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Pressure induced amorphization of $AlPO_4$

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Abstract. $AlPO_4$ has been compressed to pressures of 16 GPa in a diamond anvil cell and its X-ray diffraction pattern studied by the energy-dispersive technique. The compound is observed to become amorphous at ~ 12 GPa. This explains the loss of Raman spectrum of $AlPO_4$ reported by Jayaraman and coworkers (1987).

Keywords. Pressure-induced amorphization; $AlPO_4$; coordination tetrahedra; high-pressure energy-dispersive X-ray diffraction.

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1. Introduction

Several methods are now known that can induce a direct solid-state transition from a crystalline to an amorphous state: inter-diffusion, radiation damage and mechanical alloying (see a recent review by Johnson 1986). During the last five years the pressure variable has been added to this list. Pressure induced amorphization has so far been observed in ice (Mishima *et al* 1984), SnI_4 (Fujii *et al* 1985) TCNE (Chaplot *et al* 1986), $LiKSO_4$ (Sankaran *et al* 1988), SiO_2 (quartz and coesite polymorphs, Hemley *et al* 1988), $CaAl_2Si_2O_8$ (Williams and Jeanloz 1989), $Ca(OH)_2$ (Kruger *et al* 1989), Fe_2SiO_4 (Williams *et al* 1989) and a quasicrystal, Al_6Li_3Cu (Akahama *et al* 1989). These transitions are believed to be a response to the severe structural strains that come about with increasing pressure. In $LiKSO_4$, this transition has been attributed to the extreme distortion of the six-membered tetrahedral rings which are unable to conform to the size constraints of the very compressible potassium-oxygen linkages. In SiO_2, the onset of amorphization coincides with the bending of inter-tetrahedral Si–O–Si angle to 120° (Hazen *et al* 1989). To further check these stereochemical conjectures, we have now carried out high pressure X-ray diffraction experiments on $AlPO_4$. This compound is isostructural to SiO_2 with Al and P atoms replacing Si atoms in two adjacent tetrahedra. As a function of temperature, it exhibits a number of polymorphs similar to SiO_2 – quartz, tridymite and cristobalite. In the room temperature berlinite form, the Al–O–P angle is 142° (Thong and Schwarzenbach 1979), close to the value in the analogous quartz form of SiO_2. $AlPO_4$ is also found to exist in the amorphous form at ambient conditions. It seems likely that as in SiO_2, a crystal to amorphous phase change will occur in $AlPO_4$ too, at high pressures. The disappearance of the Raman spectrum of $AlPO_4$, above 12 GPa, reported by Jayaraman *et al* (1987) may be an indication of this.

2. Experimental

$AlPO_4$ in the berlinite form was prepared by A J Singh (Chemistry Division, BARC) by the hydrothermal bomb technique. Powder particles of the compound were placed in the gasket hole (of diameter $\sim 150\,\mu m$) in a hardened inconel foil, and subjected to pressure in a Syassen-Holzapfel diamond cell. A 16:3:1 mixture of methanol, ethanol and water, which remains hydrostatic up to 14·5 GPa and quasihydrostatic thereafter up to 20 GPa (Fujishiro *et al* 1981) was used as the pressure transmitting fluid. Pressure was estimated by monitoring the peaks of Au powder mixed with the sample. The equation of state of Au ($B_0 = 167 \pm 11$ GPa, $B_0' = 5{\cdot}5 \pm 0{\cdot}8$ GPa at room temperature, Heinz and Jeanloz 1984) was used to determine the corresponding pressure. A continuous spectrum of X-rays from a rotating copper anode X-ray generator, operating at 44 kV × 45 mA was used for recording energy dispersive X-ray diffraction patterns. The diffracted beam was collected over the full Bragg cone, of angle $\theta = 6{\cdot}1°$, by a 35 mm intrinsic Ge detector. More details of the experimental method can be found in Sikka *et al* (1989).

3. Results and discussions

Figure 1(a) shows the diffraction pattern at room pressure. It can be explained by the known structure of berlinite (space group $P3_121$, with a $c/2a$ of 1·107, Thong and Schwarzenbach 1979). Further, compression resulted in the increase of $c/2a$, which in analogy with quartz, is an indication that the Al–O–P angle is decreasing with pressure. At a pressure ~ 12 GPa, the diffraction peaks of $AlPO_4$ vanished, indicating that the compound had lost crystalline order (figure 1c).

