Recrystallization and formation of pressure-amorphized Li$_2$Ge$_7$O$_{15}$

Yuankun Lin, Guoxiang Lan† and Huafu Wang

Department of Physics, Nankai University, Tianjin 300071, People's Republic of China

Abstract. A high-pressure Raman scattering study on Li$_2$Ge$_7$O$_{15}$ up to 19 GPa reveals the occurrence of a phase transition from the crystalline to the amorphous state at 12.7 GPa. The amorphization is reversible below 15.5 GPa and irreversible above 15.5 GPa. This transformation occurs via polyhedral tilting. Crystallization processes of pressure-amorphized Li$_2$Ge$_7$O$_{15}$ are also investigated by Raman scattering. An intermediate phase (α-quartz form GeO$_2$) is crystallized at 520 °C and the stable phase of Li$_2$Ge$_7$O$_{15}$ is formed at 620 °C.

1. Introduction

Pressure-induced amorphizations in germanates have been the subject of some recent studies. Pressure Raman studies have shown that Pb$_5$Ge$_3$O$_{11}$ and Bi$_4$Ge$_3$O$_{12}$ undergo crystalline-to-amorphous phase transitions at 14.6 GPa and 12 GPa, respectively, and these transitions were attributed to extreme distortion of polyhedra [1, 2].

Lithium heptagermanate (LGO) (Li$_2$Ge$_7$O$_{15}$) is a ferroelectric crystal which undergoes a second-order phase transition at $T_c = 283.5$ K at atmospheric pressure [3]. The transition temperature exhibits a linear pressure dependence with a positive pressure coefficient ($dT_c/dP = 14.6$ K kbar^{-1}) [4]. In the ferroelectric phase, a soft optical mode associated with the phase transition has been observed by means of the Raman scattering technique [4, 5].

In the present study, we report the high-pressure Raman spectra of LGO up to 19 GPa, and a phase transition from the crystalline to the amorphous state at 12.7 GPa has been observed. The recrystallization of the pressure-induced amorphous sample was also investigated by means of Raman scattering.

2. Experimental methods

The high pressure was generated with a diamond anvil cell which is similar to that of MBC-H designed by Mao and Bell [6]. Powder particles of a LGO crystal and a few chips of ruby were loaded into a pre-indented hole 0.2 mm in diameter drilled in a gasket (T301 stainless steel). A 4:1 mixture of methanol and ethanol was used as the hydrostatic pressure medium. The pressure inside the cell was calibrated from the frequency shift of the ruby fluorescence line. In order to study the crystallization process, the pressure-quenched

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† Author to whom correspondence should be addressed.

amorphous samples in the hole of the gasket were annealed in a furnace previously heated to a desired temperature and quickly removed.

The Raman scattering was excited by the 514.5 nm line of an Ar ion laser operating at 200 mW. The spectra were recorded in the back-scattering configuration with a Spex-1403 double monochromator equipped with a Datemate. All Raman spectra were recorded at room temperature.

3. Results and discussion

3.1. Pressure-induced amorphization

Raman spectra of the LGO crystal between 360 and 640 cm^{-1} measured under different pressures are given in figure 1, and the frequencies are plotted against pressure in figure 2. From figures 1 and 2, it can be seen that all frequencies shift to higher values with increasing pressure. The dominant feature at 470 cm^{-1} broadens and decreases in intensity rapidly with increasing pressure. At 12.3 GPa, all Raman peaks are very weak. No Raman peaks are observed in the range from 12.7 to 19 GPa. The precipitous decline in Raman intensity with compression is associated with the formation of an amorphous or highly disordered state [7, 8]. We believe that the LGO crystal becomes highly disordered with increasing pressure and turns into an amorphous phase above 12.7 GPa [1, 2, 9, 10].
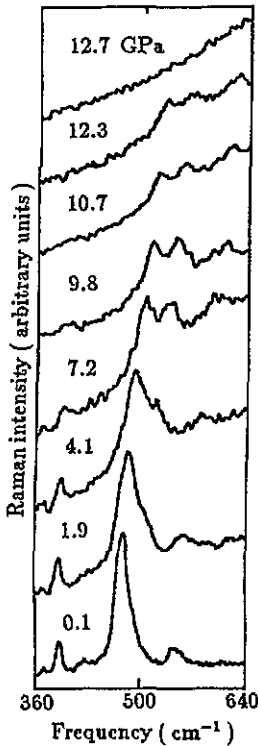

Figure 1. High-pressure Raman spectra of LGO measured under various pressures.
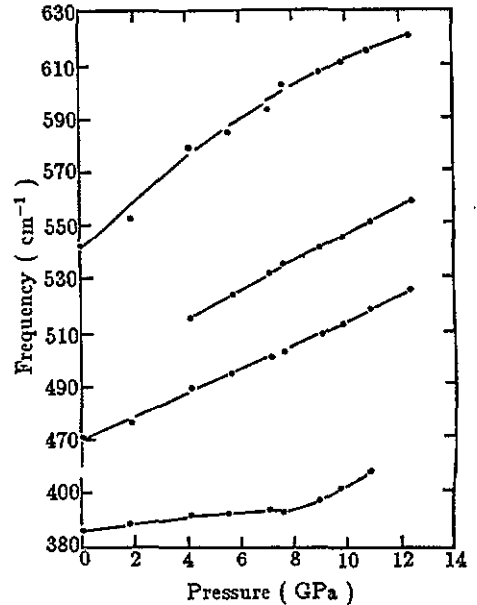
Figure 2. The pressure dependence of the Raman frequencies of LGO.

