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LETTER TO THE EDITOR

## Pressure-induced amorphization in gadolinium scandium gallium garnet by x-ray diffraction and spectroscopic studies

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**Abstract.** We report the first example of amorphization of garnets at high pressure and ambient temperature. Synchrotron x-ray diffraction and fluorescence spectroscopy at high pressure were performed on polycrystalline gadolinium scandium gallium garnet (GSGG) doped with  $\text{Nd}^{3+}$  and  $\text{Cr}^{3+}$ . X-ray diffraction measurements reveal a loss of long-range order beginning at  $58 \pm 3$  GPa. This is followed by a change in local environment for dopants at 70 GPa as indicated by the loss of fluorescence emission. The amorphous phase is retained at ambient conditions, after decompression. We present possible mechanisms for these two distinct transformations in GSGG.

The crystalline-to-amorphous ( $c \rightarrow a$ ) transformation in the solid state has been the focus of intense study in the past ten years. In 1984, Mishima *et al* [1] discovered the amorphization of  $\text{H}_2\text{O}$  ice I at 1 GPa and 77 K. Since then, this  $c \rightarrow a$  transition has been documented in more and more materials [2, 3] using x-ray diffraction and spectroscopic methods, but, to our knowledge, at ambient temperature, no pressure-induced amorphization in garnets has been reported yet.

The garnet structure was first established for a large family of naturally occurring silicates with the formula  $\text{A}_3\text{B}_2(\text{SiO}_4)_3$  in the earth's interior. Subsequent discovery of the synthetic ferrimagnetic garnets has generated a considerable interest in the crystal chemistry of the garnets. Some of the doped oxide garnets have been used as solid-state laser materials [4]. Recently, with the introduction of high-pressure, high-temperature techniques, it has become possible to investigate the transformations in garnets at the condition of the earth's interior. In high-pressure experiments, some doped oxide garnet materials have been studied for the dopants' electronic levels and also in applications as optical pressure sensors [5, 6], but, in all these high-pressure investigations, efforts were focused on the dopants, where garnet only serves as a host lattice to impose on dopants the crystal field, which is continuously tuned by pressure [4, 7]. In this letter, we for the first time report the amorphization of the gadolinium scandium gallium garnet (GSGG) crystal, which will broaden our knowledge of the crystal chemistry and thermodynamic stability of the garnet structure, which also will provide us with some clue to the understanding of the transformations in the earth's interior.

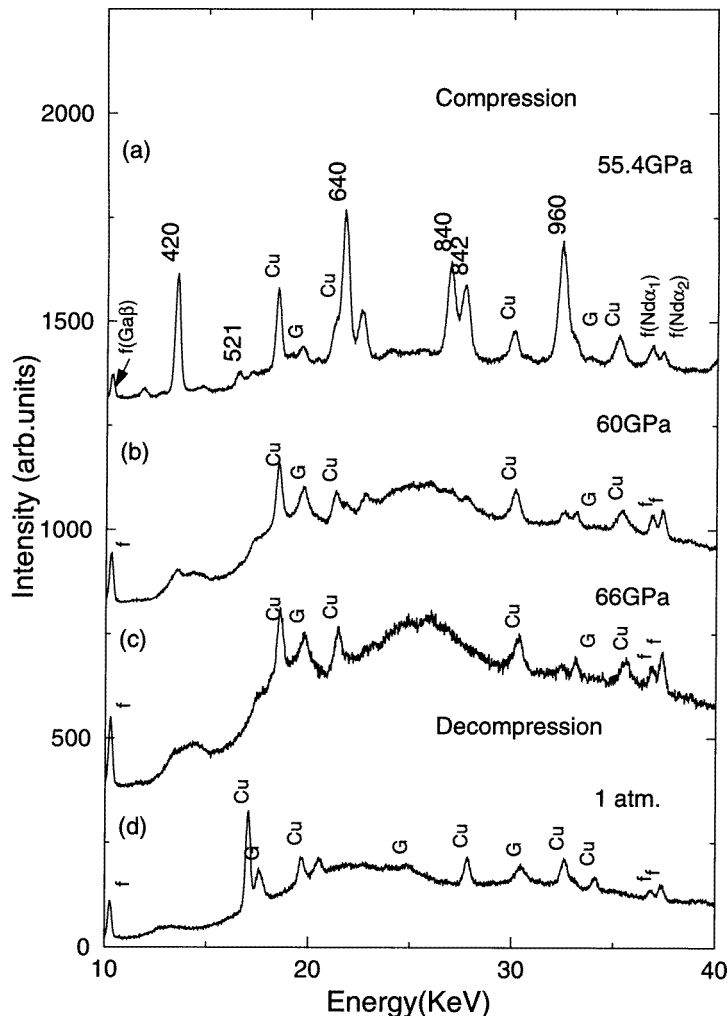
At ambient conditions, garnet crystals belong to the cubic space group  $Ia\bar{3}d-O_h^{10}$ . GSGG is one of the oxide garnets of formula  $\text{A}_3\text{B}_2\text{C}_3\text{O}_{12}$ , where A denotes the dodecahedral, B the octahedral, and C the tetrahedral sites with point group symmetries  $22_2$ ,  $\bar{3}$  and  $\bar{4}$ , respectively [4, 6]. Oxide garnets can achieve systematic changes in the crystal field strength

