentagonal bipyramidal units are present in the glass.

1. Introduction

The central goal of our work is to use pressure-induced amorphization to determine the atomic structure of non-crystalline materials, especially on the level of medium-range order (MRO). MRO, as defined by Elliott, exists on the length scale of 5–20 Å; qualitatively MRO is any pattern used to connect various local atomic groupings [1]. The determination of MRO is the major unresolved problem in the study of non-crystalline solids [1–3]. MRO at a range of about 5 Å can be studied by Raman and NMR spectroscopies; there are very few experimental techniques that can reveal MRO on the level of the third and fourth neighbours; usually only theoretical work and computer simulations are used to investigate MRO [4–6]. An exception to this is the recent work by Gaskell and co-workers [7]; they used isotopic neutron diffraction to show that a degree of order exists over a distance of 10 Å in a calcium silicate glass. The use of pressure-induced amorphization to probe the MRO of non-crystalline solids essentially asks the question, 'How much must a crystalline solid be rearranged to obtain an amorphous solid?'

The central experimental protocol is as follows.

- (a) Apply, at ambient temperature, pressures up to 10.0 GPa to a crystalline solid.
- (b) Follow the formation of an amorphous state by Raman and x-ray diffraction measurements.
- (c) Release the pressure and observe the return of the crystalline state.

The reversibility of the transformation is essential; it suggests a close relationship between ordering in crystalline and amorphous solids since only small changes are made in the crystalline structure upon compression. This allows us to surmise the

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atomic structure of the amorphous phase formed. The reversibility also shows that we are not simply crushing or shearing the material or creating crystallites too small to diffract.

The phenomenon of reversible pressure-induced amorphization has been observed for several substances: SnI_4 , AlPO_4 (berlinite), LiKSO_4 , $\text{Ca}(\text{OH})_2$, lizardite and $\text{Ca}(\text{NO}_3)_2\text{-NaNO}_3$ [8, 9]. Recently we found that barium fluorozirconate crystals also transform under compression, albeit with residual ordering [10]. We report in this paper the effect of pressure on crystalline $\beta\text{-BaZr}_2\text{F}_{10}$. The high-pressure states of crystalline $\beta\text{-BaZr}_2\text{F}_{10}$ are compared with its glassy analogue prepared by melt quenching at ambient pressure. The comparison leads us to suggest that glassy $\text{BaZr}_2\text{F}_{10}$ contains tightly packed pentagonal bipyramidal units.

The remainder of the paper is organized as follows: first we describe briefly experimental procedures, next we show the effect of pressure on the Raman spectrum and x-ray diffraction pattern of $\beta\text{-BaZr}_2\text{F}_{10}$, then we interpret these changes in terms of repacking of ions into disordered layers, and finally we make a suggestion for the MRO of glassy $\text{BaZr}_2\text{F}_{10}$.

2. Experimental methods

The high-pressure apparatus, Raman measurements and sample preparation have been described in detail in [11]. We summarize the experimental methods employed here. A modified Merrill-Bassett-style diamond anvil cell (DAC) was used to generate high pressures [12]. Inconel gaskets (10/1000 of an inch thickness) were used to contain the samples within the DAC; the gaskets were pre-indented and then a hole, 0.3 mm in diameter, was drilled into the gasket. The samples were powders; the particles were smaller than 100 mesh. The pressure-transmitting medium used was KBr (Fisher, ACS Certified grade). The pressure-transmitting medium of choice for most high-pressure experiments is a mixture of 4:1 methanol:ethanol [13]. We tried to use this mixture but found that it interacted with the sample; it tended to destroy the Raman features immediately upon application. We found that KBr maintained a quasi-hydrostatic environment to the highest pressures reached in our experiments; the ruby fluorescence signal did not broaden significantly as the sample was compressed [14]. All the pressure-induced phenomena were reproducible. The 514.5 nm line of a Spectra-Physics model 2020-5W argon laser was used for the excitation of Raman effects. The scattered light is gathered at 160° to the incident exciting beam by a Spex 1403 double monochromator. Data points were taken every 2 cm^{-1} . Approximately 800 mW of power was incident on the sample for all experiments. The National Bureau of Standards' ruby calibration method was used to monitor the pressure in the DAC [14].

