

Pressure-induced amorphization and orientational disorder in potash alum

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

2000 J. Phys.: Condens. Matter 12 4417

(<http://iopscience.iop.org/0953-8984/12/19/311>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 171.66.16.221

The article was downloaded on 16/05/2010 at 04:54

Please note that [terms and conditions apply](#).

Pressure-induced amorphization and orientational disorder in potash alum

T Sakuntala[†], Akhilesh K Arora[‡], N V Chandra Shekar[‡] and P Ch Sahu[‡]

[†] Solid State Physics Division, Bhabha Atomic Research Centre, Bombay, 400 085, India

[‡] Materials Science Division, Indira Gandhi Centre for Atomic Research, Kalpakkam, 603 102, India

Received 25 October 1999, in final form 20 March 2000

Abstract. Pressure-induced amorphization in potassium aluminium sulphate dodecahydrate (potash alum) has been studied using Raman spectroscopy in a diamond anvil cell up to a pressure of 15 GPa. In potash alum, some of the sulphate ions are misoriented with their S–O bond pointing towards potassium rather than aluminium, leading to an ‘orientational disorder’ which ranges from 10 to 24% at ambient conditions. The disorder is quantified from the intensities of the Raman lines characteristic of the two orientations. The samples with low initial disorder exhibit a sequence of two structural phase transitions occurring at 1.5 and 9 GPa respectively. The phase above 1.5 GPa, which could be pressure quenched to ambient conditions, is found to be free from orientational disorder. On the other hand, in the samples with high initial disorder, the disorder is found to grow as a function of pressure and beyond a critical value the system turns amorphous, which is confirmed from the disappearance of sharp diffraction peaks. In view of these results it is apparent that the orientational disorder is the driving mechanism of amorphization in potash alum. The different initial disorders in different samples are believed to arise from a combination of a dynamic disorder (equilibrium) and a static disorder arising from the defects. This defect could possibly be a missing molecule in the water octahedra around the potassium ion.

1. Introduction

Since its first report [1] in 1984, the phenomenon of pressure-induced amorphization (PIA) has generated considerable interest. A crystalline solid turning amorphous at high pressure is considered as ‘anomalous’ or unusual because the amorphous solids are usually found to crystallize [2] when subjected to high pressure. This is because the amorphous solids have excess free volume which is distributed. This excess free volume is released during crystallization and the system acquires stable equilibrium structure. In view of this, the pressure-amorphized state is considered to be metastable [3] and is believed to be arising due to kinetic hindrance [4] of equilibrium phase transitions. Theoretical models involving diffusion and coupling of ‘structure-forming defects’ via a stress field have also been developed [5] to explain the PIA reported in some crystalline solids.

Up to now, PIA has been found to occur in a few tens of compounds [6]. The bondings in the systems that exhibit PIA are found to be of widely different natures, e.g., covalent [7, 8] in SiO₂ and AlPO₄, ionic [9, 10] in LiKSO₄ and Ca(OH)₂, van der Waals [11, 12] in SnI₄ and C₂(CN)₄, and hydrogen bonding [1] in ice. In view of the diversity of the systems exhibiting this phenomenon, the underlying mechanisms are also expected to be different for different classes of materials. For example, in quartz, breaking of Si–O bonds due to the bending of Si–O–Si angles beyond their energetic limit has been proposed to be the cause

of PIA [13]. Recently, high-pressure polymorphism has also been proposed as an alternative explanation [14, 15] for the occurrence of the phenomenon in SiO_2 . Dimerization of tetrahedral molecules is believed to be responsible [11] for PIA in SnI_4 . On the other hand, the high-pressure phase of LiKSO_4 was found to have ‘orientational disorder’ (OD) of sulphate ions [16]. Other double sulphates have also been found to exhibit similar behaviour [17, 18]. In view of these results, orientational disorder of sulphate ions was conjectured to be responsible for amorphization in double sulphates [19]. Consequences of OD have been investigated further in potash alum [20], a crystal which is known to have OD of sulphate ions even at ambient temperature and pressure. Although the preliminary results confirm that OD does indeed drive the amorphization [20], a detailed study of the evolution of disorder as a function of pressure has not been carried out. In the present work we report the results of detailed Raman spectroscopic studies of phase transitions and amorphization in potash alum at high pressure. Amorphization is confirmed from the angle-resolved x-ray diffraction (XRD) measurements at high pressure. The behaviours of the samples with different initial disorders are compared. A model for the static disorder is also presented.

2. Background information on potash alum

Alums belong to a family of cubic crystals with four formula units per unit cell having a general formula $\text{AB}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ where A represents a trivalent metal atom and B denotes a monovalent alkali atom. Among these, potash alum $\text{AlK}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ belongs to a class of alums called α -alum crystallizing in the cubic space group $T_h^6 (Pa\bar{3})$. In the alum structure, the sulphate groups are located at the C_3 sites and, in the case of α -alums, all the S–O bonds point towards the trivalent metal ion [21]. Two other types of alum, namely the β - and the γ -alums, also exist; these also crystallize in a closely related structure with the same space group. The size of the trivalent cation is generally small and consequently the water octahedron around the Al ion is also small. For example, in the case of potash alum, the Al– H_2O distance is only 1.91 Å and hence the water molecules around Al almost touch each other [21]. On the other hand, the monovalent cation size, which could vary over a large range (0.97 Å for Na to 1.67 Å for Cs), determines the size of the water octahedron around alkali ion B. For potash alum the K– H_2O distance is 2.98 Å. For larger alkali cations such as Cs one gets β -alum structure, where the oxygen atoms of the sulphate ions are also at nearly the same distance from the cation as the oxygens of the water octahedra, leading to a twelvefold oxygen coordination around Cs [21]. For β -alums also, the S–O bonds point towards the trivalent cation. On the other hand, if the monovalent cation is smaller, such as in sodium alum, one gets γ -alum where S–O bonds point towards the B ion.

