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Abstract

In situ x-ray diffraction studies on α-cristobalite GaPO$_4$ have found that the orthorhombic α-cristobalite GaPO$_4$ (I) transforms into a monoclinic phase (II) at about 2 GPa, then to the VCrO$_4$-type orthorhombic phase (III) at 4 GPa, which persists to 52 GPa, and no further transformation was observed. The volume changes for (I)–(II) and (II)–(III) transitions are $\sim$<1% and 17%, respectively, at the transition pressure. Upon releasing the pressure to atmospheric pressure, the orthorhombic phase (III) either reverses back to the phase (I) or persists as the metastable phase, depending upon the loading process. By fitting the P–V data to the Murnaghan equation of state, we obtained values of the zero-pressure bulk modulus (K_0) and its pressure derivative (K_0') at 12.1 $\pm$ 2.1 GPa and 11.5 $\pm$ 3.5 for phase (I), and 144.1 $\pm$ 6.1 GPa and 5.2 $\pm$ 0.4 for phase (III).

(Some figures in this article are in colour only in the electronic version)

1. Introduction

GaPO$_4$ is a structural analog of SiO$_2$, and it crystallizes in various polymorphs as in SiO$_2$, such as the quartz type, the low (α-)cristobalite and the high (β-)cristobalite types. Knowledge of the phase transformation of GaPO$_4$ at high pressure would provide valuable information regarding the possible dense high-pressure phases in the ABO$_4$ compounds, including SiO$_2$, and has therefore received continual attention in the past two decades. Experimental studies of Robeson *et al*, [1] on α-cristobalite GaPO$_4$ found that at 15.9 GPa it transforms into an orthorhombic *Cmcm* phase as predicted from molecular dynamic (MD) calculations [2–4]. The orthorhombic *Cmcm* phase is very interesting because it contains an equal number of four- and six-coordinated Si atoms. The MD calculations based on α-cristobalite (SiO$_2$) also

suggested that at higher pressure, the *Cmcm* phase will further transform into a rutile-type structure. Such calculations have raised some interesting questions: How stable is the *Cmcm* phase? Will the *Cmcm* phase transform into a rutile-type structure as predicted? What is the compressibility of the α-cristobalite and the *Cmcm* phases? These questions have motivated us to carry out *in situ* high-pressure x-ray diffraction studies on α-cristobalite $GaPO_4$ to 52 GPa. The results obtained are reported and discussed in this paper.

2. Experimental methods

A modified Bassett-type diamond-anvil cell (DAC) was used in both studies. The cell consists of a pair of gem quality anvils of 1/3 carat with a culet of 400 μm and a gasket (T301, fully hardened, 0.25 mm thick) with a 100–200 μm hole serving as the sample chamber. A 4:1 mixture of methanol–ethanol was used as the pressure medium, and sample pressure was determined by the ruby fluorescence method. X-ray diffraction data were recorded using either conventional x-ray film with an in-house x-ray source at the University of Hawaii or with an imaging plate at the Photon Factory at the National Laboratory for High Energy Physics (KEK). The in-house x-ray diffraction experiment used a finely focused Zr-filtered Mo Kα radiation from a 3 kW Nonius–Enraf x-ray generator. With the operating voltage and current at 50 kV and 26 mA, respectively, and with a collimated beam of 110 μm in diameter, the average exposure time for each run was ~100 h. In experiments using the synchrotron radiation source, monochromatic radiation ($\lambda = 0.6174$ Å) from a bending magnet beamline (BL-18C) was used. With the storage ring operating at 2.5 GeV and 360 mA and a collimated beam of 60 μm diameter, each diffraction pattern was collected for 10–30 min in real time. The starting material obtained from Bell laboratories was confirmed by powdered x-ray diffraction to be the orthorhombic phase with lattice parameters $a_0 = 6.9810 \pm 0.0023$ Å, $b_0 = 6.9582 \pm 0.0056$ Å and $c_0 = 6.8799 \pm 0.0023$ Å. These values are in good agreement with those reported earlier for α-cristobalite $GaPO_4$ with space group $C222_1$ [5, 6]. Three experiments were carried out in this study with the first one up to 10.8 GPa using in-house x-ray diffraction facilities, and the second and the third runs up to 6.8 and 52 GPa, respectively, using synchrotron radiation.