$\beta\text{-BaZr}_2\text{F}_{10}$ was prepared as follows. A mixture of BaF_2 (purity, 99.995%; metal basis from Alfa Products) and ZrF_4 (purity, 99.9%; from Aldrich Chemical Company) was inserted into a tightly lidded platinum crucible at room temperature and heated to 900°C and left there for 15 m. It was cooled in the furnace to 560°C . The mixture was held there for $1\frac{1}{2}$ d and then quenched in liquid nitrogen. The melting-and-quenching procedure was performed in a dry box through which high-purity nitrogen flowed continuously. The samples were characterized in two ways: first in all cases the ambient-pressure Raman spectra of the samples agreed exactly with the spectra in the literature [15]; secondly the x-ray diffraction pattern obtained agreed well with

that reported in the literature [16]. (The instrumentation used is discussed below.) Glassy β -BaZr₂F₁₀ was prepared as follows. A mixture of ZrF₄ and BaF₄ was put in the crucible at room temperature and heated to 900 °C for 20 min. The molten mixture was then quenched between two brass plates. The x-ray pattern for this glass showed clearly that it was x-ray amorphous; the Raman spectrum matches that obtained by Almeida and Mackenzie [15].

Three different instruments were used to measure the x-ray diffraction patterns of the samples.

(1) Ambient-pressure measurements on large amounts of sample (about 1 mg) were done on a standard Rigaku D-Max instrument with a CuK α source. The instrument can detect crystalline regions greater than about 30 Å. The resolution of the instrument at 23° is about 0.3°.

(2) The *in situ* high-pressure x-ray diffraction patterns were measured by energy-dispersive x-ray diffraction (EDXD) at the Cornell High-Energy Synchrotron Source (CHESS) using a Ge solid state detector [17]. The resolution of the instrument is limited by the detector. Typically two peaks must be separated by 0.05–0.5 keV to be resolved, although the resolution can be improved by non-linear least-squares fitting [17]. Baublitz *et al* reported 0.4 keV as typical; this would correspond to about 0.4° at 23°—this value is provided for comparison with the other x-ray instruments used in this work. *Ed* for all measurements was determined, with a piece of gold foil, to be 89.34 keV Å. The same high-pressure cells and experimental protocol were used as for the Raman measurements, except that no pressure-transmitting fluid was used. The pressure was monitored by mixing 10 vol% gold powder (Alpha: purity, 99.95%; grain size, 1–3 μ m) with the sample. The change in the (1,1,1) diffraction line of gold was monitored; the pressure was then calculated using an equation of state [18]. The gold was mixed homogeneously throughout the sample. No broadening of the Au(1,1,1) line was observed as the pressure was increased, thus suggesting that there is very little shear in the sample. The gold also served to show that the diffraction patterns of the samples were truly lost and did not occur because of an error in aligning the cell with the synchrotron beam. The diffraction spectra from the synchrotron were fitted using a non-linear least-squares fitting routine [17].

(3) We used a third instrument to make *ex-situ* measurements on microsamples (about 2 μ g) pressurized in the diamond cell. The pressure-induced transformations were irreversible when pressures greater than 10.0 GPa were applied; since the samples at CHESS were taken above this pressure, a release spectrum of β -BaZr₂F₁₀ was obtained *ex-situ* on a sample pressurized to about 4.5 GPa. An Elliott GX21 CuK α rotating-anode x-ray generator (Enraf-Nonius Service Corporation, Bohemia, NY) was used with a Braun position-sensitive detector (PSD). The angular resolution of this instrument, at 23°, is about 0.2°. The response of the PSD is not completely linear; it has a 'dip' at about 22.4°. This area of the release spectrum has been removed from figure 4. A microsample was enclosed in a capillary tube and placed in the sample chamber. Note that this apparatus has a higher resolution than the *in-situ* EDXD measurements. For example, the diffraction peaks that we have labelled (1,1,1) in figure 3 are actually the (1,-1,1) and (1,1,1) diffraction peaks combined. As can be seen in figure 4, the two peaks can be resolved with the GX21 instrument.

