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In situ Raman spectroscopy of pressure-induced changes in LaBGeO₅ glass: hysteresis and plastic deformation

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Abstract

In situ micro-Raman spectroscopy was performed on lanthanum borogermanate (LBG) glasses, compressed in a diamond anvil cell at ambient temperature. Up to 5.6 GPa the structural changes are reversible, whereas experiments performed at 10 GPa and higher are characterized by hysteresis loops. A noticeable change of evolution of the main Raman band at 800 cm⁻¹ has been evidenced around 8 GPa. Indeed, at such a pressure, this Raman band is shifted in the opposite direction while the pressure is still increasing. This change of slopes may be the sign of a pressure-induced coordination number change. Upon decompression the Raman shift of this band follows a different path from the one during compression. When the sample is returned to ambient pressure, it shows a shifted and lightly modified Raman spectrum, suggesting that a new amorphous phase for LBG glass is reached under high pressure and still exists at atmospheric pressure. However, a comparison with LaBGeO₅ crystals with the same composition shows that this material has a full elastic behaviour in the same pressure range.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Over the last decades, numerous experiments have been performed in diamond anvil cells to study the behaviour of tetrahedral glasses and liquids under the influence of pressure. SiO₂ [1] and GeO₂ glasses [2, 3], extensively investigated, prove to be a model for pressure-induced transformation in such glasses, even if the structural changes occurring during densification

are not yet fully understood, especially because short-, medium- and long-range orders are implied in these amorphous materials. However, some of these experiments strongly suggest that transformations from one structure to another take place under pressure. Vitreous silica, like other glass-forming systems such as ice [4], aluminate [5], germania [6] and boron [7] oxides, has shown different amorphous structures under pressure. In most cases, the materials recover their original structure at ambient pressure, but in some cases the high-density amorphous (HDA) phase still exists at ambient conditions. This phenomenon, which is called ‘polyamorphism’, was evidenced for the first time by Mishima, who discovered a new high-pressure phase of amorphous ice. Grimsditch *et al* [8] analysed the microscopic changes occurring in vitreous B_2O_3 during pressure-induced densification. They observed changes in ring statistics. By measuring the velocity of sound, Nicholas *et al* [7] showed evidence that vitreous polymorphs exist in this material and that the transition may be abrupt. The polyamorphism of glasses originates from a plastic deformation, which corresponds to a non-reversible deformation: a permanent change of the shape of the material occurs when the pressure is released.

Our work is focused on oxide lanthanum borogermanate (LBG) glass, which presents interesting properties thanks to bulk and surface precipitation of ferroelectric $LaBGeO_5$ crystals, including nanocrystallization and grain-oriented crystallization, allowing synthesis of ferroelectric and pyroelectric glass-ceramics [9]. Nonlinear optical and photo-induced properties of LBG glasses may be initiated by nanostructuring, thermal or ultraviolet (UV) poling [10, 11]. The ternary oxide glass, called LBG, has a completely unknown behaviour under pressure, and here we present the first *in situ* experiments with it in a diamond anvil cell. The glass under investigation has a molar composition $La_2O_3-B_2O_3-2GeO_2$, which corresponds to the $LaBGeO_5$ crystal stoichiometry. This crystal has a stillwellite-like structure [12], and it is composed of chain-framed structural units. The chains are helical and are made of BO_4 tetrahedra connected by shared O atoms. Each of the two neighbouring BO_4 tetrahedra are connected with a GeO_4 tetrahedron via other bridging O atoms to form rings composed of three tetrahedra. The helical chains are linked together by lanthanum atoms located in between. LBG glasses have a short- and medium-range structure close to the corresponding crystal $LaBGeO_5$ in which all boron atoms have coordination number equal to four. Although there exist some boron atoms which are three-fold coordinated [13, 20], LBG glass is considered as a predominantly tetrahedron-coordinated network glass, where BO_4 and GeO_4 tetrahedra are bonded to each other.