by variation of the unit cell size. Generally, this is obtained in a systematic way through the chemical composition. Along the series YAG ( $\text{Y}_3\text{Al}_5\text{O}_{12}$ ), YGG ( $\text{Y}_3\text{Ga}_5\text{O}_{12}$ ), GGG ( $\text{Gd}_3\text{Ga}_5\text{O}_{12}$ ), GSAG ( $\text{Gd}_3\text{Sc}_2\text{Al}_3\text{O}_{12}$ ), GSSG ( $\text{Gd}_3\text{Sc}_2\text{Ga}_3\text{O}_{12}$ ), LLGG ( $\text{La}_3\text{Lu}_2\text{Ga}_3\text{O}_{12}$ ) the unit cell size increases and the strength of the crystal field decreases progressively [4]. Among them, GSSG gives an intermediate field strength on doped ions. In doped GSSG,  $\text{Cr}^{3+}$  ions have a strong preference for the  $\text{Sc}^{3+}$  sites, while  $\text{Nd}^{3+}$  substitute mainly for the  $\text{Gd}^{3+}$  site [4, 6].

In the present experiments, GSSG single crystals containing approximately 0.6 at.wt% for  $\text{Nd}^{3+}$  and 1.0 at.wt% for  $\text{Cr}^{3+}$  were ground to a grain size of less than  $5\ \mu\text{m}$ , and placed into a gasketed diamond anvil cell (DAC) with diamonds of  $300\ \mu\text{m}$  culet. A 4:1 methanol–ethanol mixture served as pressure medium that provided the hydrostatic pressures below 15 GPa. Both x-ray diffraction and fluorescence experiments have been performed on this material. The energy dispersive x-ray diffraction spectra were taken at X-17 C beam line, National Synchrotron Light Source (NSLS), Brookhaven National Laboratory, using copper as an internal pressure standard [8, 9]. Fluorescence spectra were obtained by using a micro-Raman and fluorescence spectrometer as described in [10]. The 514.5 nm wavelength of an argon ion laser was utilized to excite the fluorescence spectra. Ruby was used as internal pressure standard in fluorescence studies at high pressure [11].

Several typical patterns taken in x-ray diffraction experiment are shown in figure 1. We found that up to  $P = 55.4\ \text{GPa}$ , the diffraction pattern from the GSSG sample consists of sharp diffraction peaks that could be readily indexed as cubic phase. The lattice parameter of the cubic phase changes from  $12.53\ \text{\AA}$  at 1 atm to  $11.84\ \text{\AA}$  at 55.4 GPa (figure 1(a)). However, the diffraction peaks of the cubic phase disappear abruptly as pressure approaches 60 GPa (figure 1(b)), leaving only several very broad and weak peaks in the energy region corresponding to those sharp peaks. The loss of sharp diffraction peaks indicates that long-range order is lacking while the broad peaks indicate that some short-range order exists. Thus this material starts to transform to the amorphous state at a pressure of  $58 \pm 3\ \text{GPa}$ . At 66 GPa, the highest pressure for this experiment, long-range order in crystalline garnet is almost completely destroyed (figure 1(c)). Additionally, after total decompression from the highest pressure of 66 GPa, no recurrence of sharp peaks indicative of the sample's crystalline state was observed at ambient conditions (figure 1(d)).