3. Effect of pressure on crystalline β -BaZr₂F₁₀

We have studied the effect of compression on the Raman spectrum and x-ray

diffraction pattern of crystalline β -BaZr₂F₁₀. The Raman measurements have been reported previously; they are included here for completeness [11]. The barium fluorozirconate composition discussed here can be prepared, at ambient pressure, as both a crystalline solid and a melt-quenched glass. The crystal has a low temperature (α) and a high-temperature (β) form; the glass is a precursor to the high-temperature form, since β -BaZr₂F₁₀ crystallizes from the glass at temperatures between 380 and 440 °C, even though β -BaZr₂F₁₀ is *not* thermodynamically stable at this temperature [19]. Also, EXAFS, x-ray and molecular dynamics studies suggest a relationship between the glass and β -BaZr₂F₁₀. The density of the glassy state is greater than that of β -BaZr₂F₁₀—4.5–4.6 g cm⁻³ versus 4.35 g cm⁻³—suggesting that, when compressed, β -BaZr₂F₁₀ may form glassy BaZr₂F₁₀ [20].

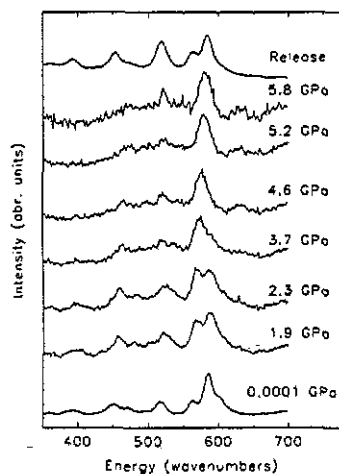


Figure 1. Effect of pressure on the Raman spectrum of β -BaZr₂F₁₀. The scale of the intensity axis is expanded for the high-pressure spectra. The amount of noise in a spectrum is an indicator of its weakness relative to other spectra within a pressure run. If the high- and low-pressure spectra were plotted on the same scales, then the features in the high-pressure spectra would not be visible.

The effect of pressure on the Raman spectrum is shown in figure 1. The general trends are as follows: a loss of intensity and broadening of the spectral features with increasing pressure; the selective retention, for pressures above 2.9 GPa, of a peak initially at about 560 cm⁻¹; the return of the crystalline spectral features and intensity when the pressure is released. The Raman spectrum of the melt-quenched glass (formed at ambient pressure) and the high-pressure state are compared in figure 2. They are very similar, although the major feature of the high-pressure state is narrower. This feature is due to the zirconium-terminal fluorine stretch within the pentagonal bipyramids, which exist in both β -BaZr₂F₁₀ and glassy BaZr₂F₁₀ [21]. The narrower feature in the high-pressure state indicates that the distortions in the pentagonal bipyramids are less severe than in ambient-pressure melt-quenched BaZr₂F₁₀. The precipitous loss of intensity is characteristic of a disordered solid [22,23]. In figure 1 the intensity scale varies from spectrum to spectrum; the scale becomes elongated as the pressure increases. The amount of noise in a spectrum is an indicator of its weakness relative to other spectra within a pressure run. If the high-

and low-pressure spectra were plotted on the same scales, then the features in the high-pressure spectra would not be visible. In summary, the Raman measurements suggest the formation of a disordered phase at a pressure between 2.9 and 3.7 GPa.

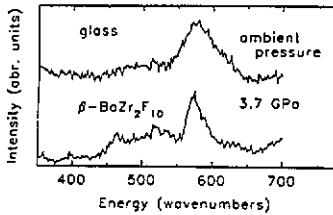


Figure 2. Comparison of Raman spectra of β -BaZr₂F₁₀ at a pressure of 3.7 GPa and glassy BaZr₂F₁₀.