2. Samples and experimental methods

LBG glasses have the nominal composition 25% La_2O_3 , 25% B_2O_3 and 50% GeO_2 . They were prepared in platinum crucibles by heating at 1300–1320 °C for 40 min by a conventional melting technique, mixing appropriate amounts of reagent-grade powders of La_2O_3 , H_3BO_3 and GeO_2 [14]. The glasses obtained were transparent and free of crystalline inclusions. A small sample of LBG glass was cracked in a pestle and one obtained ‘grain’ was meticulously introduced by means of a needle into the 200 μm hole of the gasket of a diamond anvil cell (DAC). The pressure was estimated by the shift of ruby fluorescence lines. Methanol was used as the pressure-transmitting medium instead of methanol + ethanol because the Raman bands at 430 and 880 cm^{-1} from ethanol interfere with the LBG glass spectra. The use of methanol as transmitting fluid ensures hydrostaticity up to 8.6 GPa [15]. Our previous experiments on the width of the ruby fluorescence line showed us that differences from hydrostaticity of methanol are small up to 18 GPa. Experiments were then performed up to 18 GPa with the hypothesis that quasi-hydrostaticity was still provided by methanol.

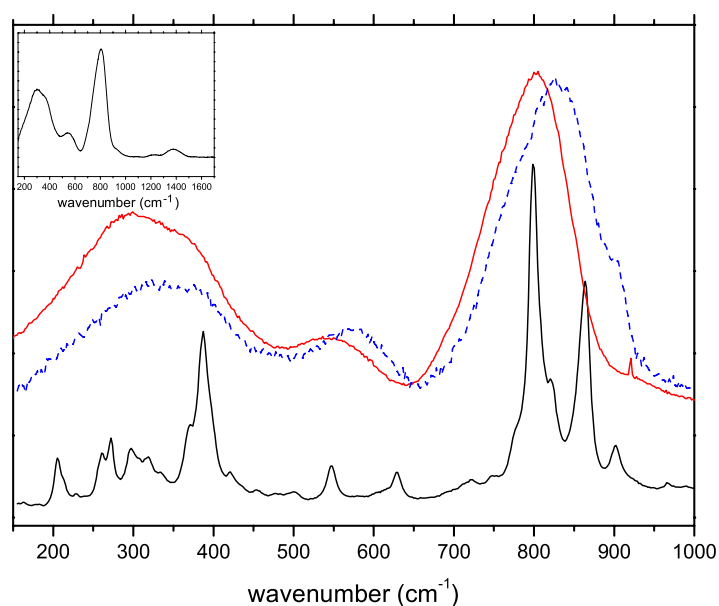


Figure 1. Raman spectra of stillwellite-like crystal LaBGeO_5 (below) and of LBG glasses recorded at ambient pressure and 5.6 GPa (dashed line). In the top left corner is reported the spectra of LBG glass at ambient conditions recorded from 150 to 1700 cm^{-1} and showing high-frequency bands resulting from BO_3 unit vibrations.

In situ micro-Raman spectra were measured in the DAC using the 514.5 nm line of an Ar-ion laser delivering a 50 mW signal. Spectra were recorded using an RM 1000 Renishaw monochromator in a backscattering configuration via a microscope equipped with a $50\times$ objective. The detection of the signal was carried out by a cooled CCD camera.

Raman spectra of LBG glass were measured in the range 150–1000 cm^{-1} . The pressure was recorded before and after each Raman LBG spectrum, to be sure that the pressure did not evolve during the measurement. Several runs were carried out in order to observe reversible and irreversible behaviours. In the first run, the sample was pressurized to 5.6 GPa, then it returned to near atmospheric pressure, and finally it was reloaded to 4.6 GPa before returning to atmospheric pressure again. In the second run, another sample was pressurized to 10 GPa and then returned to atmospheric pressure. In the last run, the sample was loaded at a pressure of 18.9 GPa and then returned to atmospheric pressure. An experiment was devoted to compressing the corresponding crystal LaBGeO_5 up to 18.3 GPa.