3. Experimental results and discussion

Figure 1 shows a series of diffraction patterns up to 10 GPa, showing clearly that the $C222_1$ phase (I) is stable to up 1.9 GPa and changes to a new high-pressure phase (III) at 3 GPa, which persists to 10 GPa. Upon decompression, all peaks of the new high-pressure phase persist, along with three additional peaks (111), (201), (112) from phase (I) showing that although the new phase could remain metastable at ambient conditions, it starts to convert back to phase (I). All the diffraction peaks of the new phase at ambient conditions could be explained using an orthorhombic unit cell with lattice parameters $a_0 = 5.188$ Å, $b_0 = 7.662$ Å, and $c_0 = 6.212$ Å and with Z (number of molecular formulas per unit cell) = 4. The molar volume is calculated as 37.193 cm^3 mol^{-1}, which gives $\Delta V_0 = 26\%$ at atmospheric pressure. Our results are in good agreement with the values from molecular dynamics calculations ($a_0 = 5.11$ Å, $b_0 = 7.47$ Å, $c_0 = 5.97$ Å, and $\Delta V_0 = 24\%$) based on the proposed *Cmcm* phase [2, 3]. Very similar results ($a = 5.12$ Å, $b = 7.31$ Å, and $c = 5.92$ Å) were also obtained for the high-pressure phase of α-cristobalite $GaPO_4$ at 17.5 GPa [1].

In order to characterize the structural behavior of phases (I) and (III) under high pressure and the phase transition between the two phases, we repeated the above experiment with synchrotron radiation and took a series of diffraction patterns with increasing pressure to 6.8 GPa and then gradually decreased the pressure to atmospheric pressure. As shown in
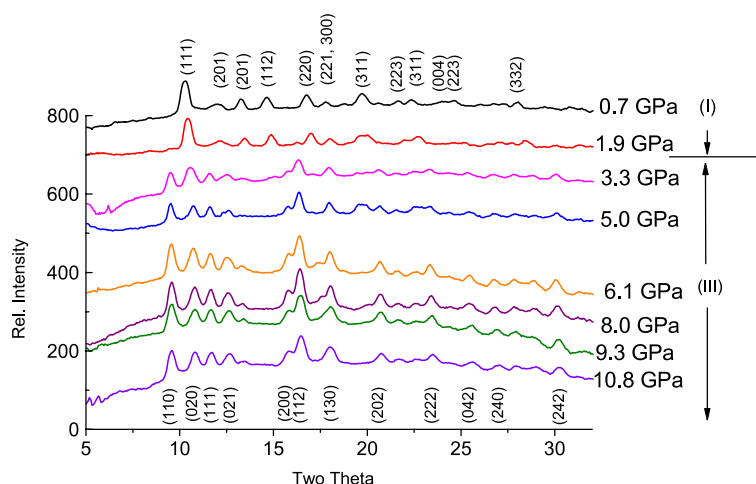
Figure 1. *In situ* x-ray diffraction patterns of the α-cristobalite GaPO$_4$+ alcohol mixture as a function of pressure to 10.8 GPa at room temperature.
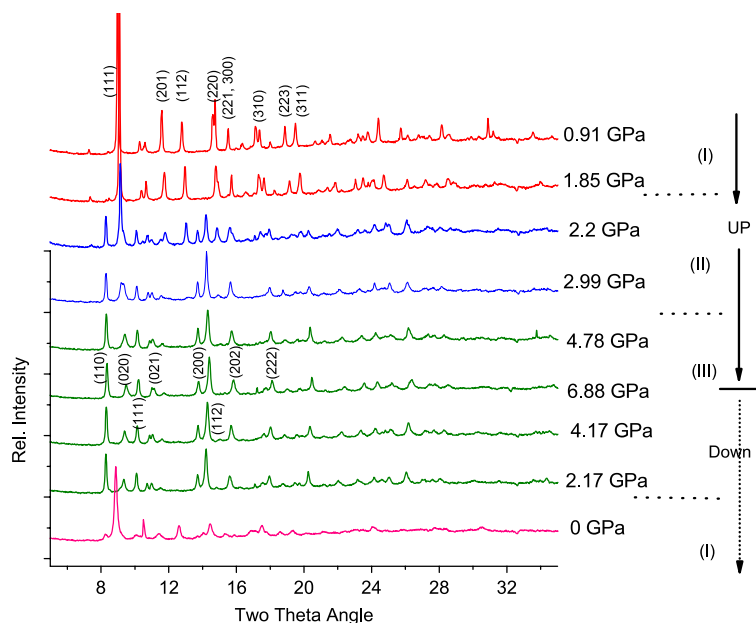