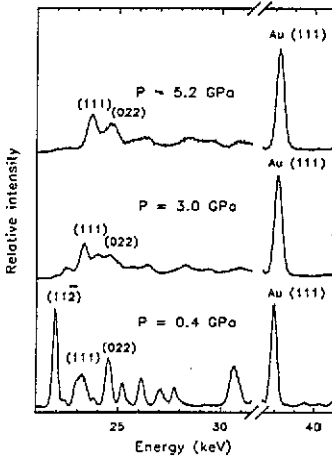


Figure 3. EDXD patterns of β -BaZr₂F₁₀ at various pressures. The gold (111) diffraction peak is scaled to 100 units in each spectrum.

To determine whether the high-pressure state is completely amorphous, we monitored the x-ray diffraction pattern as a function of pressure (figure 3). As the pressure is increased, all the diffraction peaks begin to shift and change in relative intensity (see table 1). For a pressure above 3.0 GPa the x-ray spectrum 'collapses'; at this point the density of the sample, as calculated from lattice parameters, is about 4.6 g cm^{-3} ; this is the same as that of the melt-quenched glass. Above 3.0 GPa the only distinct diffraction peaks left are those associated with the (1,1,1) and (0,2,2) planes; note the complete loss of the (1,1,-2) diffraction peak. Upon release of the pressure the major x-ray diffraction peaks return, although broadened (see figure 4). Note, particularly, the return of the (1,1,-2) plane which vanishes completely above 3.0 GPa. The return of the x-ray and Raman spectra after release shows that the structure of the material is substantially the same as that in the initial state. As noted above, the agreement between the initial and the release Raman spectra was excellent.

Table 1. Change in the lattice parameters of β -BaZr₂F₁₀ with pressure.

Pressure (GPa)	d spacing (Å)				Lattice parameters (Å)			β (deg)	Density (g cm ⁻³)
	(1,-1,-2)	(1,1,1)	(0,2,-2)	(0,4,1)	a	b	c		
0.3	4.07	3.89	3.64	3.41	6.2	14.9	9.0	113	4.4
0.5	4.06	3.89	3.63	3.41	6.2	15.0	9.0	113	4.4
1.4	4.02	3.87	3.62	3.40	6.1	15.0	9.0	112	4.4
3.0	3.98	3.83	3.64	3.38	5.9	14.8	9.0	111	4.6

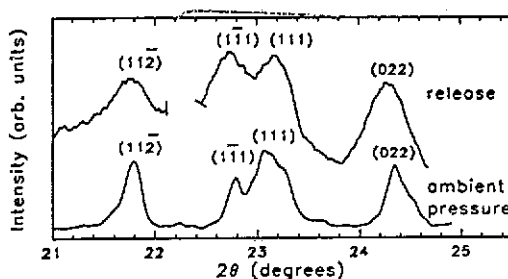


Figure 4. Comparison of x-ray diffraction patterns of β -BaZr₂F₁₀ before pressurization and after pressurization to about 4.5 GPa. Note that the spectra were taken on different instruments. (See section 2 for a discussion).

The x-ray diffraction pattern does not change significantly at pressures above 5.2 GPa. The pattern observed at the highest pressure reached, 19 GPa, is very similar to that at 5.2 GPa. Above about 10.0 GPa the transformation is irreversible. We have no explanation for this irreversibility above a threshold pressure. This effect may be related to shear; it is well known that shear-induced amorphizations are irreversible [1].

The x-ray spectra show that with compression a completely amorphous phase is not attained, but rather a disordered state arises. Kruger and Jeanloz [8] have suggested that pressure-induced amorphizations occur due to an impeded phase transition. Adams *et al* [24] have suggested that a pressure-induced disordered phase results because a high-pressure crystalline phase is kinetically inaccessible at room temperature. The diffraction pattern that we observe at high pressures is similar to that observed by Adams *et al* [24] for the pressure-induced disordered state of ammonium metavanadate. It is likely that an impeded phase transition explains why β -BaZr₂F₁₀ is becoming disordered, although the large loss of Raman intensity and the lack of any new features in the x-ray and Raman scattering give no hint as to what crystal-crystal transformation is being impeded. Note that this transformation is not caused by crushing or shearing the sample since first it is observed by two techniques, namely Raman and x-ray, which probe different length scales (about 10 Å and about 1000 Å, respectively), secondly the pressure indicators show a quasi-hydrostatic environment when the transformation takes place and thirdly the transformation is reversible. To understand the residual ordering, we must examine the crystalline structure of β -BaZr₂F₁₀.