3. Results

The Raman scattering spectra of LBG glasses presented in figure 1 have three major peaks, located around 320, 550 and 800 cm^{-1} at atmospheric pressure. The last band is narrow and the most intense, and it is sensitive to the increase of pressure. Therefore it appears to be of great interest and ensures precision for our experiments. The position of this band is given by its wavenumber at maximum Raman intensity. On figure 1, the Raman spectrum of the corresponding crystal of the stillwellite-like structure is also presented. The glass indeed has a structure close to that of this crystal.

A first set of Raman measurements was performed up to 5.6 GPa. Raman spectra at limit pressures (atmospheric pressure and 5.6 GPa) are shown in figure 1. After the decompression,

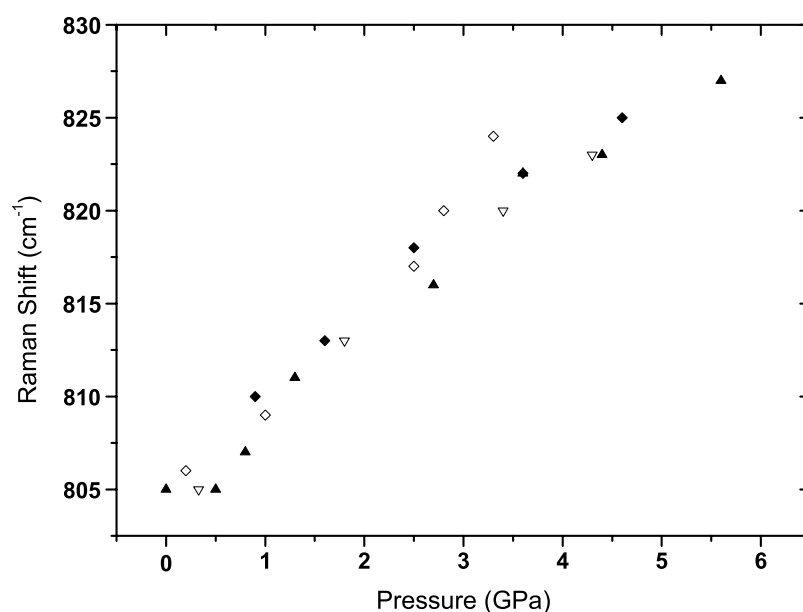


Figure 2. Elastic deformation of the 800 cm^{-1} Raman band of LBG glass loaded up to 5.6 GPa (solid triangles) then decompressed (open triangles) and loaded again up to 4.6 GPa (solid rhombus) and then decompressed (empty rhombus).

the same LBG sample was loaded once more up to 4.6 GPa and then returned to atmospheric pressure. The Raman shift of the band at 800 cm^{-1} according to the pressure is given in figure 2. The Raman shift increases linearly with pressure and follows the same path upon first and second compression–decompression cycles. This confirms good reproducibility of the elastic response of LBG glass to pressure. A second set of measurements was carried out up to a pressure of 10 GPa, and the results are shown in figure 3. The Raman band at 800 cm^{-1} is shifted toward higher frequencies up to 7.5 GPa; then, when the pressure is increased to 10 GPa, the Raman band shifts in the opposite direction. On decompression, the Raman band at 800 cm^{-1} does not follow the same path. A hysteresis loop is then described, and when the sample returns to atmospheric pressure, it recovers its original structure.

In the last experiments, the pressure reached 18.9 GPa, and the results are reported in figures 3 and 4. In figure 3, the data of the two experiments concerning the Raman band at 800 cm^{-1} are superimposed. During compression, the Raman shifts follow the same path. We still observe a change of slopes around 7.5 GPa. A hysteresis is still seen, but the noticeable change comes from the fact that the hysteresis is not closed, meaning that the glass does not recover its original structure but is in another amorphous structural state at atmospheric pressure than before the compression–decompression cycle. In figure 4 are reported the shifts of the two other Raman bands during this cycle. The first large band at 320 cm^{-1} evolves linearly with pressure during the whole cycle, and returns to the initial position at atmospheric pressure. The second band at 550 cm^{-1} also increases linearly with pressure up to 13 GPa, but it then becomes indistinguishable from the band located at 800 cm^{-1} . That is the reason why the graph is not complete. This band is no longer visible afterwards, even after decompression.

