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Pressure-induced amorphization of bismuth orthosilicate

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Abstract

High-pressure behaviour of bismuth orthosilicate ($\text{Bi}_4\text{Si}_3\text{O}_{12}$) is investigated in a diamond anvil cell up to a pressure of 20 GPa using Raman spectroscopy. A new broad peak observed in the Raman spectra above 6 GPa is assigned to resonantly excited photoluminescence from self-trapped Frenkel excitons. Two phonons are found to have negative Gruneisen parameter, suggesting instability of the structure at high pressure. Broadening and disappearance of most of the Raman lines suggest amorphization of this system above 16 GPa. Amorphization is found to be reversible, unlike the case of $\text{Bi}_4\text{Ge}_3\text{O}_{12}$, where it is irreversible. In light of a recent model of pressure-induced amorphization it is argued that amorphization in bismuth orthosilicates and germanates arises due to kinetic hindrance of decomposition into mixtures of daughter compounds with dense-packed structures.

1. Introduction

Pressure-induced amorphization (PIA) has been a subject of considerable interest ever since its first report in ice [1] at 77 K and 1 GPa. Now more than 60 compounds with bonding natures as different as covalent [2] (SiO_2), ionic [3] (LiKSO_4), molecular [4] ($\text{C}_2(\text{CN})_4$) and hydrogen bonding (ice) have been found to exhibit this phenomenon. In addition, a number of silicates [5, 6], germanates [7, 8], molybdates [9, 10] and other minerals [11] have shown amorphization under pressure. PIA was originally proposed to arise due to kinetic hindrance of equilibrium phase transitions [12]. On the other hand, computer simulation studies have predicted an elastic instability [13] (Born criterion) to drive amorphization. In addition, factors such as poly-tetrahedral packing [14], increase in the coordination number [15] and orientational disorder of polyatomic ions [16] are found to be associated with PIA. These

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features are not necessarily all distinct, i.e. more than one may be applicable simultaneously in some cases and hence could be related. Although it is widely accepted that kinetic hindrance of equilibrium phase transitions is the cause of the PIA, the 'final phase', which the system should have ideally transformed to, remained speculative or unknown in most instances. Based on reports of PIA at ambient temperature in some silicates and the observations of pressure-induced decomposition (PID) in those systems into mixtures of simple oxides at high pressure and high temperature (HPHT), a unified model of pressure-induced amorphization and decomposition has been proposed recently [17]: that amorphization at high pressure could also arise from kinetic hindrance of equilibrium decomposition. It may be pointed out that pressure-induced solid–solid decomposition, also known as disproportionation, can occur only at elevated temperatures as the process of nucleation and growth of macroscopic phases of daughter compounds is diffusion controlled. Only at elevated temperatures is diffusion kinetics sufficient for the evolution of a disordered assemblage of the phases of daughter compounds. On the other hand, at ambient temperature the system is likely to be trapped in a metastable amorphous (disordered) state while attempting to decompose under the application of pressure. Furthermore, the condition for the occurrence of PID at elevated temperatures (i.e. total volume of daughter compounds being less than that of the parent compound) can be taken as a simple criterion for PIA at ambient temperature. Several compounds that exhibit PIA at ambient temperature have been found to satisfy this condition [17].

Orthosilicates and germanates of bismuth, which crystallize in the eulytite structure, are important scintillator detector materials [18], and when suitably doped with rare earths such as Nd serve as laser materials. These crystals are also photo-refractive and find applications in optical devices [19]. Bismuth orthogermanate $\text{Bi}_4\text{Ge}_3\text{O}_{12}$ has been reported to amorphize irreversibly at 12 GPa [7]. Quite interestingly $\text{Bi}_4\text{Ge}_3\text{O}_{12}$ indeed satisfies the condition for decomposition. In view of this it is important to examine whether $\text{Bi}_4\text{Si}_3\text{O}_{12}$ also satisfies the condition for decomposition, and whether it exhibits amorphization. In the present work we report results of high-pressure studies of isostructural bismuth orthosilicate $\text{Bi}_4\text{Si}_3\text{O}_{12}$ investigated using Raman spectroscopy. Gruneisen parameters of all the modes are obtained. Amorphization in this system and in $\text{Bi}_4\text{Ge}_3\text{O}_{12}$ is analysed in the light of the new model of amorphization [17]. Pressure-induced amorphization is predicted to occur also in other silicates and germanates of bismuth.