The Raman spectra of pressure-quenched and polycrystalline LGO are presented in figure 3. The Raman spectrum of the sample on releasing pressure from 13.1 GPa is similar to that of polycrystalline LGO, but two very weak and broad bands centred at 485 and 840 cm^{-1} were observed in the background. The sample evidently reverted to the initial polycrystalline phase, but there is a little amorphous phase in it. On releasing the pressure from 19.0 GPa some weak and diffused bands appeared instead of the peaks. The Raman spectrum is apparently different from that of polycrystalline state but is similar to that of the melt-quenched glassy analogue [11]. Bands centred at 485 and 840 cm^{-1} are ascribed to the internal modes of the distorted GeO_4 tetrahedra [12]. The band at 540 cm^{-1} is ascribed to the internal mode of the distorted GeO_6 [13]. The Raman spectrum on releasing the pressure from 15.5 GPa is quite different from that of the polycrystalline state but slightly different from the glassy analogue. These results indicate that the amorphization is irreversible above 15.5 GPa and reversible below 15.5 GPa. We have no explanation for this irreversibility above a threshold pressure. This effect may be related to shear in the methanol–ethanol medium [14]. It is well known that shear-induced amorphizations are irreversible [15].
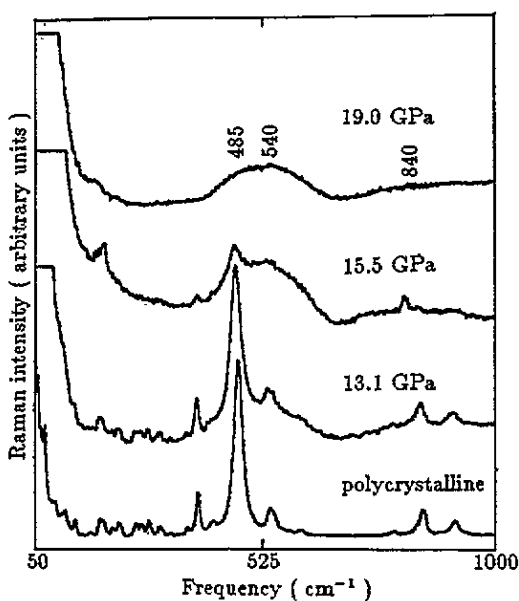

Figure 3. Raman spectra of pressure-quenched and polycrystalline LGO.

We must describe the ambient pressure structure of LGO in order to understand the mechanism responsible for the pressure-induced amorphization. The crystal structure of LGO at room temperature (above T_c) is orthorhombic which contains puckered layers of GeO_4 tetrahedra linked by GeO_6 octahedra forming a three-dimensional network and the space group is D_{2n}^{14}-$(Pbcn)$ [16]. All polyhedra units share corners and the lithium atoms sit in 'holes' between the polyhedra. Hazen and Finger [17] found that the volume of a crystal is often reduced by changing the angles between the polyhedra rather than by significantly shortening the ionic bonds within them if the polyhedra in a structure of a crystal share corners and that this polyhedral tilting is responsible for a dramatic phase transition in some compounds. We suggest that the pressure-induced amorphization of LGO may occur from tilting of GeO_4 tetrahedral and GeO_6 octahedral units about the lithium atoms in different

manners. In some cases such as β-BaZr$_2$F$_{10}$, SiO$_2$ and LiKSO$_4$ [7, 9, 18], the pressure-induced amorphization was also explained by the 'polyhedral tilt' mechanism of Hazen and Finger.