Finally, in figure 5 we present the Raman spectra at ambient pressure before compression, at 18.9 GPa after compression, at 2 GPa and at ambient pressure after decompression. The spectrum recorded at low pressure is very noisy but is however different from the first spectrum

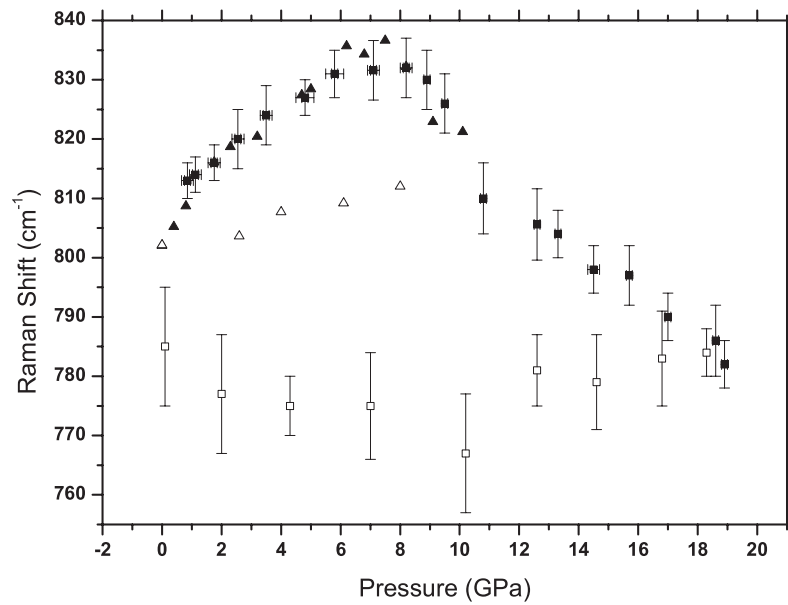


Figure 3. Raman shifts of the 800 cm^{-1} band obtained from compression (solid symbols)–decompression (open symbols) up to 10 GPa (triangles) and up to 19 GPa (squares). The hysteresis is closed for a 10 GPa compression and open for a 19 GPa compression.

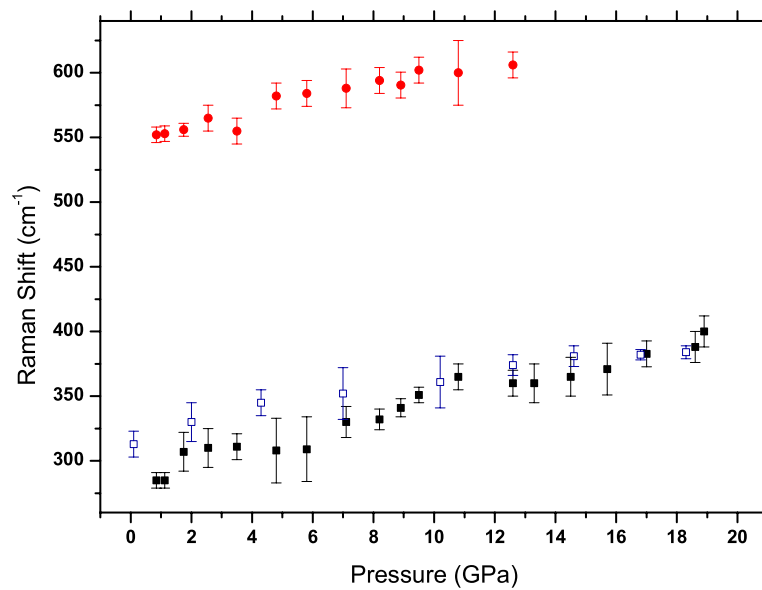


Figure 4. Raman shift of the Raman bands located around 320 and 550 cm^{-1} after a compression–decompression cycle up to 19 GPa. The 320 cm^{-1} Raman band has an elastic behaviour whereas the 550 cm^{-1} Raman band disappears near 13 GPa. Solid and open symbols represent compression and decompression, respectively.