In GSSG, the  ${}^4\text{F}_{3/2} \rightarrow {}^4\text{I}_{9/2}$  transition at the  $\text{Nd}^{3+}$  dopant site gives rise to a dominant emission in the wavelength range of 850–900 nm ( $11\,000\text{--}11\,800\ \text{cm}^{-1}$  in wavenumber). We employed high resolution ( $1200\ \text{grooves mm}^{-1}$  grating) to study this region. At ambient pressure, our fluorescence spectrum (figure 2) features the splitting of Stark levels of the ground state  ${}^4\text{I}_{9/2}$  as well as the excited state  ${}^4\text{F}_{3/2}$  as follows:  $103\ \text{cm}^{-1}$  ( $Z_2$ ),  $166\ \text{cm}^{-1}$  ( $Z_3$ ), and  $255\ \text{cm}^{-1}$  ( $Z_4$ ) for the splitting of  ${}^4\text{I}_{9/2}$ , and  $11\,429\ \text{cm}^{-1}$  ( $R_1$ ) and  $11\,488\ \text{cm}^{-1}$  ( $R_2$ ) for the splitting of  ${}^4\text{F}_{3/2}$ . These values are very close to those obtained by earlier investigations for  $\text{Nd}^{3+}:\text{GSSG}$  [4]. Figure 3 shows the typical spectra taken upon compression, which demonstrate the dramatic position, intensity and width changes with pressure of the first four peaks defined in figure 2. We noticed a very dramatic and abrupt loss of fluorescence signal at a pressure of 70 GPa (figure 3) and attribute this to another transformation in the amorphous phase. This change in the fluorescence spectra is irreversible on decompression. It is necessary to mention here that for dopant  $\text{Cr}^{3+}$  in GSSG, the narrow  ${}^2\text{E} \rightarrow {}^4\text{A}_2$  emission band which emerges at high pressure in the region of 650–750 nm also suddenly disappears at 70 GPa upon compression, which also provides supporting evidence of this transformation. In this fluorescence experiment, we cannot determine the onset of amorphization because the host lattice GSSG unit cell where  $\text{Nd}^{3+}$  lies is large (about  $12.53\ \text{\AA}$  in lattice constant at ambient conditions), thus the loss of some

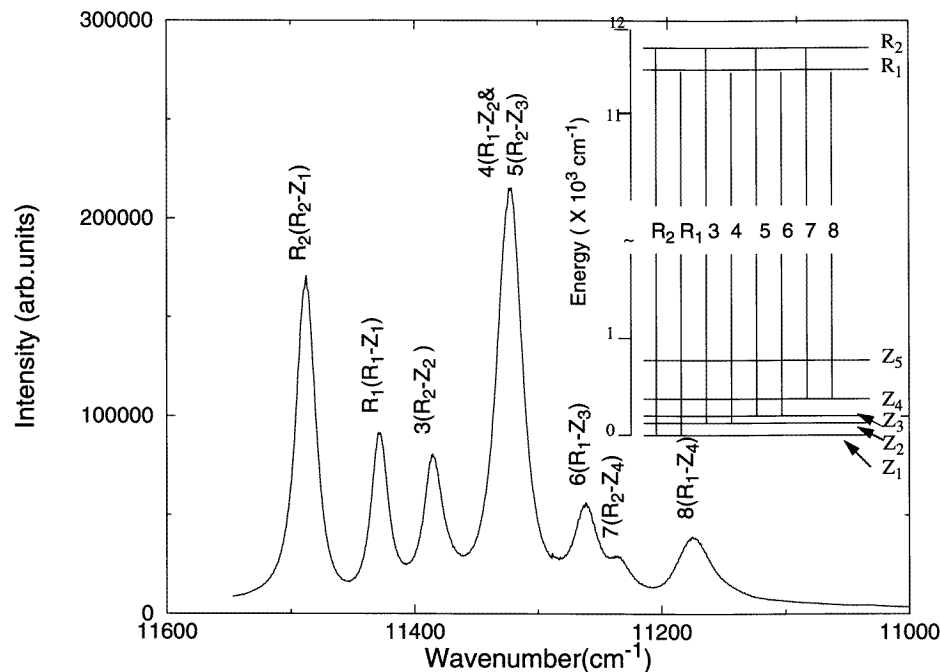


**Figure 1.** Energy dispersive x-ray diffraction spectra obtained at beam line X-17C of the GSGG sample mixed with copper pressure standard.  $E_d = 35.56 \text{ keV } \text{\AA}$ . (a) Crystalline cubic phase at 55.4 GPa; (b) amorphous at 60 GPa; (c) completely amorphous state at 66 GPa and (d) amorphous at ambient pressure after decompression. Cu, G, and f represent copper, gasket, and fluorescence peaks respectively.

long-range order at the beginning does not have much influence on the optical spectra.

