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XAS Study of the High Pressure Behaviour of Quartz-Like Compounds

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Abstract. EXAFS spectroscopy experiments have been carried out on quartz-like α -GaAsO₄ and α -AlAsO₄ at high pressure and room temperature. It has been shown that these materials exhibit two structural phase transitions; the first transition to a high pressure crystalline form occurs at 9 GPa and is reversible upon decompression, whereas the second transition occurs at higher pressures and is irreversible. In α -GaAsO₄, EXAFS measurements agree with the predicted transition from four- to six-fold coordination of oxygen atoms around the cations, but the two local coordination transformations are *not* dissociated; in fact, both As and Ga atoms exhibit a coordination change at the onset of the *first* phase transition, the rate of transformation being significantly higher for Ga atoms. In both cases, the average bond length increases very rapidly with pressure thus yielding the first compression stage after the transition. In the second stage, the average bond lengths increase slowly, ultimately reaching six-fold coordination above 28 GPa and 24 GPa for As and Ga respectively. The behaviour of the As K-edge EXAFS is the same for both compounds, and enables us to link the behaviour of Ga and Al atoms. The local transformations are well described and a direct link with phosphate berlinites seems timely.

1. Introduction

Quartz and quartz-like compounds are among nature's most interesting minerals, because their various structures in different regions of thermodynamic phase space are simple yet common ones. The low pressure polymorphs consist of tetrahedrally coordinated cations whereas the higher pressures forms have octahedral cation arrangements, in which oxygen atoms are packed in a body-centred cubic (bcc) sublattice around the cations. At room temperature, the kinetics of these four- to six-coordinated transitions are very slow leading to a pressure-induced amorphization (PIA) process in quartz. This phenomenon has been observed by different probes¹⁻⁴ on the SiO₂ system. The room temperature compression and PIA of isostructural α -GeO₂ has also been studied by X-ray diffraction and EXAFS spectroscopy⁵ and the study has shown that germanium coordination increases from four to six through the crystal-to-amorphous transition. Molecular dynamics (MD) simulations⁶⁻¹⁰ have shown that changes in the local structure during the transition in quartz are very similar to those observed in GeO₂.

In quartz-like berlinites, it was first thought that α -AlPO₄ exhibited the same room temperature and high pressure behaviour as quartz¹¹, and underwent PIA at 15 GPa. A later Raman scattering study¹² as well as Brillouin spectroscopy measurements¹³ have shown that this transition is not a PIA, but a polymorphic crystalline phase transition, the high pressure form being very poorly crystallized, and therefore yielding very poor X-ray diffraction patterns. MD simulations associate the transition with a destabilization of the AlO₄ tetrahedron and its transition towards an AlO₆ octahedron; they also have concluded that PIA would occur only when the PO₄ tetrahedra became unstable, at a predicted pressure of 80 GPa, which has not yet been produced experimentally using AlPO₄. *In-situ* EXAFS experiments were performed¹⁴ on an isostructural compound, GaPO₄, at the Ga K-edge, and the polymorphic phase transition observed at 12 GPa is associated with a four- to six-fold oxygen coordination change around gallium atoms.

2. Experimental

Quartz-structured aluminium and gallium arsenate powders were used for this high pressure dispersive EXAFS study. The samples were loaded in a stainless steel inconel gasket with a 250 μ m hole diameter and 50 μ m thickness and high pressures were generated by a membrane driven diamond anvil cell (DAC). Silicon oil was used as a pressure transmitting medium, and ruby fluorescence was used as a pressure gauge. The measurements were carried out on the D-11 dispersive^{15,16} EXAFS beamline on the DCI storage ring of the LURE synchrotron facility in Orsay, France. Each absorption measurement was accumulated for 32 times and 3.5 seconds each, and was followed by the collection of a spectrum of a GaAs sample in order to insure edge energy stability.

3. Results and Discussion

3.1. $GaAsO_4$

EXAFS spectra at the Ga and As K-edges show a very interesting pattern with increasing pressure (fig. 1); a first polymorphic transition¹⁷ occurs around 9 GPa and is observed for *both* Ga and As. The average Ga-O distance rises rapidly and then levels off above 12 GPa corresponding to an octahedral arrangement of gallium atoms. Meanwhile, the As-O mean distance also increases between 9 and 12 GPa at which point another compression regime appears and the As-O bond lengthens in a slower manner, until a plateau is reached at about 25 GPa. These distance variations are related to the rate of transformation from 4-fold to 6-fold coordinated cations; the arsenic atoms have two transformation regimes, the second being much slower because the six-coordinated structure of gallium atoms renders the system less compressible. This would therefore imply that the coordination of both As and Ga atoms transform at 9 GPa, and that the Ga 4-to-6 transformation is faster, permitting the As 4-to-6 transformation to continue up to 25 GPa. At this pressure, the system consists of a pseudo-rutile type structure, the XANES spectra for As and Ga atoms being very similar to the XANES spectrum of GeO_2 at high pressure⁵. A recent X-ray diffraction study¹⁸ by Clark *et al.* has shown that the intermediate crystalline phase can be indexed in a triclinic (yet very close to orthorhombic) structure. It was pointed out that this phase has 2/3 of the cations in 6-fold coordination and the rest in 4-fold. Our EXAFS measurements concur with this result and it can be added that in this particular case, all Ga atoms are in six-fold coordination whereas a smaller portion of As atoms are in octahedral coordination.