X-ray studies on α -alums have indicated that the sulphate groups have finite disorder at ambient conditions [22]. In the case of potash alum, space group symmetry allows *all* the S–O bonds to point either towards aluminium or towards potassium. Refinements of the alum structure have shown that a fraction of the sulphate groups have their S–O bonds pointing towards potassium (misoriented) while for the remaining sulphate groups the S–O bonds point towards aluminium (normal). Figure 1 shows two $\frac{1}{8}$ parts of the unit cell with sulphate ions in the normal or *correct* and the *misoriented* configurations. As a result of this orientational disorder, the potassium atoms towards which the misoriented S–O bonds are pointing are found to be *pulled* towards the anion centres from their ideal $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ positions. Consequently, the normal and the misoriented sulphate ions have slightly different S–O bond lengths. Orientational disorder in potash alum is found to manifest itself in the Raman spectra also in the form of the splitting of the nondegenerate symmetric stretching mode (ν_1) of the sulphate group [23]. For this compound, group theory predicts one mode of

A 4:1 methanol–ethanol mixture was used as the pressure-transmitting medium and the pressure inside the cell was measured using the standard ruby fluorescence technique. Raman spectra were excited using the 488 nm line of an argon-ion laser. Scattered light was analysed using a SPEX double monochromator and detected using a cooled photomultiplier tube operated in the photon-counting mode. Scanning of the spectra and data acquisition were carried out using a home-built microprocessor-based data-acquisition-cum-control system. Angle-resolved x-ray diffraction measurements were carried out using a Guinier diffractometer coupled to a rotating-anode x-ray generator and a position-sensitive detector. Silver powder was used as a pressure marker in the high-pressure XRD measurements. The Birch equation of state with values of $B_0 = 110.5$ GPa and $B'_0 = 4.6$ [25] was used for obtaining the pressure. The Guinier geometry adopted for the high-pressure measurements has proven sensitivity in detecting even low-intensity peaks [26]. In order to ensure reproducibility, measurements were repeated on a number of freshly fragmented pieces of single crystals of potash alum samples of each type.

4. Results

As mentioned earlier, the degree of orientational disorder in freshly grown samples is found to be different from that of the aged crystals. Figure 2 shows the Raman spectra of the two kinds of potash alum sample in the region of the symmetric stretching mode ν_1 of the sulphate ions. The main peak at 990 cm^{-1} (labelled as M) corresponds to the sulphate ions with S–O bonds pointing towards Al while the side-band at 975 cm^{-1} (labelled as D) arises due to the misoriented sulphate ions with S–O bonds pointing towards K. The ratio of the area under the 975 cm^{-1} peak to the total area under both the peaks is taken as the fraction of

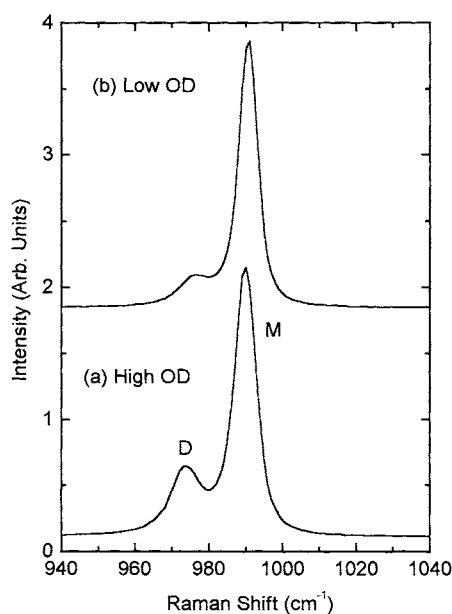


Figure 2. Ambient-pressure Raman spectra of potash alum samples of (a) high OD and (b) low OD in the ν_1 -mode region of the sulphate ion. The main peak at 990 cm^{-1} (labelled as M) arises due to sulphate ions with S–O bonds pointing towards Al, and the side-band at 975 cm^{-1} (labelled as D) arises due to the sulphate ions with S–O bonds misoriented towards K.

misoriented sulphate ions, i.e., the OD. In freshly grown crystals this fraction is found to be around 0.24, consistent with the x-ray results [22], whereas for aged crystals it reduces to 0.12 ± 0.02 .

4.1. Behaviour of samples with low disorder

In potash alum samples with low OD, the frequencies of the internal modes of the sulphate ions are found to increase monotonically with pressure up to 1.5 GPa. The symmetric stretching mode (ν_1) of the SO_4 ion in various crystals appears in the frequency range $940\text{--}1050\text{ cm}^{-1}$, whereas the asymmetric stretching mode (ν_3) lies in the region $1080\text{--}1200\text{ cm}^{-1}$, depending on the S–O bond length and the cation neighbourhood. Similarly, the symmetric and asymmetric bending modes, ν_2 and ν_4 , appear in the frequency ranges of $420\text{--}500$ and $600\text{--}680\text{ cm}^{-1}$ respectively. Figure 3 shows the Raman spectra of various internal modes of sulphate ions at various pressures. The OD increases from a value of 0.12 at ambient pressure to 0.3 at 1.5 GPa in the cubic phase (P_1). At 1.5 GPa, a new mode appears at 965 cm^{-1} . The intensity of the new mode increases rapidly at the expense of those at 975 and 990 cm^{-1} as a function of time. At still higher pressures, only this mode is present as the single strongest mode in the ν_1 -region. Discontinuous decreases in the mode frequencies of the Raman bands

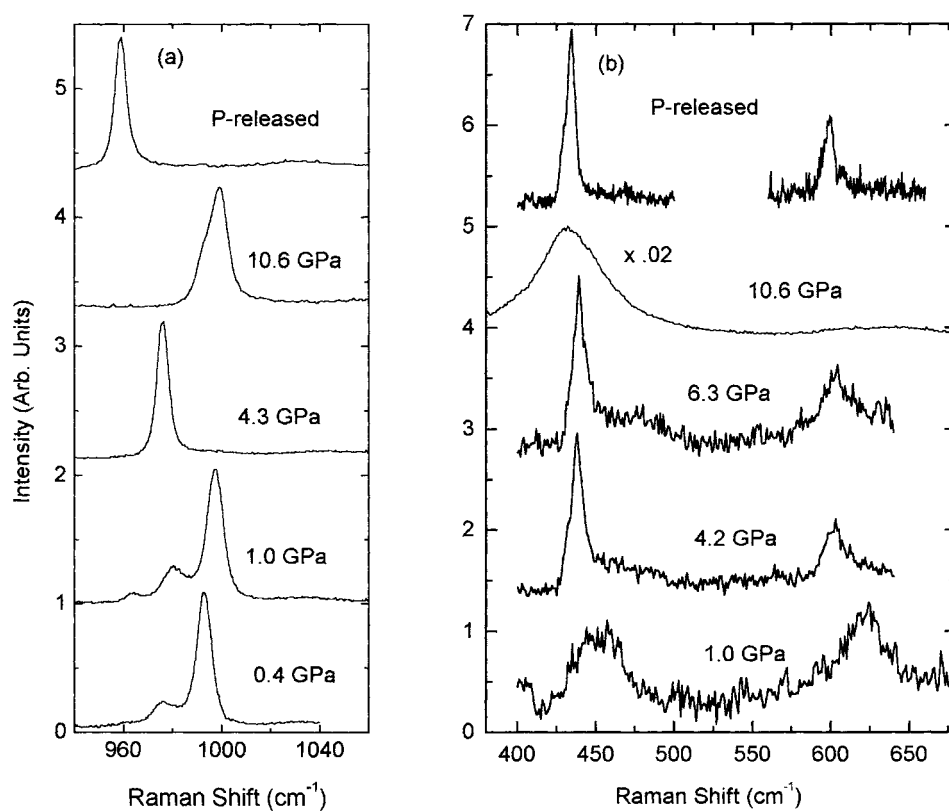


Figure 3. Raman spectra of the (a) ν_1 -modes and (b) ν_2 - and ν_4 -modes of sulphate ions in potash alum with low OD at various pressures.