The first two peaks shown in the spectra in figure 3, which are labelled as  $R_2$  and  $R_1$ , are due to transitions  $R_2 \rightarrow Z_1$  and  $R_1 \rightarrow Z_1$ , respectively. From these two peaks, we can find the effect of pressure on the energies of the  $^4F_{3/2}$  levels, which is presented in figure 4. With increasing pressure, the separation between the two levels of the  $^4F_{3/2}$  state decreases at first, and approaches a minimum separation of about  $32.2 \text{ cm}^{-1}$  at 12.6 GPa. After that, the splitting increases up to about  $125 \text{ cm}^{-1}$  at 69.4 GPa. Above 70 GPa, the  $R_1$  and  $R_2$  peaks disappear altogether.

We also carried out an additional experiment on GSGG to monitor the optical

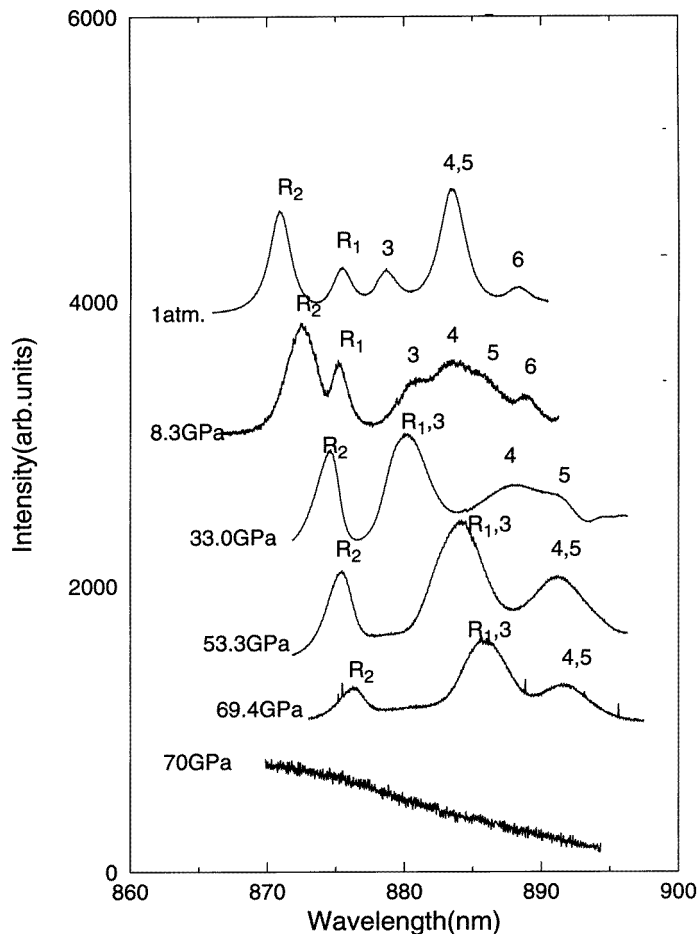


**Figure 2.** The fluorescence spectra of  $\text{Nd}^{3+}$  recorded at ambient conditions showing the transitions  ${}^4\text{F}_{3/2} \rightarrow {}^4\text{I}_{9/2}$ , from Stark levels  $Z_2$  ( $103 \text{ cm}^{-1}$ ),  $Z_3$  ( $166 \text{ cm}^{-1}$ ), and  $Z_4$  ( $255 \text{ cm}^{-1}$ ) of the ground state  ${}^4\text{I}_{9/2}$ , to  $R_1$  ( $11429 \text{ cm}^{-1}$ ) and  $R_2$  ( $11488 \text{ cm}^{-1}$ ) of the excited states  ${}^4\text{F}_{3/2}$ . The spectrum is excited by the 514.5 nm line of an argon laser.

transparency of the sample between 1 atm and 70 GPa. Figure 5 shows an optical micrograph of the GSGG sample at 70 GPa taken with transmitted light to demonstrate the optical transparency of the sample. We did not document any visible change in the sample absorbance at transformation pressures of 58 and 70 GPa. Thus the sudden change of fluorescence spectra (figure 3) can only be due to a change of site symmetry or coordination of the  $\text{Nd}^{3+}$  in GSGG.