2. Experimental details

$\text{Bi}_4\text{Si}_3\text{O}_{12}$ crystals were synthesized from high-purity bismuth trioxide (Bi_2O_3 —99.99%, Aldrich) and silicon dioxide (SiO_2 —99.999%, Aldrich) in 2:3 molar ratio [20]. These were thoroughly mixed in a mortar and pestle, and melted in a platinum crucible at 1050 °C and left to homogenize for 12 h, after which the furnace temperature was decreased gradually. Powder x-ray diffraction (XRD) was used to confirm the purity of the phase.

Raman spectra of unoriented single-crystal chips of dimensions about 100 μm were recorded [21] in the back-scattering geometry using a Mao–Bell-type gasketed diamond anvil cell (DAC). A 4:1 mixture of methanol and ethanol was used as the pressure transmitting medium. The standard ruby fluorescence technique was used for pressure calibration. The 488 nm line of an argon ion laser was used as the excitation source. The scattered light was analysed by a SPEX double monochromator and detected by a photomultiplier tube in the photon counting mode. Scanning and data acquisition were carried out by a home-built microprocessor-based data-acquisition-cum-control unit. Subsequent to the completion of a scan, the data were transferred to a personal computer for further analysis.

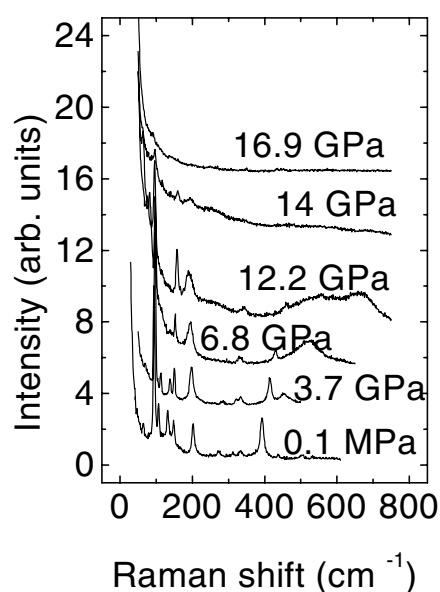


Figure 1. Raman spectra of $\text{Bi}_4\text{Si}_3\text{O}_{12}$ at various pressures. Almost all the lattice and the internal modes disappear above 16 GPa.

3. Results

Crystals of $\text{Bi}_4\text{Si}_3\text{O}_{12}$ were analysed for their structure using powder XRD. The d -spacings were found to agree well with the reported JCPDS data [22]. $\text{Bi}_4\text{Si}_3\text{O}_{12}$ crystallizes in the cubic (eulytite) structure belonging to the space group $I\bar{4}3d$ (T_d^0) with a lattice constant of 10.288 Å, with four formula units per unit cell [23]. The structure consists of SiO_4 tetrahedra at S_4 site and bismuth cations on the C_3 axis. Each bismuth ion is coordinated to a distorted octahedron of oxygen atoms of neighbouring silicate ions [24], three oxygen atoms at 2.19 Å, and the other three at 2.67 Å. The primitive cell contains two formula units, leading to 46 optical phonons ($4A_1 + 5A_2 + 9E + 14F_1 + 14F_2$), out of which 27 are Raman active: $4A_1 + 9E + 14F_2$ [25]. Raman spectra of $\text{Bi}_4\text{Si}_3\text{O}_{12}$ at several pressures are shown in figure 1. This region covers the lattice modes and the ν_2 and ν_4 internal modes of the SiO_4 tetrahedron. The spectrum at ambient pressure is in good agreement with those of earlier reports [25, 26]. At high pressures only 11 out of the 27 Raman active modes could be observed with measurable intensity. ν_1 and ν_3 modes of SiO_4 tetrahedra, which lie in the range of 700–900 cm^{-1} , are about 40 times weaker than ν_2 and ν_4 modes [26]. These modes could not be observed either at high pressures. The behaviour of several of the lattice modes (below 300 cm^{-1}) and the ν_2 , ν_4 internal bending modes of SiO_4 tetrahedra were investigated as a function of pressure. A broad peak at about 520 cm^{-1} appears in the Raman spectra above 6 GPa, whose frequency exhibits anomalously high pressure coefficient. The intensity of this peak increases dramatically as a function of pressure and exhibits a maximum around 9.3 GPa. The origin of this peak will be discussed later.