The diffraction peaks of Au, which were as prominent as earlier, served the dual purpose of providing a measure for pressure, and of confirming that the disappearance of the spectrum of $AlPO_4$ was due to some intrinsic change within the sample, and not due to an experimental error like misalignment of the cell or displacement of sample from the gasket hole.

$AlPO_4$ reverted to crystallinity on the release of pressure, for then the diffraction pattern reappeared. This observation is similar to that of SnI_4, $LiKSO_4$ and $Ca(OH)_2$ which also show a reversible crystal to glass transition. Further, the pressure of amorphization ~ 12 GPa, is close to that of quartz, suggesting that the decrease of Si–O–Si and Al–O–P angles is similar.

The loss of long range order and reversibility of the crystal-amorphous transitions can generally be understood on the basis of a three level energy diagram of the kind shown in figure 2. For such a system, in order to create an amorphous state, a crystalline solid has to be driven into a high energy state (Go). The free energy of this state can be lowered either by the formation of a metastable amorphous phase (Ga) or the formation of the more energetically favoured crystalline phase (Gc). However, the kinetics of the system is such that though the transition from Go to Gc brings the system to a lower energy, the transition from Go to Ga is favoured. In most cases, the phase Gc can be identified as one in which the coordination number of the cation is higher. The changes in the inter-tetrahedral angle facilitate this increased coordination. To attain the new crystalline phase Gc, some atomic rearrangements are necessary. The low temperature of the experiments, however, precludes these

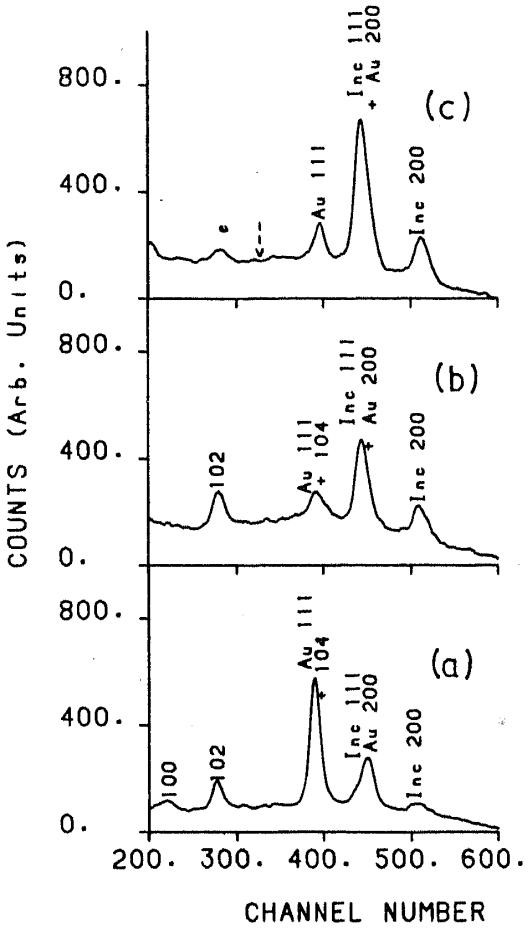

Figure 1. EDXRD pattern of $AlPO_4$ (**a**) ~ 0·1 GPa (**b**) 2·5 GPa (**c**) 14 GPa.

Note that in (**b**) the 111 peak of Au and the 104 peak of $AlPO_4$ occur very close, and thus the composite peak appears very broad. In (**c**), where the sample no longer contributes to the crystalline pattern, this peak is noticeably sharper. '*e*' denotes the escape peak. The arrow in 1 (**c**) shows the position where the 102 peak of $AlPO_4$ is expected.

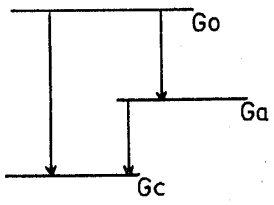

Figure 2. The three-level energy diagram which explains the pressure-induced crystal-to-amorphous transition. The kinetic conditions require $\tau_{0\to a} \ll \tau_{0\to c}$ and $\tau_{0\to a} \ll \tau_{a\to c}$.

motions, with the consequence that the system attains a lower energy by losing long range order.

A further confirmation of this picture in $AlPO_4$ will come with the discovery of the stishovite like form of $AlPO_4$.

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