are found in other regions also at around this pressure (see figure 3). These abrupt changes observed in the internal mode frequencies suggest a structural transition to a new phase—say P_{II} . It may be mentioned that in some of the runs, even at pressures below 1.5 GPa, there is a small but noticeable intensity at 965 cm^{-1} , indicating nucleation of the new phase P_{II} at lower pressures, as may be noted from figure 3 also. However, above 1.5 GPa only the mode at 965 cm^{-1} is present. The disappearance of the mode arising due to disorder and the emergence of a single sharp peak in the ν_1 -region suggest that the sulphate ions have a unique orientation in the new structure (disorder free). Further, compression of the S–O bond is known to increase the ν_1 -mode frequency. In view of this, a decrease of ν_1 -mode frequency across a phase transition implies that the S–O bonds of the sulphate ions in the new structure are relaxed. While the linewidths of the stretching (ν_1 and ν_3) modes do not change much, those of the bending (ν_2 and ν_4) modes are found to reduce across this transitions. It may be mentioned that a very weak (intensity about 2% of that of the 965 cm^{-1} peak) and broad peak at 1040 cm^{-1} is also observed in the P_{II} phase. The origin of this peak will be discussed later.

Upon increasing pressure further, the frequencies of all the internal modes increase in the β -phase up to 9 GPa. The width of the ν_4 -mode is found to increase rather monotonically in the P_{II} phase and no appreciable change in mode frequency is noted at around 9 GPa. Above this pressure, ν_1 develops a noticeable asymmetry towards the low-frequency side. Upon resolving ν_1 into two components, no noticeable broadening of the individual components is found up to 15.5 GPa, i.e., the full widths at half-maximum (FWHM) of these modes remain as 7 cm^{-1} over the pressure range investigated in the present study. In addition to the changes found in the ν_1 -region, the frequency of the ν_2 -mode is found to decrease, while its FWHM increases from 8 to 48 cm^{-1} above 9 GPa. The intensity of this mode increases severalfold while those of the ν_3 - and ν_4 -modes become too low to be followed above this pressure. These observations suggest another transition around 9 GPa to a further phase—say P_{III} . In view of this, the sequence of phase transitions in the low-disorder samples can thus be written as

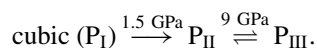


Figure 4 shows the pressure dependence of the mode frequencies in the samples with low OD. Note the discontinuous changes in the mode frequencies across the two transitions. During the pressure-reducing cycle, the $P_{II} \rightarrow P_{III}$ transition is found to be reversible, while the cubic phase (P_I) is not recovered upon releasing the pressure. This shows that the disorder-free P_{II} phase can be pressure quenched to ambient conditions [27].

4.2. Behaviour of samples with high disorder

Freshly grown single crystals of potash alum, which have OD around 0.24 ± 0.01 , were found to exhibit a completely different behaviour at high pressure as discussed below. The complete Raman spectra of these samples are investigated. Due to the large Rayleigh background, external and lattice modes could not be detected with sufficient intensity from the samples inside the DAC. Nevertheless, at ambient pressure, rather weak external modes were found. Similarly, upon pressurizing, the intensities of the ν_3 -modes are found to be too low for us to carry out any meaningful quantitative analysis. Figure 5 shows the Raman spectra of potash alum at various pressures in the ν_1 -, ν_2 - and ν_4 -regions of the sulphate internal modes at various pressures. The frequencies of all the modes are found to increase as functions of pressure. The intensity of the mode at 975 cm^{-1} is found to increase, implying that more and more of the sulphate ions are misoriented towards the potassium. If, guided by the positive pressure coefficient of the phase transition temperatures in a variety of systems [28], one treats the increase in pressure as being qualitatively analogous to a decrease in temperature,

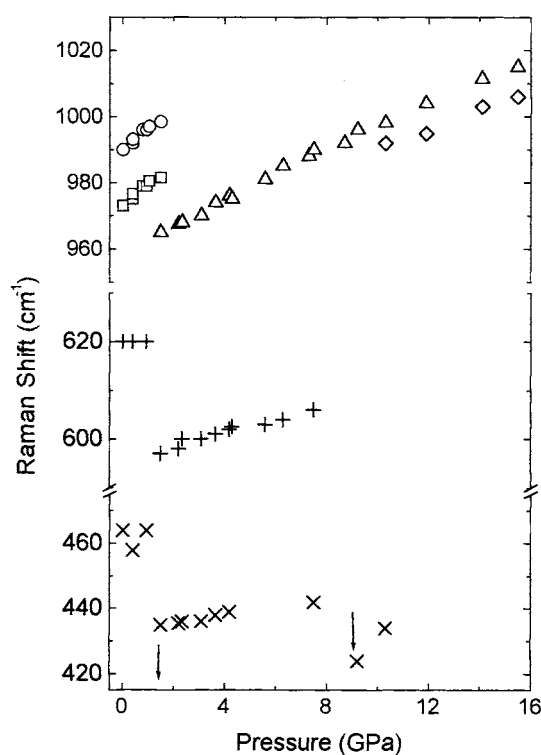


Figure 4. The pressure dependence of Raman mode frequencies in potash alum samples of low OD. Arrows indicate the phase transition pressures.

the increase in OD as a function of pressure is the 'opposite' of that reported as a function of temperature [24]. While carrying out the structure refinement of the alums, Larson and Cromer reported that as the size of the alkali cation reduces, the fraction of the reversed sulphate group increases [22]. In view of this, the behaviour of potash alum at high pressure may be viewed as a tendency to evolve towards the γ -alum.