Figure 2 shows the pressure dependence of the frequencies of the various phonons. The mode at 202 cm^{-1} exhibits softening, implying lattice instability [27] and consequent phase transition [28]. In the isostructural $\text{Bi}_4\text{Ge}_3\text{O}_{12}$ a mode around 202 cm^{-1} was also found to exhibit softening [7]. From this one could conclude that this mode in the two compounds

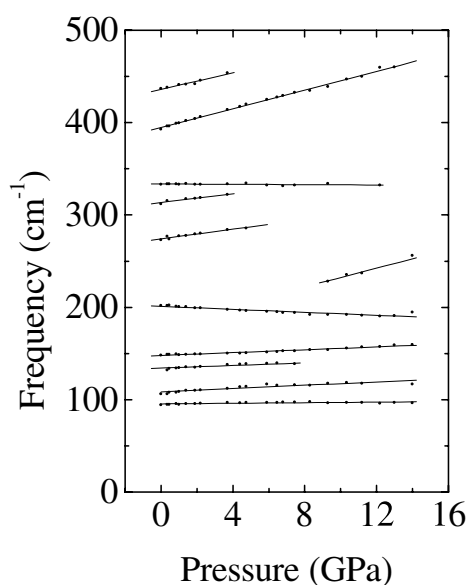


Figure 2. Pressure dependence of mode frequencies of $\text{Bi}_4\text{Si}_3\text{O}_{12}$. Modes at 202 and 334 cm^{-1} exhibit softening.

has the same symmetry. From polarized Raman measurements on oriented single crystals of $\text{Bi}_4\text{Si}_3\text{O}_{12}$, this mode is identified to be a lattice mode of A_1 symmetry [25]. Mode Gruneisen parameters, which are important from the point of view of testing lattice dynamical models and other theoretical calculations, are obtained from the high-pressure data using the relation $\gamma_i = (B_0/\omega_i)(\partial\omega_i/\partial P)$, where ω_i is the mode frequency, B_0 the bulk modulus (230 GPa [20] for $\text{Bi}_4\text{Si}_3\text{O}_{12}$) and P the pressure. The values of γ_i for the various modes are given in table 1 along with the mode assignment and correspondence between the modes of $\text{Bi}_4\text{Si}_3\text{O}_{12}$ and $\text{Bi}_4\text{Ge}_3\text{O}_{12}$. In addition to the 202 cm^{-1} mode, another mode at 332 cm^{-1} exhibits marginal softening. On the other hand, the corresponding mode of $\text{Bi}_4\text{Ge}_3\text{O}_{12}$ exhibits only normal behaviour (see figure 2 of [7]). In $\text{Bi}_4\text{Ge}_3\text{O}_{12}$ a mode at 246 cm^{-1} was reported to soften, while the corresponding mode in the orthosilicate at 274 cm^{-1} exhibits the opposite behaviour. This difference in the behaviour of other soft modes in the two systems is not well understood at present.

Intensities of all modes including the most prominent lattice mode near 95 cm^{-1} decrease rapidly above 13 GPa and disappear above 16.2 GPa. Raman line-width (FWHM) of several of the modes increases dramatically across amorphization (figure 3). Disappearance of lattice modes [29] and broadening of internal modes by a large factor [3, 30, 31] are often taken as evidence for amorphization. Thus the present results suggest occurrence of PIA above 16 GPa. However, a quantitative analysis is non-trivial because models of PIA are qualitative in nature and a theoretical formalism for the behaviour of these quantities has not yet been evolved. When the pressure was increased above 16.2 GPa no further changes in the spectrum were observed. After reaching 20.2 GPa, the pressure was gradually reduced. Several Raman lines corresponding to the lattice, namely, at 95 , 160 , 192 and 250 cm^{-1} , reappeared, suggesting reversibility of the crystalline to amorphous transition. A hysteresis of only about 1 GPa was found. Recent high-pressure energy dispersive XRD measurements carried out on powdered samples of $\text{Bi}_4\text{Si}_3\text{O}_{12}$ in a DAC up to a pressure of 20 GPa have confirmed [20] the occurrence

Table 1. Mode Grüneisen parameters of the various Raman modes of $\text{Bi}_4\text{Si}_3\text{O}_{12}$, their assignments and correspondence with the Raman modes of bismuth orthogermanate. The numbers in the parentheses are the standard errors in the least significant digit.