In this material, we can also obtain from the fluorescence spectra additional information about the energy level of the dopants, which can indicate changes in the symmetry and strength of the crystal field at the dopants' sites [12]. We generally assume that, in the garnet lattice,  $\text{Nd}^{3+}$  is located in the  $D_2$  site symmetry (which belongs to orthorhombic symmetry) [4, 6]. For the  ${}^4\text{F}_{3/2}$  state of  $\text{Nd}^{3+}$ , cubic symmetry gives no splitting, while symmetry lower than cubic will give the splitting into levels  $R_1$  and  $R_2$ . As shown in figure 4, the decrease in the splitting in the pressure range 0–12.6 GPa implies that there is a tendency toward a cubic site symmetry in that range for  $\text{Nd}^{3+}$ . This change in site symmetry can be either due to the movement of  $\text{Nd}^{3+}$  ions in the garnet lattice or due to the internal coordination's change of the garnet lattice itself. The increasing in the splitting of the levels  $R_1$  and  $R_2$  after 13 GPa indicates that the site symmetry is lowered, progressively until the irreversible change is encountered at 70 GPa.

Various models have been proposed to understand the thermodynamics and driving mechanism of the crystalline-to-amorphous transition. Sikka [3] gave a review of these models and suggests that this  $c \rightarrow a$  transition is a consequence of a competition between the

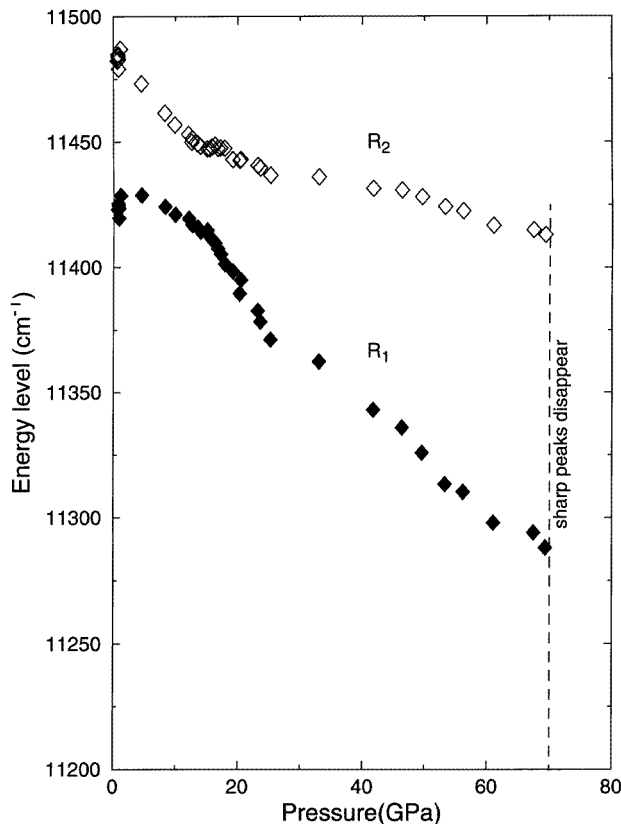


**Figure 3.**  $\text{Nd}^{3+} \ ^4\text{F}_{3/2} \rightarrow \ ^4\text{I}_{9/2}$  fluorescence spectra of  $\text{Nd}^{3+}$ ,  $\text{Cr}^{3+}$ :GSGG at various pressures upon compression. The labels ( $R_2$ ,  $R_1$ , 3, 4, 5, 6) are defined in figure 2. The fluorescence emission signal completely disappears at 70 GPa. These spectra are excited by the 514.5 nm line of an argon laser and pressures are based on the ruby fluorescence technique.