At ambient pressure, modes M and D have FWHM of 6.5 and 9 cm^{-1} respectively and these do not show any change up to 4 GPa. Above 5 GPa, the linewidths of the individual components exhibit broadening, the rate of broadening of mode D being larger than that of mode M. More striking changes take place above 6.0 GPa where the two distinct peaks disappear and a very broad, nearly symmetric peak labelled as C appears. Figures 6(a) and 6(b) respectively show the pressure dependencies of the mode frequencies and the FWHM of modes M, D and C. Note from figure 6(a) that the two modes have nearly the same pressure coefficients, of about 5 $\text{cm}^{-1} \text{GPa}^{-1}$, and do not show any tendency to merge even up to 6.0 GPa. It is important to point out that even around 6.0 GPa, mode M could be resolved into two components separated by about 12 cm^{-1} (figure 6(a)). The appearance of a nearly symmetric peak with a FWHM of 24 cm^{-1} cannot be interpreted as arising from the combined width of the two individual components. Further, the Raman linewidths of the ν_2 - and ν_4 -modes are also found to increase abruptly at this pressure. Upon increasing the pressure further, the linewidth of the ν_1 -mode continues to increase from 24 cm^{-1} at 6.3 GPa to about 32 cm^{-1} at 10.4 GPa. Note that the pressure range in which the broadening takes place is well within the hydrostatic limits of the pressure-transmitting medium and hence broadening due to an inhomogeneous pressure

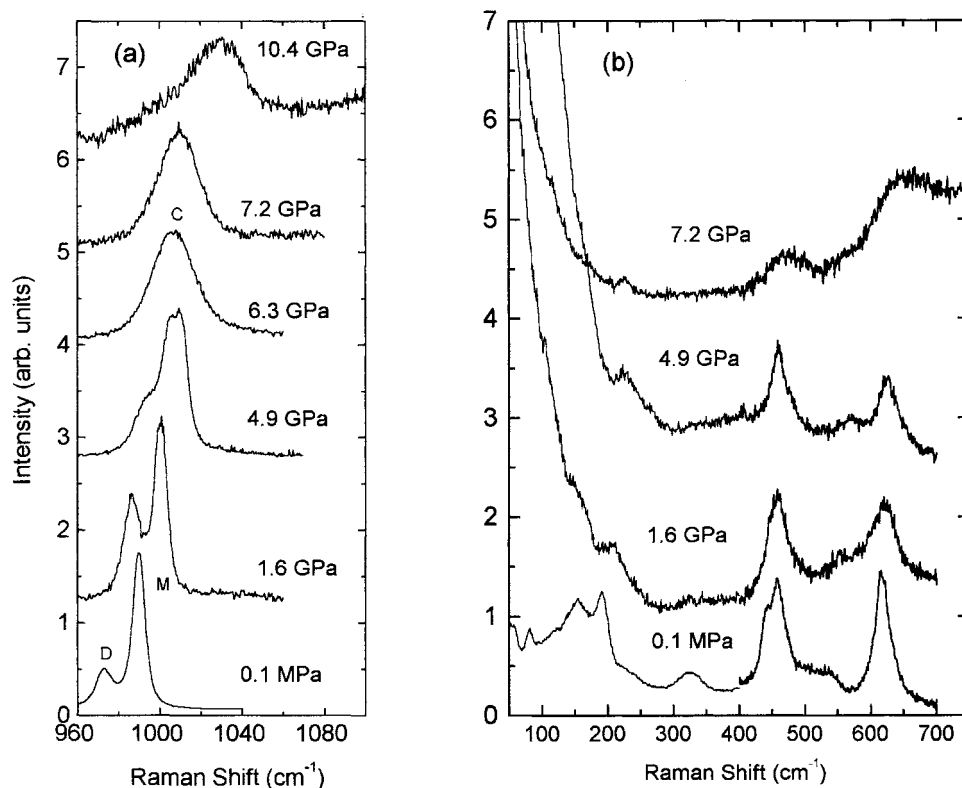


Figure 5. Raman spectra of potash alum samples with high OD in (a) ν_1 -regions and (b) ν_2 - and ν_4 -regions of internal modes of sulphate ions at various pressures. Above 6 GPa only one mode (labelled as C) is observed in the ν_1 -region.

distribution can be ruled out. Such an abrupt increase in the linewidths of the internal modes suggests a disorder in the system with a much broader distribution in the bond lengths and the bond angles of the molecular ions. This can arise if the system has turned amorphous due to a continuous growth of the OD. An increase of the linewidths of the internal modes by a factor of about four has often been found during the PIA [9,29]. Broadening of internal and external modes and disappearances of lattice modes are expected across crystalline–amorphous phase transitions, as the amorphous phase lacks periodicity. Amorphization has often been identified from spectroscopic techniques [8, 10] as well as from the disappearance of XRD peaks [8].

Figure 7 shows the evolution of the OD as a function of pressure. In some of the pressure runs, a rather weak and broad mode around 1040 cm⁻¹, similar to that found for low-disorder samples, was also observed at high pressures. This could arise due to a different kind of orientational configuration present in the samples whose origin will be discussed later. In such cases the total area under both of the disorder peaks (excluding the main peak at 990 cm⁻¹) was taken to correspond to the OD. Note that the OD increases with pressure in two stages and reaches saturation above 5 GPa, where the distinction between the modes M and the D ceases to exist. Thus the critical disorder at the onset of amorphization turns out to be around 0.75. As mentioned earlier, the OD of sulphate ions in potash alum has indeed been found to have an associated positional disorder of potassium atoms. Hence it is understandable that increasing the OD subsequently leads to positional disorder of the cation sublattice. Hence