4. Interpretation of changes

The crystalline structure of $\beta\text{-BaZr}_2\text{F}_{10}$ consists of layers of barium separated by layers of zirconium atoms [20]. Each zirconium atom is coordinated by seven fluorine atoms arranged in the shape of a pentagonal bipyramid. These zirconium layers are composed of two interpenetrating chains running along quasi-orthogonal directions. One chain is composed of bipyramids sharing corners along the $[-1,0,1]$ direction; the other chain consists of bipyramids sharing corners and edges along the $[2,0,1]$ direction (see figure 5). The barium atoms sit in 'holes' where the polyhedral units share corners.

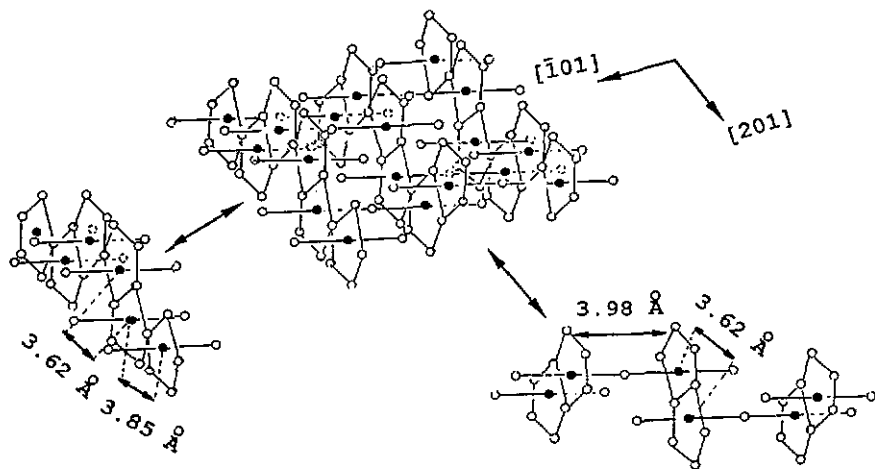


Figure 5. Crystalline structure of $\beta\text{-BaZr}_2\text{F}_{10}$. This figure shows a zigzag layer of zirconium polyhedra; the black atoms are zirconium, and the white atoms are fluorine. (This figure is adapted from [20]).

The $(1,1,1)$ diffraction plane is orthogonal to the $[-1,0,1]$ direction; the plane reflects order in the corner-and-edge-sharing chain. The $(1,1,-2)$ plane is associated with the corner-sharing chain since the plane is orthogonal to the $[2,0,1]$ direction. The other diffraction planes cut across the layers at various angles, none orthogonal to either the $[-1,0,1]$ or the $[2,0,1]$ direction.

The x-ray diffraction data show that by 3.0 GPa the layer is compressed by about 0.2 Å in the $[2,0,1]$ direction and by about 0.3 Å in the $[-1,0,1]$ direction. This means that the layer is becoming more dense by compression along the chains. Also, the x-ray spectrum and knowledge of the crystalline structure of $\beta\text{-BaZr}_2\text{F}_{10}$ suggest that there is disorder along the layer in the $[-1,0,1]$ direction and some residual ordering along the corner-and-edge-sharing chain. The 'rigid' edge between the zirconium units is retained while losing order in the $[-1,0,1]$ direction. This is not unexpected since the edge is rigid as compared with the solely corner-sharing chain. Since the transformation is reversible, it must be largely displacive and involve only small changes in the atomic positions, distances and coordination numbers. We suggest that the compression will occur from a repacking of the zirconium polyhedral units about the barium atoms. This is a form of the 'polyhedral tilt' mechanism of Hazen and Finger [25].