Mode frequency ω_i (cm^{-1})	γ_i	Assignment ^a	Modes of $\text{Bi}_4\text{Ge}_3\text{O}_{12}$ ^b
64	4.1(1)	Lattice F_2	63
95	0.36(7)	Lattice A_1	92
107	1.9(2)	Lattice F_2	99
133	1.2(1)	Lattice E	125
149	1.21(5)	Lattice E	144
202	-0.91(8)	Lattice A_1	203
274	1.9(3)	Lattice E	246
314	1.8(3)	Lattice E	268
334	-0.06(3)	Lattice F_2	284
394	2.97(4)	$\nu_2(\text{SiO}_4)$	363
436	2.4(3)	$\nu_4(\text{SiO}_4)$	396

^a Reference [25].

^b Reference [26].

of amorphization at 16 GPa and also its reversibility. This is in contrast to the behaviour of $\text{Bi}_4\text{Ge}_3\text{O}_{12}$, which has been reported to exhibit an irreversible amorphization at 12.3 GPa [7]. Possible reasons for this difference are discussed in the next section.

As mentioned earlier, the peak around 520 cm^{-1} in the 6.8 GPa spectrum exhibits an unusually large pressure coefficient of $25 \text{ cm}^{-1} \text{ GPa}^{-1}$, whereas most other phonons have values between 1 and $2 \text{ cm}^{-1} \text{ GPa}^{-1}$. Figure 4 shows the Raman spectra between 8 and 13 GPa, highlighting this peak. Note that its line width is also much higher than most other phonons. In view of these facts it is likely that the origin of this peak is different from that of the other phonon Raman lines. It is possible that this peak is a photoluminescence (PL) peak because PL peaks originating from direct interband electronic transitions are known to overlap with phonon Raman lines in the Raman spectra. Guided by its large pressure coefficient and large line width we assign this peak to a PL peak. The apparent Raman shifts of this peak (57 meV at 4 GPa to 85 meV at 13 GPa) would then correspond to absolute emission energies of 2.484 eV at 4 GPa and 2.456 meV at 13 GPa. Figure 5 shows the energy of this PL emission as a function of pressure. The pressure coefficient of this emission energy (-3 meV GPa^{-1}) is of the same order of magnitude [7] as that from europium levels ($-0.75 \text{ meV GPa}^{-1}$) in isostructural $\text{Bi}_4\text{Ge}_3\text{O}_{12}$. Recently PL emission bands at 2.8, 2.45 and 2.1 eV have been reported [32] in undoped $\text{Bi}_4\text{Si}_3\text{O}_{12}$. The high-energy bands are assigned to self-trapped Frenkel excitons associated with $(\text{BiO}_6)^{9-}$ ions, whereas the 2.1 eV peak arises from recombination at defects. The PL energy observed in the present studies (2.497 eV when extrapolated to zero pressure) is close to that of the middle band (2.45 eV) reported earlier. In view of this we assign the broad peak observed in the present crystals to one of these emission centres. The enhancement of the emission intensity in a limited range of pressures could be due to resonant excitation of the relevant energy levels, which are pressure tuned to coincide with the fixed excitation photon energy of 2.541 eV (488 nm). Other emission bands were not observed, possibly because these were not resonantly excited.

4. Discussion

In order to examine the possible reasons for the different behaviours of $\text{Bi}_4\text{Si}_3\text{O}_{12}$ and $\text{Bi}_4\text{Ge}_3\text{O}_{12}$ with respect to reversibility of amorphization, one must consider the difference

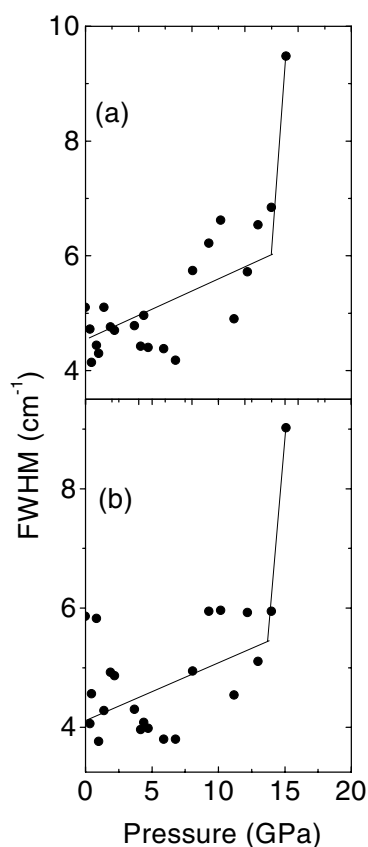


Figure 3. FWHM of two of the Raman modes, (a) 94 cm^{-1} and (b) 148 cm^{-1} , showing the dramatic rise across amorphization. Continuous lines are guides to eyes.