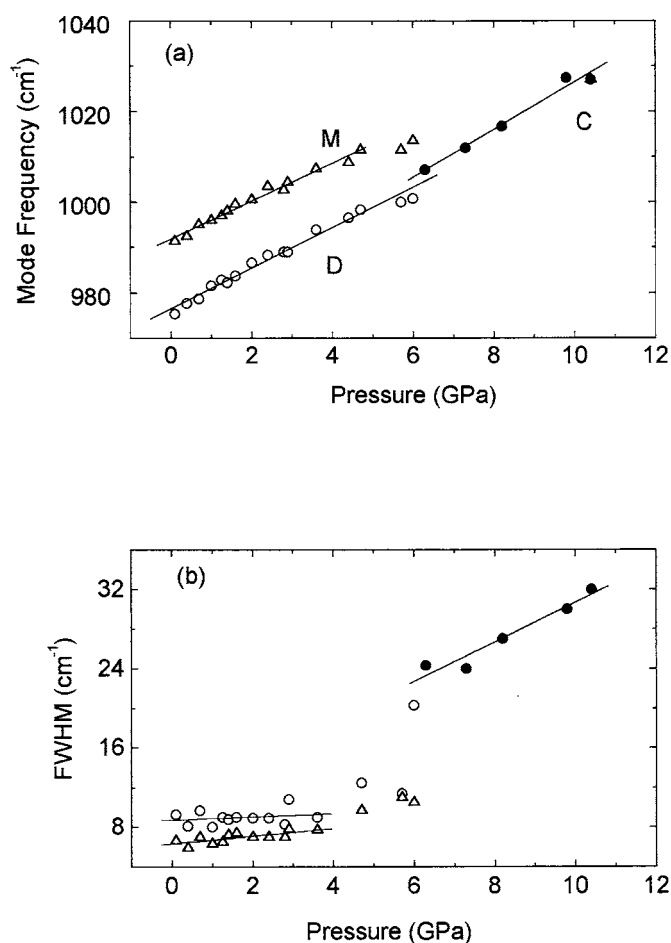
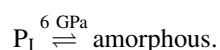


Figure 6. (a) Pressure dependences of ν_1 -mode frequencies in potash alum samples of high OD. Note that even just prior to amorphization, the mode separation remains the same. (b) Pressure dependences of the FWHM of the ν_1 -mode frequencies in potash alum.

the high-pressure behaviour of alum crystals with high initial disorder can be represented as



In order to determine whether the observed broadening of the Raman lines of the internal modes is really due to amorphization, angle-resolved x-ray diffraction measurements were carried out on this system up to 15 GPa. Figure 8 shows the diffraction pattern at several pressures. Note that sharp diffraction peaks are not found at pressures above 6 GPa; a rather broad intensity profile similar to that expected for an amorphous phase [30] is observed. It may be pointed out that broad diffraction peaks may also arise due to the existence of a poorly crystallized high-pressure phase as reported earlier in the case of AlPO_4 [14]. Conclusions regarding amorphization based on one technique alone may sometimes be misleading [8]; however, in view of the results obtained from the Raman spectroscopy and x-ray diffraction, we firmly believe that the present samples have undergone amorphization. Upon reducing the pressure, sharp diffraction peaks reappear. Some differences are found in the relative

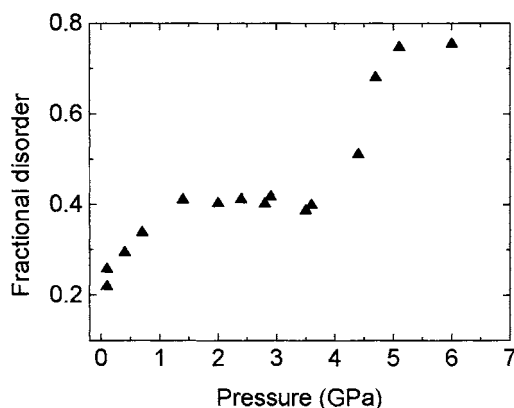


Figure 7. The variation of the orientational disorder of sulphate ions in potash alum samples with high OD as a function of pressure. Note the rapid increase in fractional OD above 4 GPa.

intensities of the diffraction peaks; however, the pattern could be indexed to the parent cubic phase P_I , indicating the reversibility of amorphization. Such intensity differences could arise due to preferred-orientation effects during recrystallization.

It is also possible to obtain further information about the bond-length distribution from the width of the stretching modes and about the bond-angle distribution from that of the bending modes. To a first approximation, the ν_1 -mode vibrational frequency of a tetrahedral ion is inversely correlated with the bond length, i.e., a decrease in bond length leads to an increase of ν_1 -mode frequency. An examination of the correlation of the average S–O bond lengths in several sulphate compounds and the corresponding ν_1 -mode frequencies has indicated a linear dependence [31]. A change in the average S–O bond length by 0.01 Å is found to result in a corresponding change in the ν_1 -mode frequency by 10 cm^{-1} . In view of this, one can visualize that a spread of ± 0.01 Å in the bond length would increase the FWHM by 10 cm^{-1} . Such an analysis has been used to get an estimate [32] of the distribution of bond lengths in the disordered phase of LiKSO_4 . In the present case, the values thus estimated show that the width of the distribution of bond lengths increases sharply to more than 0.02 Å at 6.3 GPa and subsequently to 0.03 Å at a pressure of 10 GPa.

While most of the samples with high initial disorder exhibited amorphization at around 6 GPa, a few of the fragmented single-crystal pieces underwent amorphization at 10 GPa via an intermediate transition at 3.1 GPa to a new phase—say P'_{II} —which was also found to be orientationally disordered:

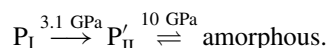


Figure 9 shows the Raman spectra of such crystals. The phase P'_{II} is distinguished from other phases by the presence of a sharp peak at 1004 cm^{-1} , a position in between those of peaks M and D, and broad peaks at 992 and 1040 cm^{-1} as seen in the 4.3 GPa spectrum. The sharp peak and the two broad peaks become better resolved as the pressure is increased to 9.6 GPa. The structural transition at 3.1 GPa also exhibited kinetics for several hours. Systems exhibiting intermediate phases prior to amorphization have been reported earlier also [9]. Upon reducing the pressure, the amorphization is found to be reversible; however, the original cubic phase is not recovered and the system remains locked in the P'_{II} phase. Note that the broad peak at 1040 cm^{-1} is still prominent even in the spectrum after releasing the pressure. Similar irreversibility upon decompression has been observed in NaVO_3 which also