3.2. Recrystallization of pressure-amorphized Li$_2$Ge$_7$O$_{15}$

Some work has been done on the crystallization of melt-quenched glassy LGO [11, 19]. The differential thermal analysis curve of glassy LGO has two exothermic peaks at T_{crys1} and T_{crys2} [19]. The presence of two exothermal peaks suggest that the crystallization occurs twice successively in glassy LGO. An x-ray diffraction study [19] shows that an intermediate phase is formed in glassy LGO heated to a temperature between T_{crys1} and T_{crys2} (but this phase was not identified) and then the crystalline LGO is formed after heating to a temperature above T_{crys2}. To compare the crystallization processes of pressure-quenched amorphous LGO with those of melt-quenched glassy LGO [11, 19], the pressure-quenched amorphous LGO was annealed. Figure 4 shows the Raman spectra of amorphous samples annealed at different temperatures for 5 min. The Raman spectrum of amorphous samples annealed at 520 °C (the temperature below T_{crys1}) for 50 min is shown in figure 5. The frequencies of Raman peak of an amorphous sample annealed at 520 °C for 5 and 50 min are tabulated in table 1. For comparison, the Raman frequencies of α-quartz form GeO$_2$ are also listed in table 1.
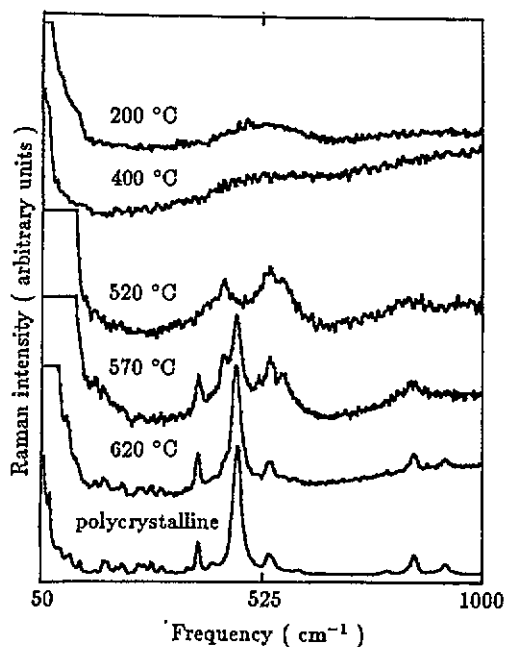

Figure 4. Raman spectra of pressure-amorphized LGO annealed at different temperatures (holding time, 5 min).

We can see from the above results that the samples annealed at 200 and 400 °C are still in the amorphous state but the Raman spectra of the latter exhibit a strong background which masked almost all the information on amorphous LGO. The Raman features of the sample annealed at 620 °C (the temperature above T_{crys2}) are almost identical with those of polycrystalline LGO, which indicates that the pressure-amorphized LGO transforms into stable crystalline LGO.

In the Raman spectrum of the amorphous sample annealed at 520 °C for 5 min a few peaks appear in an amorphous background (see figure 4). When the amorphous sample was
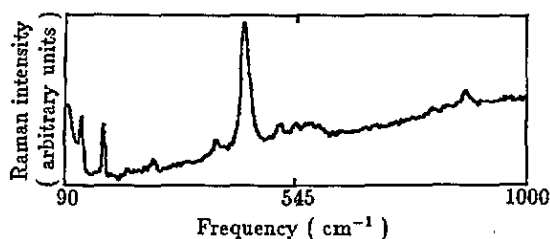
Figure 5. Raman spectrum of pressure-amorphized LGO annealed at 520 °C for 50 min.

Table 1. Frequencies of Raman peaks of amorphous Li$_2$Ge$_7$O$_{15}$ annealed at 520 °C and α-quartz form GeO$_2$: s, strong; m, medium; w, weak.

Raman peak frequency (cm^{-1})			
Amorphous LGO annealed at 520 °C		α-quartz form GeO$_2$	
For 5 min	For 50 min	From [11]	From [13]
	122 s	125 s	121
	166 s	168 s	166
	210 w	214 w	212
	248 w	250 w	
	264 m	264 m	261
	326 w	326 w	326
			372
	386 m		385
440	442 s	445 s	440
			456
			492
	516 m	519 m	512
542	548 m		
570	586 w	585 w	583
	596 w	597 w	595
		860 w	857
850	882 m	886 m	880
			949
	960 w	961 w	961
		975 w	972

annealed at 520 °C for 50 min, more peaks appear and a Raman spectrum is similar to that of α-quartz form GeO$_2$ [11, 13] (see table 1). The Raman spectrum is different from that of the amorphous sample annealed at 620 °C, indicating the existence of an intermediate phase. This agrees with the results of x-ray analysis that an intermediate phase exists in the crystallization processes of glassy LGO and we identify this intermediate phase as α-quartz form GeO$_2$.

4. Conclusions

The LGO crystal transforms into an amorphous phase above 12.7 GPa. The amorphization is reversible below 15.5 GPa and irreversible above 15.5 GPa. A few diffuse Raman bands are observed in the pressure-amorphized LGO quenched from 19 GPa and are similar to those of melt-quenched glassy LGO. The Raman spectra show that GeO$_4$ tetrahedra and GeO$_6$ octahedra are still retained but highly distorted in the pressure-amorphized LGO. The

mechanism of the pressure-induced amorphization of LGO is 'polyhedral tilt'. The pressure-amorphized LGO is recrystallized in two steps which are similar to those of the glassy analogue. First α-quartz form GeO_2 microcrystallites are formed in an amorphous matrix, and then crystalline LGO is formed.

Acknowledgments

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