close packing and long-range order. Also he found that for the substances which can vitrify under pressure there exists a three-level free energy diagram, with kinetic barriers, for the induced  $c \rightarrow a$  transitions (figure 1 in [3]). In this three-level energy diagram, the lowest free energy state is the crystalline phase which the system will go to if there is no intervention of metastable phases. It is not clear at the present time what the stable crystalline state is for garnets under high pressure. It could be a single phase or a mixture of two phases which could result from the breakup of  $\text{A}_3\text{B}_2\text{C}_3\text{O}_{12}$  into several components [13]. As indicated by Marezio *et al* [13], some synthetic garnets, such as  $\text{Y}_3\text{Fe}_5\text{O}_{12}$  and  $\text{Y}_3\text{Al}_5\text{O}_{12}$ , undergo decomposition at moderately high pressure and high temperature. Along these lines, we propose the following decomposition path of GSGG leading to a phase mixture:



where the  $\text{GdGaO}_3$  is of perovskite-like structure and  $\text{Sc}_2\text{O}_3$  of corundum structure. Marezio

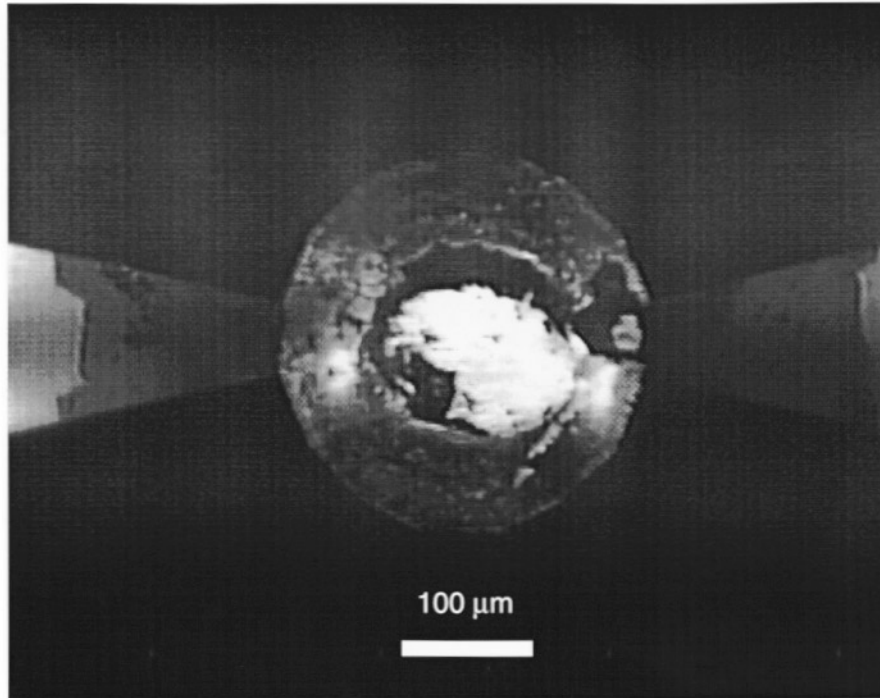


**Figure 4.** The effects of pressure on the  ${}^4F_{3/2}$  energy levels ( $R_1$  and  $R_2$ ) of  $Nd^{3+}$  in  $Nd^{3+}, Cr^{3+}$ :GSGG. Energies are given with respect to the lowest level ( $Z_1$ ) of the ground state  ${}^4I_{9/2}$ .

*et al* [13] also found that the breakdown reaction is endothermic, which is consistent with the notion of a kinetic barrier in the free energy diagram of garnet materials. Our experiments suggest that a metastable amorphous phase forms at  $58 \pm 3$  GPa with further modification of the dopants' site at 70 GPa.

In summary, we present the first example of the amorphization of crystalline garnet GSGG:Nd,Cr under high pressure at ambient temperature. Both x-ray diffraction and fluorescence techniques are used to demonstrate that the loss of long-range order (amorphization) occurs at  $58 \pm 3$  GPa followed by modification of the local environment of dopants at 70 GPa. The  $c \rightarrow a$  transition is explained using the three-level free energy diagram. Further *in situ* high-pressure–high-temperature experiments and transmission electron microscopy (TEM) of the sample are needed to probe the stable crystalline phases in this class of materials and to establish the length scale in the amorphous phase.

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**Figure 5.** A photomicrograph of the GSGG sample in a diamond anvil cell at 70 GPa in the amorphous phase. The sample is viewed in transmitted light and there is no visible change in the appearance of the sample between 10 and 70 GPa.

at the NSLS, Brookhaven National Laboratory, which is supported by the US Department of Energy, Division of Materials Sciences and Division of Chemical Sciences (DOE contract number DE-AC01-76CH00016).

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