in the experimental parameters in the two experiments. Zou *et al* [7] used solid argon as the pressure transmitting medium, which freezes at 1.2 GPa [33], while in the present measurements a 4:1 mixture of methanol and ethanol was used. Solid argon is known to be quasi-hydrostatic only up to 9 GPa, whereas the methanol–ethanol mixture freezes at 10.4 GPa and remains quasi-hydrostatic up to 20 GPa [33]. In view of this the non-hydrostatic (shear) component of the stress is likely to be much higher in the case of measurements by Zou *et al* on $\text{Bi}_4\text{Ge}_3\text{O}_{12}$ than that in the present experiments. Shear stresses arising from non-hydrostatic stresses are known to strongly influence the amorphization pressure [34] and its reversibility [35]. Another factor that is important in controlling the reversibility of pressure-induced phase transitions and amorphization is the highest pressure reached in a particular pressure run. In several systems it is known that if the highest pressure reached in the pressure run is much higher than the transition pressure, i.e. the extent to which a phase transition is over driven is high, the transition often becomes irreversible [36] or returns to an entirely different phase. It must be pointed out that the highest pressure reached in the case of $\text{Bi}_4\text{Ge}_3\text{O}_{12}$ was about 2.5 times the amorphization pressure, whereas in the present experiments it is only 1.25 times. In view of this the reported irreversibility of amorphization in $\text{Bi}_4\text{Ge}_3\text{O}_{12}$ and reversibility in the present case is understandable. The present results also suggest a need to reinvestigate $\text{Bi}_4\text{Ge}_3\text{O}_{12}$ and look for possible reversibility of amorphization.

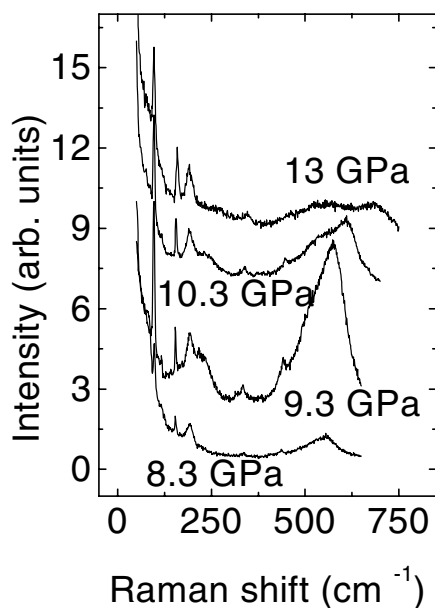


Figure 4. Raman spectra of $\text{Bi}_4\text{Si}_3\text{O}_{12}$ between 8 and 13 GPa, exhibiting a broad band around 550 cm^{-1} . The broad band is assigned to resonantly excited PL.

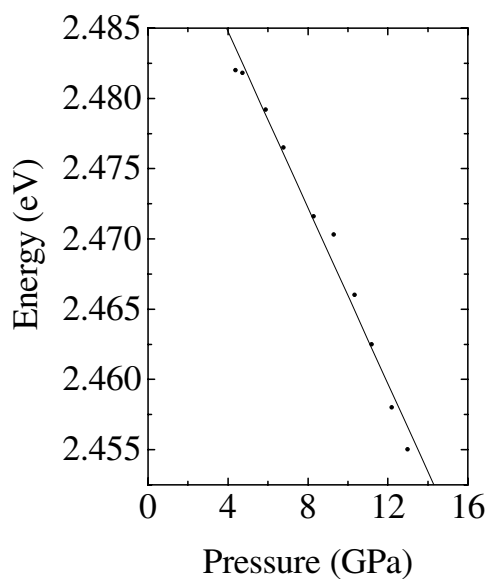


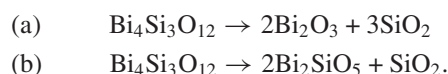
Figure 5. Dependence of resonantly excited self-trapped Frenkel exciton energy on pressure.