Why does β -BaZr₂F₁₀ exhibit residual ordering when compressed rather than become completely amorphous? As described above, β -BaZr₂F₁₀ contains zirconium fluoride layers separated by large barium atoms. The mechanism operating to repack the layer cannot propagate through the solid because it lacks a three-dimensional connectivity. Crystalline β -BaZr₂F₁₀ becomes disordered, rather than completely x-ray amorphous, because it contains layers well separated by barium atoms, which have an irregular coordination of 11 fluorine atoms.

5. Suggestions for the atomic structure of glassy BaZr₂F₁₀

We have noted above the similarities between the densities and the Raman spectra of glassy BaZr₂F₁₀ and the pressure-induced state of β -BaZr₂F₁₀. These similarities and the notion of connectivity discussed above suggest a model for the MRO of glassy BaZr₂F₁₀.

Specifically, the observations suggest that the MRO of the glass is very similar to that of the high-pressure state of β -BaZr₂F₁₀ with the exception that the tightly packed pentagonal bipyramidal layers in the glass are somewhat 'defective'. They are either not continuous or are topologically flat rather than geometrically flat, i.e. they are creased or wrinkled. Also, the sheets of zirconium polyhedra could have some tears in them. We do not know how large or extensive these layers would be in the melt-quenched glass. It is easy to see how these defects arise when the glass emerges from the melt; as the melt is cooling, crystalline β -BaZr₂F₁₀ is being formed, but the melt is quenched before the zirconium polyhedral layers have a chance to form and connect fully, resulting in a 'defective' layer. We are *not* suggesting that the melt-quenched glass contains perfect pentagonal bipyramids, but rather that it is the layer structure on which the glass structure is based. There could well be a distribution of bond angles and distances.

The MRO proposed above is consistent with the analysis by Le Bail *et al* [26] of their neutron and x-ray diffraction data on glassy BaZr₂F₁₀. Using 'quasi-crystalline' modelling they found that strained β -BaZr₂F₁₀ provided a reasonable description of the glassy structure, although the glass must have some deviations from the mean local organization of the crystal.

Our suggestion is consistent with the annealing studies of glassy BaZr₂F₁₀. It is also consistent with EXAFS and x-ray studies which show the coordination number of zirconium to be 7–7.5 and the coordination number of the barium atoms to be 10–11 in the melt-quenched glass [27–31]. Molecular dynamics and other computer simulations suggest a zirconium coordination number of 7–8 [28, 32–34]. Computer calculations also yield information about the proportions of corner and edge sharing between the zirconium fluoride polyhedra, although the calculations do not agree on this ratio [28, 30, 32–34]. Also, the high-pressure transformation observed here confirms the suggestion of Laval *et al* [20] that the zirconium fluoride units of crystalline β -BaZr₂F₁₀ are retained in the melt-quenched glass.

Several workers [33, 34] have pointed out that fluoride glasses are highly ionic and can be described by potentials lacking any directional character. This implies that the structure of ionic glasses is determined by the tendency to maximize the coordination number [34]. The high-pressure results presented here suggest that packing and charge-balancing considerations are the dominant criteria for determining the structure of ionic glasses just as they are in ionic crystals [35]. The key difference

is that in the non-crystalline case the packing lowers the energy locally, while for the crystalline case the packing increases the energy locally but lowers it globally by the formation of a periodic lattice.

6. Conclusions

We have demonstrated with high-pressure Raman and x-ray data that crystalline β -BaZr₂F₁₀ transforms reversibly under compression to a disordered state. Comparison of glassy BaZr₂F₁₀ and β -BaZr₂F₁₀ provides important structural insight into the MRO of ionic glasses. Specifically we believe that layers of tightly packed pentagonal bipyramidal units are present in the glass.

More generally, the results suggest the following.

(i) Local packing and charge-balancing considerations are important in determining the structure of an ionic glass.

(ii) Amorphous solids can have extensive MRO existing with long-range randomness.

(iii) Models based on 'defective' order are appropriate for ionic glasses.

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