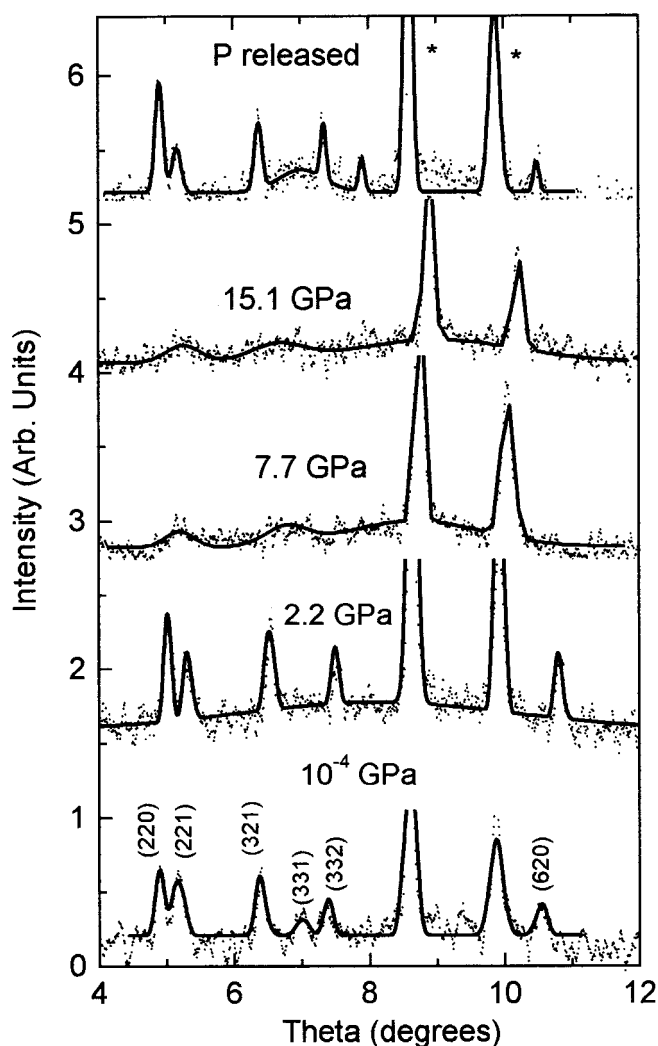


Figure 8. Angle-resolved x-ray diffraction patterns of potash alum samples with high OD at various pressures. Peaks marked with asterisks are due to pressure marks. Note the absence of sharp diffraction peaks in the pattern at 7.7 GPa. The reversibility of the amorphization is also confirmed by the reappearance of the diffraction peak.

amorphizes [33] at moderate pressures around 6 GPa. Thus all the samples with high OD are found to exhibit PIA. Those samples which exhibit an intermediate phase eventually amorphize at higher pressure than those that amorphize directly.

We now examine the origin of the 1040 cm^{-1} peak. This mode is most prominent in the intermediate P'_{II} phase of the high-OD samples, whereas it is extremely weak (intensity only 2% of that of the 965 cm^{-1} peak) in the P_{II} phase of the low-OD samples. In order to assign this peak, one must examine the sulphate-ion frequencies in other types of sulphate. In the case of double sulphates and di-sulphates the ν_1 -mode frequency is known to increase as the cation size reduces [34]. The highest ν_1 -mode frequencies are found in Li_2SO_4 [35] and LiKSO_4 [9]; these occur at around 1012 cm^{-1} . In KHSO_4 , where H is bonded to the

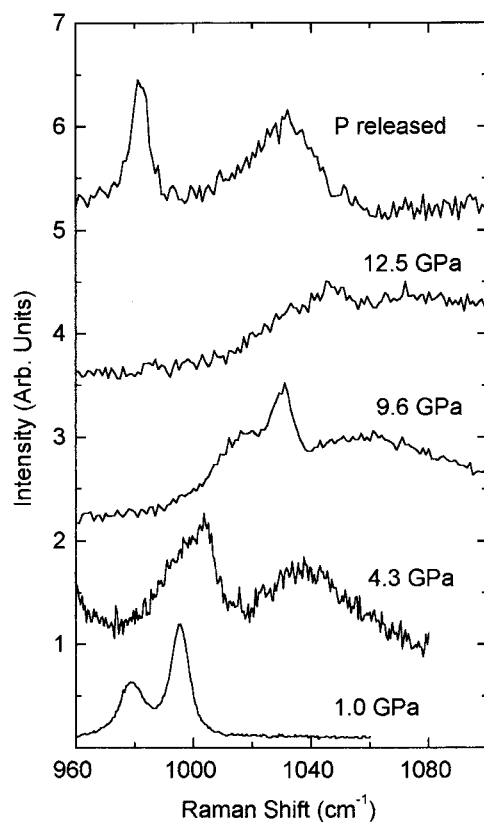


Figure 9. Raman spectra of the potash alum samples with high OD, which exhibit a transition to another phase at 3.1 GPa before amorphization at 10 GPa, at different pressures (see the text).

sulphate ion, ν_1 is found [36] to be around 1040 cm^{-1} . In the case of potash alum, there are water octahedra around both the cations. In view of this, it is likely that the hydrogens of some of the water molecules may be so oriented with respect to SO_4 that an HSO_4 -like bonding (a different orientational configuration) evolves at high pressure. This suggests that the hydrogen atoms of some of the water molecules are also shared by sulphate ions in the formation of HSO_4 -like units. Although the transformation of SO_4 to HSO_4 is not 100%, the present scenario is analogous to hydrogen bonding. In view of these results, it appears that hydrogen bonding might play a significant role in polymorphism in alums at high pressure. The appearance of this new configuration only in some of the samples may either be due to slightly different orientation of the water octahedra around the cations or be due to marginal differences in the magnitudes of the OD in high-disorder samples. In summary, the low-disorder samples undergo only structural transitions, while those with high disorder exhibit amorphization irrespective of the path chosen.

5. Discussion

As mentioned earlier, a number of compounds with strongly bound polyatomic groups/ions such as sulphates [9], molybdates [37] and germanates [38] are reported to amorphize at high pressure. Earlier reports of OD in the high-pressure crystalline phases of LiKSO_4 prior to

amorphization [16] led to speculation that OD could be responsible for amorphization [19]. A mechanism of amorphization involving the coupling of the positional disorders of various sublattices and the orientational disorder has also been proposed [9]. From the completely different behaviour of potash alum samples with different initial disorders, it unambiguously emerges that OD can indeed drive amorphization at high pressures.

It may be mentioned that the amorphous solids are considered to be metastable. In addition to the application of high pressure, amorphous solids are also produced by rapid solidification of melts and directly from crystalline solids by subjecting them to extreme conditions such as mechanical alloying [39], irradiation [40], hydrogen charging [41] and interfacial interdiffusion [42]. These methods invariably induce sufficient chemical disorder or defect density. Loss of long-range order occurs when the positional disorder (displacement from equilibrium positions) is more than a critical fraction of the interatomic distance. In the context of understanding the phenomenon of solid-state amorphization (i.e., amorphous phases produced without fusion and resolidification), Fecht has argued [43] that an isentropic condition limits the stability of a crystal as a function of defect concentration. Beyond a certain defect concentration, the crystal melts into a liquid if the temperature is above the glass transition temperature, whereas below that, it becomes an amorphous solid. Irradiation-induced amorphization has also been understood on the basis of a critical disorder model [44]. The present results also indicate that amorphization occurs beyond a critical disorder, which is orientational in nature. A comparison of the high-pressure behaviour of the low- and high-OD samples further suggests that the phase P_{II} is probably the stable high-pressure structure for potash alum. The remarkable result of the present study is the striking difference in high-pressure behaviour between samples with different initial disorders. While the transition $P_I \rightarrow P_{II}$ could proceed in the case of samples with low OD, the transition is impeded in those cases with high OD, resulting in an amorphous/highly disordered phase. Hence, one can conclude that the observed PIA in the present case is primarily entropy driven.