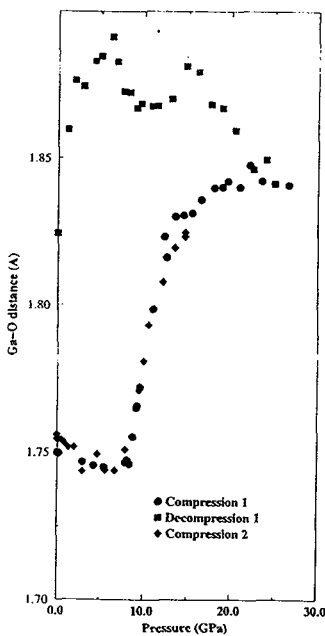


Figure 1a: Ga-O average distance from Ga K-edge EXAFS on $GaAsO_4$ as a function of pressure

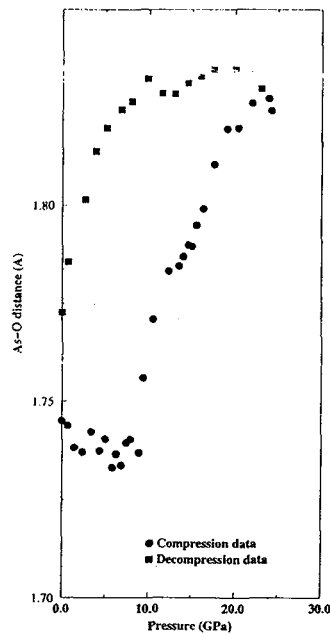


Figure 1b: As-O average distance from As K-edge EXAFS on $GaAsO_4$ as a function of pressure

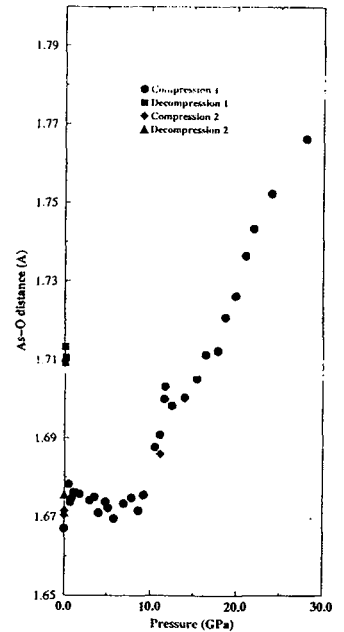


Figure 2: As-O average distance from As K-edge EXAFS on $AlAsO_4$ as a function of pressure

In a $GaAsO_4$ sample quenched from 15 GPa, after all Ga atoms have become six-fold coordinated and before all As clusters turn into octahedra, the Ga atoms undergo a back-transformation to a tetrahedral arrangement with partial amorphization of the sample, whereas the sample decompressed from 25 GPa has a much more complex history and shows amorphous character after decompression, mainly consisting of octahedral configurations.

3.2. $AlAsO_4$

A recent X-ray diffraction study¹⁹ has shown that $AlAsO_4$ undergoes a crystal-to-crystal phase transition between 7.6 and 8.4 GPa. This study also claimed that the high pressure crystalline phase undergoes PIA between 8.4 and 9.4 GPa. Our X-ray diffraction and Raman scattering experiments disagree with these conclusions. In fact, Raman scattering on single crystals as well as X-ray powder diffraction clearly agree with the first crystal-to-crystal transition between 8.5 and 9.5 GPa, but crystalline reflections of the high pressure phase are observed up to 35 GPa and Raman spectra show new crystalline features between 9.6 and 13.3 GPa.

The As K-edge EXAFS show a rapid increase in As coordination between 9 and 12 GPa (fig. 2) followed by a lightly less rapid rise in As-O distance up to 28 GPa, exactly as seen in $GaAsO_4$. A direct comparison with $GaAsO_4$ in which both cations can be monitored by in-situ EXAFS, would imply that Al coordination should rise rapidly from 4 to 6 and should level off at about 12 GPa at which point only As coordination increases ultimately reaching a value of 6. Upon decompression, the transition is reversible below 13 GPa and becomes irreversible above this pressure.

4. Conclusions

We have shown that both aluminium and gallium arsenate undergo two phase transitions at high pressure and 300 K. The first transformation is a crystalline polymorphic phase transition and is associated, as opposed to phosphates¹⁷, with a local transition from four- to six-fold coordination of *both* cations. The second transition occurs over a large pressure domain, for it is not a usual first order transformation, but a PIA, and starts slightly above the point where one of the cations reaches complete six-fold coordination. As with quartz, samples decompressed from these pressure domains are more or less amorphous, depending on the maximum pressure reached. The first transition is locally reversible yet producing some amorphous material, whereas the second transition leading to a 'pressure glass' is not.

The destabilization of tetrahedral clusters in both $GaAsO_4$ and $AlAsO_4$ has been demonstrated by in-situ EXAFS, and is in good agreement with MD studies on berlinite. Experimental and numerical studies are converging on the reversibility of the first transition; the remaining tetrahedral clusters (PO_4 for phosphates, and AsO_4 for arsenates) seem to form an undeformed sublattice that forces the transformed octahedra back into their original positions when pressure is released. In the case of arsenates, if these strong clusters are transformed into octahedra, the back-transformation is not possible for the driving force has vanished, and the systems becomes amorphous. In the case of phosphates, the critical pressure needed to destabilize the PO_4 tetrahedra has not yet been reached.

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