taken before compression. The higher spectra in figure 5 are very similar. They differ from the first spectrum recorded at ambient pressure. The main differences are that the Raman band

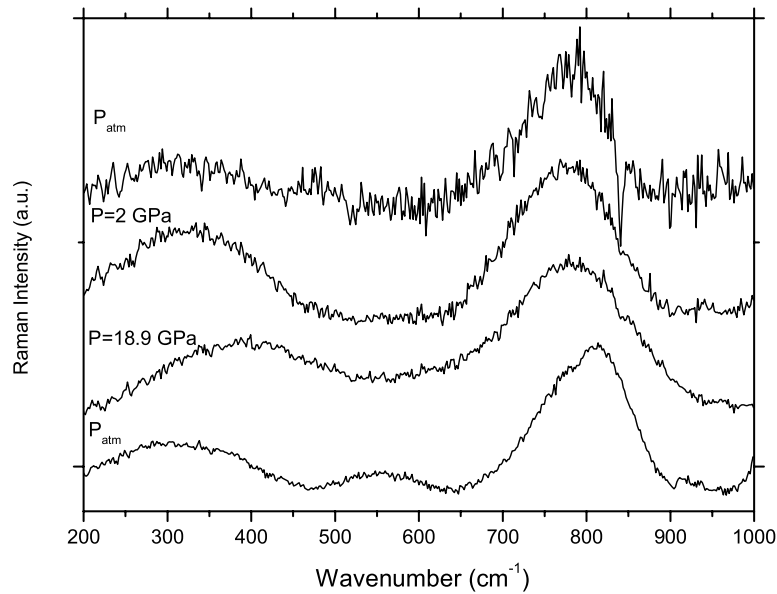


Figure 5. Raman spectra of LBG glass close to atmospheric pressure before compression (down spectrum), then at 18.9 and 2 GPa after compression; the noisy spectrum at the top was obtained at ambient pressure after decompression.

at 800 cm^{-1} is shifted toward smaller frequencies and that the middle band at 550 cm^{-1} is no longer visible on spectra recorded at 18.9 GPa and during decompression.

The last experiment was devoted to observing the behaviour of the corresponding crystal LaBGeO_5 under pressure. The crystal has the stillwellite-like structure, and as shown in figure 1, the Raman spectrum of the glass looks like a broadened spectrum of the crystal. The pressure was increased in the same range as before, i.e. up to 18.3 GPa. The Raman spectra obtained before and after the compression–decompression cycle do not reveal any difference. Up to these high pressures, in contrast to the LBG glass, the crystal has a reversible behaviour, as shown in figure 6, where the positions of the two main peaks located around 805 and 866 cm^{-1} follow the same path upon compression and decompression.

4. Discussion

We supposed that LBG glasses have a short-range order like that of the corresponding stillwellite-like crystal. This means that LBG glass is a random network of BO_4 and GeO_4 tetrahedra. However, Sigaev *et al* [13] have provided evidence from infrared (IR) spectra of the unexpected presence of BO_3 units in LBG glasses melted in a platinum crucible. The presence of BO_3 groups is confirmed by two bands centred at 1210 and 1370 cm^{-1} on the Raman spectrum at ambient pressure [19] (see figure 1). From nuclear magnetic resonance (NMR) data [20] the three-fold and four-fold coordinated boron atoms were estimated to be in about equal amounts, but this depends on the experimental conditions used to obtain the glass. When the LBG glass is crystallized in a stillwellite-like structure, all boron atoms become four-fold coordinated [20]. According to the literature [12, 16–18], the Raman band at 320 cm^{-1} is attributed to the La–O vibration mode and the Raman band at 550 cm^{-1} is assigned to a combination of the bending vibrations of T–O–T (T = Ge or B) bonds. The