In view of the diversity of the systems that exhibit PIA, the mechanisms of amorphization are also expected to be different for different systems. For example, orientational disorder of polyatomic ions has been shown to be responsible for amorphization in a number of binary sulphates [16], whereas in the case of SiO_2 bond breaking due to bending of Si–O–Si angles beyond their stability limit was argued to cause PIA [37]. In the case of metal hydroxides, disordering of the anion sublattice has been found prior to amorphization [38]. Among

the systems that exhibit PIA a large number of systems have covalently bonded tetrahedral molecules [39] such as SnI_4 or molecular ions such as sulphates [3, 16], molybdates [9], silicates [6] or tungstates [40]. In addition, several of these systems are also found to have negative pressure coefficients of melting temperature [2]. These tetrahedral units are corner linked in some compounds [2, 41], while in others these are isolated and form interpenetrating sublattices with cations [3, 7, 40]. In general these compounds have open structure and are susceptible to densification under the application of pressure. While transforming to more dense-packed structures the tetrahedral units often exhibit distortion and orientational disorder [16] prior to amorphization. On the other hand, in the systems where tetrahedral units are corner linked, the distortion of these units may be sufficient to break the bonds [37], resulting in a coordination number more than four [13, 42]. However, in the present system the SiO_4 tetrahedra are isolated and hence are expected to show orientational disorder. The excessive broadening of internal modes found in the present measurements is consistent with this conclusion.

As mentioned earlier, PIA can also be viewed as a metastable state arising due to a kinetically constrained decomposition. An outcome of this model is that the final state, which remained speculative or unknown in most instances, can now be identified as a decomposed state. In analogy with the condition for structural phase transitions, a decomposition into daughter compounds would be favourable if the total volume of the daughter compounds were lower than that of the parent compound [43], i.e. if volume change upon decomposition $\Delta V = V_D - V_P < 0$, where V_P and V_D are respectively the total volumes of the parent and the daughter compounds [44]. It may be pointed out that the reported PIA at ambient temperature and PID at HPHT in Fe_2SiO_4 [5, 45], CuGeO_3 [41, 46], Mg_2SiO_4 [47, 48] and $\text{Zr}(\text{WO}_4)_2$ [40, 49] are consistent with the model. Thus, negative ΔV for a possible decomposition at elevated temperatures is considered a criterion for PIA at ambient temperature.

In order to examine whether a decomposition of $\text{Bi}_4\text{Si}_3\text{O}_{12}$ is favourable, one can consider two possible decomposition routes,



Other systems such as KHSO_4 have also exhibited more than one decomposition path [43]. While calculating ΔV , the equilibrium high-pressure structures of the daughter compounds should be considered. Under HPHT conditions, the fourfold-coordinated quartz phase of SiO_2 is known to transform to the sixfold-coordinated stishovite structure [2, 15], which is the equilibrium high-pressure phase. The mechanism of this transformation has been extensively reviewed [50]. The quartz phase (volume 39.15 \AA^3 per formula unit) consists of SiO_4 tetrahedra that are corner linked. As dense packing of tetrahedra is not possible without breaking bonds, the structure becomes increasingly unfavourable at high pressure and tetrahedra experience extreme distortion (flattening) [37]. If temperature is increased at high pressure to accelerate atomic motion, the coordination number increases to six, resulting in the dense-packed stishovite phase (volume 23.27 \AA^3 per formula unit). The formation of stishovite phase during HPHT decomposition of Fe_2SiO_4 (fayalite) has indeed been confirmed [45]. In view of this it is reasonable to use the stishovite unit-cell volume for the decomposition reactions (a) and (b). Using the reported unit-cell volume data of bismuth silicates and these oxides we obtain $V_P = 272.47 \text{ \AA}^3$ and $V_D(\text{a}) = 235.07 \text{ \AA}^3$, $V_D(\text{b}) = 245.17 \text{ \AA}^3$. Thus the estimated volume reductions upon possible decomposition turn out to be rather large fractions of the original volume, i.e. 13.7 and 10.0% for reactions (a) and (b) respectively. Table 2 gives the estimated volume change upon possible decomposition of orthosilicates and germanates of bismuth. For GeO_2 the volume of high-pressure rutile phase is used in the calculation.

Table 2. Calculated changes in the volume upon possible decomposition of different silicates and germanates of bismuth.