In order to understand the factors which may lead to widely different degrees of OD in freshly grown and aged single crystals of potash alum, we first consider the 12 water molecules constituting the water of crystallization. It is likely that the water of crystallization may change upon aging. The structures of the compounds with different waters of crystallization could also be different. For example, potash alum with $12H_2O$ is cubic, that with $11H_2O$ is monoclinic, while the anhydrous alum has a hexagonal structure [45] very similar to that of $LiKSO_4$. In order to examine whether the two different behaviours in the samples with low and high OD arise from any possible changes in the water of crystallization resulting from storage, Raman spectra of both types of sample were recorded for the O–H stretching mode region. Figure 10 shows the Raman spectra of these samples in the O–H stretching mode region. Differences are seen in the linewidths and relative intensities of the bands, suggesting possible redistribution of water molecules around the cations. In order to look for a possible correlation between the water of crystallization and the OD of sulphate ions, the total area under the curve of the low- and high-OD samples in the O–H stretching mode region is compared after normalizing with respect to the total area under the curve for the stretching modes of sulphate ions. Though such a comparison cannot give the absolute amount of water of crystallization, information about the relative changes can be obtained. The integrated intensity of the O–H stretching mode is found to be higher for low-OD samples as compared to the samples with high OD. If one assumes that the integrated O–H band intensity is proportional to the number of water molecules in the samples, the present results suggest that the water of crystallization in low-OD samples is marginally higher (about 0.083 ± 0.008) than that in high-OD samples. On the other hand, the OD in the two batches of samples are found to be widely different. This suggests that the difference in magnitude of OD between the two types of sample cannot solely arise

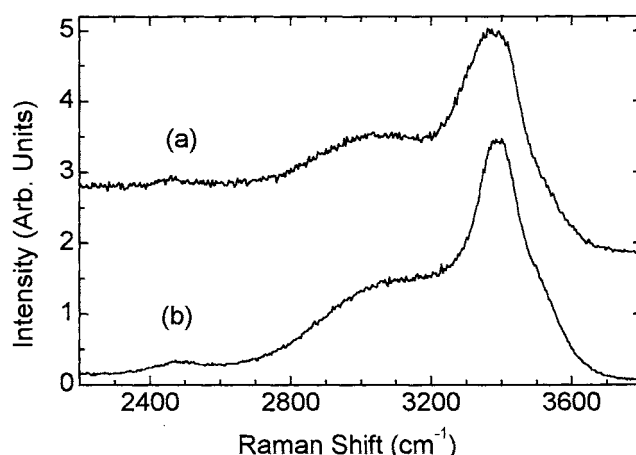


Figure 10. Raman spectra of potash alum in the O–H stretching mode region of the water molecules in (a) low-disorder and (b) high-disorder samples.

due to the difference in the water of crystallization. Hence it is reasonable to consider the OD in the two samples to be composed of a static (defect-related) and a dynamic part. It is important to point out that by doing so it is also possible to quantitatively interpret the reported departure of the area ratio from the Arrhenius law without invoking an *ad hoc* temperature-independent cooperative reorientation mechanism [24] for pairs of sulphate ions. The dynamic part, which represents the thermal equilibrium between the two orientations in the absence of defects, is expected to disappear at low temperatures [23]. Hence we estimate the fraction of static OD in the high-OD samples by extrapolating the reported [24] temperature dependence of the OD to 0 K. The fractions of sulphate ions exhibiting static and dynamic disorders in high-OD samples turn out to be 0.14 and 0.10 ± 0.01 respectively. The dynamic disorder is expected to be the same for both types of sample. In view of this, the static disorder in low-OD samples appears to be rather low ($\sim 2\%$) and most of the disorder happens to be dynamic in nature. Aging of samples at ambient conditions probably anneals the defects and leads to more perfect crystals. The opposite correlation of the O–H intensity with the OD suggests that the defect could be a missing water molecule around one of the cations. As mentioned earlier, the water octahedron around K is bigger than that around Al. In view of this, it is likely that the vacancy (defect) related to the water octahedron is located at a potassium site rather than at an aluminium site. The presence of this defect could create a sufficiently deep potential minimum in the orientational space for the S–O bond, leading to a permanent trapping of a sulphate ion in that orientation. In order to find out whether the observed difference in water of crystallization between the two samples has also led to a change in the ambient structure, powder x-ray diffraction measurements were carried out on both batches of samples. Small differences in the relative intensities of some of the reflections were found; however, the two-theta values agree very well and both sets of data could be fitted to the cubic (T_h^6) structure with a good figure of merit. These results also suggest that changes in the water of crystallization are only marginal—not sufficient to change the ambient structure.

The present model of a defect (a water vacancy around potassium) leading to static disorder is based on the assumption that the integrated intensity of the O–H band represents the total water of crystallization. However, it is also likely that the presence of some other kind of defect around the K ion may cause changes in the polarizability of the OH vibration, leading to

different intensities of the O–H band. In such a case, there is no need to consider the waters of crystallization in the two samples to be different; nevertheless, one can certainly conclude that whatever the nature of the defect, prolonged aging at ambient conditions leads to a decrease in the concentration of such defects.

The reversibility of this PIA suggests that the atomic arrangements in the amorphous and in the cubic phase are closely related, involving distortions and tilting of the polyatomic group, consequently leading to disorder in the cation and anion positions. Reversibility has been reported in other systems such as $\text{NaLa}(\text{MoO}_4)_2$ [37] and $\text{Ca}(\text{NO}_3)/\text{Na}(\text{NO}_3)$ [46] also. The amorphization is expected to be reversible wherever it does not involve breaking/forming of new bonds [31]. On the other hand, results on low-disorder samples suggest that cubic alum structure is unstable at high pressure against transformation to a stable disorder-free structure. It is interesting to note that the presence of a moderate amount of static disorder stabilizes the cubic alum structure, as found from the present studies.