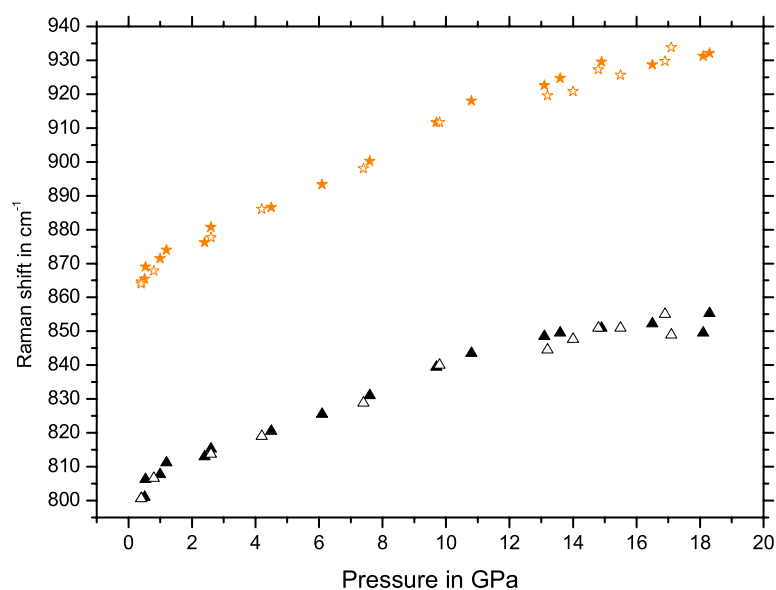


Figure 6. Raman shifts of the 805 and 866 cm^{-1} bands in the LaBGeO_5 crystal obtained from compression (solid symbols)–decompression (open symbols) up to 18.3 GPa.

Raman band at 800 cm^{-1} is attributed to antisymmetric stretching of four-fold coordinated B and Ge. However, vitreous B_2O_3 , where boron atoms are three-fold coordinated, presents a Raman band at 808 cm^{-1} which is assigned to vibrations of boroxol rings [24]. Therefore the 800 cm^{-1} Raman band in LBG glass whose width is ten times larger than in vitreous B_2O_3 corresponds to B–O vibration where boron atoms are four-fold and three-fold coordinated and where there is no vibrational decoupling of boroxol cycles.

Recalling that LBG glass contains a large part of GeO_2 (50% of the molar composition), it is relevant to look in the literature at the behaviour of GeO_2 glass under pressure. Durben *et al* recorded *in situ* Raman spectra of GeO_2 glass up to 56 GPa [21]. They deduce from their experiments that a compression up to 5.6 GPa leads to a continuous increase of distortion of the GeO_4 tetrahedra and to a decrease of the intertetrahedral bond angle. This was revealed by the positive frequency shift, the broadening and loss of intensity of the main band located at 419 cm^{-1} which is assigned to symmetric stretching modes of bridging oxygens in predominantly six-membered rings. These results are consistent with our first experiment, which shows that, at least up to 5.6 GPa, the LBG glass has a reversible behaviour, meaning that such pressures are too small to induce any irreversible plastic transformation.

In further experiments, Durben [21] confirmed with Raman spectroscopy the results found earlier by Itie *et al* with x-ray absorption spectroscopy (XAS) [6]. They both found a transition around 10 GPa (between 5.6 and 13 GPa for [21] and between 7 and 9 GPa for [6]) which is attributed to a pressure-induced four-fold to six-fold Ge coordination change. This transformation is characterized by a change of the derivatives of the frequency shifts, a broadening and weakening of the main band in the Raman spectra [21], and by an increasing Ge–O distance close to the expected value in octahedral coordination deduced from XAS experiments [6]. In B_2O_3 glasses [7], it is supposed that, at atmospheric pressure, boron atoms are entirely three-coordinated and a change from three to four of the boron coordination number is supposed to occur by increasing the pressure. This structural rearrangement under pressure is

gradual, in contrast to the reverse transformation during decompression, which is characterized by a dramatic decrease of the velocity of sound around 3 GPa.