Compound	Possible decomposition products	$\Delta V / V_P$ (%)
$\text{Bi}_4\text{Si}_3\text{O}_{12}$	$2\text{Bi}_2\text{O}_3 + 3\text{SiO}_2$	-13.7
$\text{Bi}_4\text{Si}_3\text{O}_{12}$	$2\text{Bi}_2\text{SiO}_5 + \text{SiO}_2$	-10.0
$\text{Bi}_4\text{Si}_3\text{O}_{12}$	$\text{Bi}_2\text{O}_3 + \text{Bi}_2\text{Si}_3\text{O}_9$	— ^a
$\text{Bi}_4\text{Ge}_3\text{O}_{12}$	$2\text{Bi}_2\text{O}_3 + 3\text{GeO}_2$	-14.7
$\text{Bi}_4\text{Ge}_3\text{O}_{12}$	$2\text{Bi}_2\text{GeO}_5 + \text{GeO}_2$	-11.6
$\text{Bi}_4\text{Ge}_3\text{O}_{12}$	$\text{Bi}_2\text{O}_3 + \text{Bi}_2\text{Ge}_3\text{O}_9$	-0.26
$\text{Bi}_{12}\text{SiO}_{20}$	$6\text{Bi}_2\text{O}_3 + \text{SiO}_2$	0.6
$\text{Bi}_{12}\text{GeO}_{20}$	$6\text{Bi}_2\text{O}_3 + \text{GeO}_2$	0.2
Bi_2SiO_5	$\text{Bi}_2\text{O}_3 + \text{SiO}_2$	-4.6
Bi_2GeO_5	$\text{Bi}_2\text{O}_3 + \text{GeO}_2$	-5.2
$\text{Bi}_2\text{Ge}_3\text{O}_9$	$\text{Bi}_2\text{O}_3 + 3\text{GeO}_2$	-20.2
$\text{Bi}_2\text{Si}_3\text{O}_9$	$\text{Bi}_2\text{O}_3 + 3\text{SiO}_2$	— ^a

^a The volume change could not be estimated for these reactions as the crystal structure of $\text{Bi}_2\text{Si}_3\text{O}_9$ is not well known.

This analysis thus suggests that orthosilicates and germanates of bismuth are likely to exhibit decomposition under suitable HPHT conditions. The reaction path the system adopts and its kinetics will be determined by the difference in the total free energies ΔG of the daughter and the parent compound and the activation energy Δg for the reaction. Theoretical investigations of free energies similar to those carried out for alkaline-earth chromates [51] could throw further light on the energetics of the phenomena. Furthermore, the PIA found at ambient temperature arises most probably due to the kinetic hindrance of decomposition rather than a phase transition.

It may be mentioned that Bi_2O_3 and SiO_2 are known to form several compounds with different molar ratios between them. Some of these are Bi_2SiO_5 , $\text{Bi}_2\text{Si}_3\text{O}_9$ and $\text{Bi}_{12}\text{SiO}_{20}$. Similarly various bismuth germanates have also been found to form from Bi_2O_3 and GeO_2 . One can now examine whether other silicates and germanates are likely to amorphize at ambient temperature. Table 2 also gives the calculated volume changes upon decomposition of other silicates and germanates. All these compounds, except $\text{Bi}_{12}\text{SiO}_{20}$ and $\text{Bi}_{12}\text{GeO}_{20}$, have negative ΔV and hence could possibly decompose when subjected to HPHT conditions and are likely to exhibit PIA at ambient temperature. The predictions about the decomposition under HPHT conditions and PIA at ambient temperature in these compounds need to be confirmed from appropriate HPHT experiments.

5. Summary and conclusions

High-pressure Raman spectroscopic measurements carried out on bismuth orthosilicate suggest a crystalline to amorphous transition above 16 GPa. Amorphization is found to be reversible, in contrast to the reported behaviour of isostructural $\text{Bi}_4\text{Ge}_3\text{O}_{12}$. The difference between these behaviours is understood on the basis of the highest pressure reached in the respective pressure runs. The intensity of a new broad peak observed in the Raman spectra exhibits enhancement over a limited pressure range and is understood to be due to PL arising from self-trapped Frenkel excitons around 2.45 eV. Analysis of the crystal unit-cell volumes suggests that the PIA in bismuth orthosilicates and germanates arises because a decomposition into dense-packed daughter compounds is kinetically constrained. The present results could motivate further

experimental studies on these silicates and germanates under high- P - T conditions for possible decomposition and at ambient temperature for possible PIA. Theoretical investigations of free energies of various phases would also throw further light on the energetics of the phenomena of PIA/PID.

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