6. Summary and conclusions

To summarize, the present investigations clearly show that the cubic alum structure is not stable at high pressures. Samples with low OD undergo structural transformation to a disorder-free phase at 1.5 GPa irreversibly. This phase is found to be stable up to 9 GPa. No signatures of disorder or amorphization are seen up to 15.5 GPa in these samples. On the other hand, samples with high OD remain in the cubic phase and subsequently become amorphous upon further pressurizing. This PIA in potash alum appears to be primarily entropy driven, with the static orientational disorder of the sulphate ion acting as defects in the alum structure. The different high-pressure behaviours of these two types of sample indicate the presence of a critical OD beyond which transition to other crystalline phases is impeded.

Acknowledgments

The authors gratefully acknowledge Dr G V N Rao for XRD characterization of the low- and high-disorder potash alum samples and Dr K G Rajan for making available the high-pressure XRD facility. The authors also thank Dr T S Radhakrishnan for keen interest in the work, and Dr Baldev Raj for support and Dr P Rodriguez for encouragement.

References

- [1] Mishima O, Calvert L D and Whalley E 1984 *Nature* **310** 393
- [2] Shekar N V C, Yousuf M, Sahu P Ch, Mahendran M and Rajan K G 1993 *Pramana* **40** 367
- [3] Hemley R J, Chen L C and Mao H K 1989 *Nature* **338** 638
- [4] Mishima O 1996 *Nature* **384** 546
Serghiou G C and Hammack W S 1993 *J. Chem. Phys.* **98** 9830
- [5] Demishev S V, Ischenko T V, Blundell S J and Singleton J 1997 *J. Phys.: Condens. Matter* **9** 9199
- [6] Sharma S M and Sikka S K 1996 *Prog. Mater. Sci.* **40** 1
- [7] Hemley R J, Jephcoat A P, Mao H K, Ming L C and Manghanani M H 1989 *Nature* **334** 52
- [8] Kruger M B and Jeanloz R 1990 *Science* **249** 647
- [9] Arora A K and Sakuntala T 1992 *J. Phys.: Condens. Matter* **4** 8697
- [10] Kruger M B, Williams Q and Jeanloz R 1989 *J. Chem. Phys.* **91** 5910
- [11] Sugai S 1985 *J. Phys. C: Solid State Phys.* **18** 799
- [12] Chaplot S L and Mukhopadhyay R 1986 *Phys. Rev. B* **33** 5099
- [13] Hazen R M, Finger L W, Hemley R J and Mao H K 1989 *Solid State Commun.* **72** 507
- [14] Gillets P, Badro J, Varrel B and McMillan P F 1995 *Phys. Rev. B* **51** 11 262
- [15] Teeter D M, Hemley R J, Kresse G and Hafner J 1998 *Phys. Rev. Lett.* **80** 2145

- [16] Arora A K and Sakuntala T 1990 *Solid State Commun.* **75** 855
- [17] Sashikala M N, Chandrabhas N, Jayaram K, Jayaraman A and Sood A K 1993 *J. Raman Spectrosc.* **24** 129
- [18] Sashikala M N, Chandrabhas N, Jayaram K, Jayaraman A and Sood A K 1994 *J. Phys. Chem. Solids* **55** 107
- [19] Arora A K and Sakuntala T 1992 *Recent Trends in High Pressure Research* ed A K Singh (New Delhi: Oxford-IBH) p 262
- [20] Sakuntala T, Arora A K, Shekar N V C and Sahu P Ch 1998 *Europhys. Lett.* **44** 728
- [21] Wyckoff R W G 1963 *Crystal Structure* 2nd edn, vol 3 (New York: Wiley)
- [22] Larson A C and Cromer D T 1967 *Acta Crystallogr.* **22** 793
- [23] Eysel H H and Schümacher G 1977 *Chem. Phys. Lett.* **47** 168
- [24] Sood A K, Arora A K, Dattagupta S and Venkataraman G 1981 *J. Phys. C: Solid State Phys.* **14** 5215
- [25] Liu L and Bassett W A 1973 *J. Appl. Phys.* **44** 1475
- [26] Sahu P Ch, Yousuf M, Shekar N V C, Subramanian N and Rajan K G 1995 *J. Alloys Compounds* **223** 49
- [27] Arora A K and Sakuntala T 1994 *14th Int. Conf. on Raman Spectroscopy* ed N T Yu and X Y Li (Chichester: Wiley) p A277
- [28] Fujimoto S, Yasuda N and Hibino H 1984 *Phys. Lett. A* **140** 42
- [29] Klug D D, Mishima O and Whalley E 1986 *Physica B* **139+40** 475
- [30] Fujii Y, Kowaka M and Onodera A 1985 *J. Phys. C: Solid State Phys.* **18** 789
- [31] Arora A K 1997 *Advances in High Pressure Science and Technology* ed M Yousuf, N Subramanian and K G Rajan (Hyderabad: Hyderabad University Press) p 162
- [32] Arora A K 1996 *15th Int. Conf. on Raman Spectroscopy* ed S A Asher and P B Stein (Chichester: Wiley) p 1056
- [33] Shen Z X, Ong C W, Tang S H and Kuok M H 1994 *Phys. Rev. B* **49** 1433
- [34] Sakuntala T 1997 *PhD Thesis* University of Madras
- [35] Sakuntala T and Arora A K 2000 *Physica B* **279** 282
- [36] Sakuntala T and Arora A K 1998 *Rev. High Pressure Sci. Technol.* **7** 373
- [37] Jayaraman A, Wang S Y and Sharma S K 1995 *Solid State Commun.* **93** 2356
- [38] Li Y and Lan G 1997 *J. Phys. Chem. Solids* **58** 789
- [39] Eckert J, Schulz L and Urban K 1991 *J. Mater. Res.* **6** 1874
- [40] Nair K G M, Vijayalakshmi M and Krishan K 1993 *Scr. Metall.* **29** 913
- [41] Samwer K, Fecht H J and Johnson W L 1994 *Glassy Metals III* ed H Beck and H J Güntherodt (Heidelberg: Springer) p 5
- [42] Johnson W L 1986 *Prog. Mater. Sci.* **30** 81
- [43] Fecht H J 1992 *Nature* **356** 133
- [44] Riviere J P 1977 *Radiat. Eff.* **33** 21
- [45] *Powder Diffraction File* 1982 JCPDS International Center for Diffraction Data, Swarthmore, PA, cards # 3-337 and # 17-133
- [46] Winters R R, Serghiou G C and Hammack W S 1992 *Phys. Rev. B* **69** 3751