For the crystal of LaBGeO₅, we observed that a compression up to 18.3 GPa does not strongly affect the Raman spectrum and that, after decompression, no modification in the Raman spectrum was obvious. If we compare the Raman shift of the two bands located around 805 and 870 cm⁻¹ of the LaBGeO₅ crystal (see figure 6) to the main Raman band of the glass located around 800 cm⁻¹ (see figure 3), we find similar slopes: respectively 3.3 ± 0.2 cm⁻¹ GPa⁻¹ and 3.8 ± 0.2 cm⁻¹ GPa⁻¹ for the crystal and 4 ± 0.4 cm⁻¹ GPa⁻¹ for the glass during elastic deformation. The very close values of slopes between crystal (which contains exclusively four-fold coordinated germanium and boron) and glass suggest that, below 7.5 GPa, the elastic deformation is mainly due to BO₄ and GeO₄ tetrahedra. The pressure reached was not high enough to induce an irreversible transformation in the LaBGeO₅ crystal. For comparison, only a compression up to 30 GPa is able to provoke an irreversible amorphization of α -quartz. For lower pressures, the densified phase returns to quartz phase upon decompression [22].

The sudden change of slope of the 800 cm⁻¹ Raman band frequency shift corresponds to the domain of pressures for which a change of Ge coordination number from four to six has been observed. The slope of the curve passes from 4 ± 0.4 to -4.5 ± 1 cm⁻¹ GPa⁻¹ in LBG glass at 7.5 GPa. BO₃ and BO₄ units are also present in this glass and we cannot exclude a transition of the boron coordination from three to four or/and from four to six. However, the change of coordination number of BO₃ units is supposed to be smooth [7] and the dramatic alteration in the Raman spectrum at 7.5 GPa does not act in favour with this assumption. Moreover, the presence of a large amount of non-bridging oxygens in LBG glass makes a coordination number change easier, because less breakdown of the network structure is needed to ensure this coordination transition [21, 23]. The change of slope sign observed around 7.5 GPa could be explained in the following manner: the compression applied on the sample leads first to a decrease of Ge–O and/or B–O bond lengths, and the 800 cm⁻¹ Raman band is then shifted toward high frequencies. But when non-bonding repulsive forces between neighbouring cations of Ge or B become preeminent because of a decrease of intertetrahedral bonding angles (7.5 GPa is assumed to mark this limit), the Ge–O and/or B–O bonds are lengthened, allowing a coordination change, and therefore the bond angles change. The 800 cm⁻¹ Raman band then shifts in the opposite direction.

At ambient pressure, after decompression, the 800 cm⁻¹ Raman band shift is negative compared to unloaded LBG. The assumed non-reversible coordination number of LBG glass, in contrast to GeO₂ glass [6], may explain this negative shift. Another difference between Raman spectra recorded before and after compression (see figure 5) is the disappearance of the 550 cm⁻¹ band. This band may be hidden by the neighbouring 800 cm⁻¹ band, which is closer in compressed LBG glass than before compression. Moreover, the two initial peaks of the 800 cm⁻¹ band are no longer visible in compressed glass, although the width of this band is similar after decompression. Finally, the band located around 320 cm⁻¹ is very large and is attributed to La–O vibration modes. Taking into account the maximum value of this band, we observed a reversible behaviour under pressure. Indeed the lanthanum atoms do not participate in the rings but they interconnect them. It is then consistent that pressure does not strongly permanently affect this band.

5. Conclusion

The ability of a ternary 25La₂O₃–25B₂O₃–50GeO₂ glass to manifest different polyamorphous structures at atmospheric pressure has been established. Experiments showed the behaviour of

this glass under pressure and gave evidence of the existence of hysteresis curves that are open or closed, depending on the highest pressure reached, and which are the signs of permanent or non-permanent plastic deformations. Although the path drawn upon decompression differs from the path upon compression, the glass recovers its original structure after a compression up to 10 GPa, whereas the densification is permanent after a compression up to 19 GPa. The change of slopes observed in Raman shifts relative to pressure may be interpreted as a change of coordination number of one kind of unit.

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