Figure 2. *In situ* x-ray diffraction pattern taken at various pressures for α-cristobalite GaPO$_4$ to 6.8 GPa on the loading cycle as well as on the unloading cycle to atmospheric pressure.

figure 2, several new peaks appear at ~2 GPa, indicating that the phase transformation has taken place, and above 4 GPa a different pattern appears, which is consistent with the *Cmcm* phase observed in our in-house experiment described above. Upon decompression, the *Cmcm* high-pressure phase persists to ~2 GPa and then reverts back to phase (I) at atmospheric pressure. A gradual transition between the $C222_1$ and the *Cmcm* phases was suggested earlier [1]. Although the patterns at 2.2 and 2.99 GPa seem to be the mixed phases of (I) and (III), our
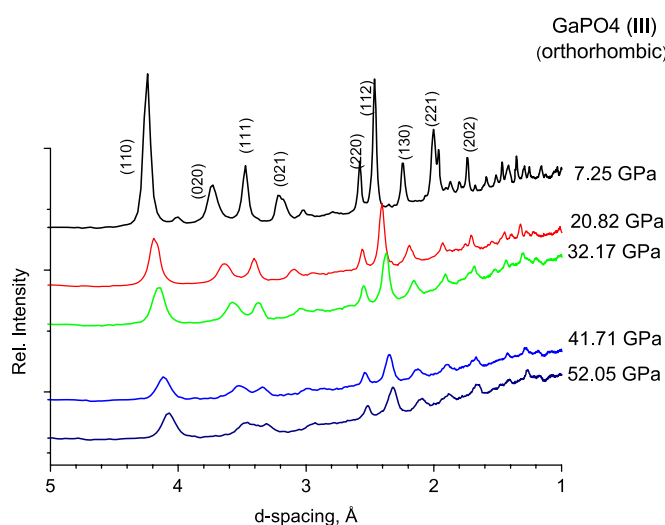
Figure 3. *In situ* x-ray diffraction pattern taken at each pressure for α-cristobalite GaPO$_4$ to 52 GPa in the loading cycle.
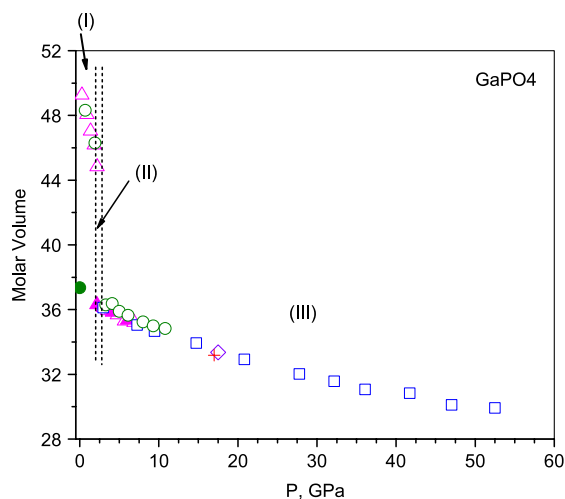

Figure 4. Molar volume as a function of pressure for phases (I), (II) and (III) in GaPO$_4$, where different symbols represent data from different, runs with open and solid ones for the pressure increases and pressure decreases, respectively. The circles are data from the in-house experiment. Both upward triangles and the squares are data from the synchrotron experiment. The two data points represented by a cross at 17 GPa and an open diamond at 17.5 GPa are taken from [9] and [1], respectively.

recent Raman measurements [7] clearly show that new phases appear in a narrow pressure region between 2 and 4 GPa. Diffraction data obtained at 2.2 GPa are, therefore, indexed on the basis of a single phase. A monoclinic unit cell with $a = 13.431$ Å, $b = 6.752$ Å, $c = 13.142$ Å, $\beta = 93.12$ fits well with the diffraction data. With $Z = 16$, the molar volume is 44.826 cm^3 mol^{-1}. The volume change between the orthorhombic phase (I) and the monoclinic phase (II) is less than 1% at 2 GPa. The transition between the α-cristobalite phase (I) and the

monoclinic phase (II) in GaPO$_4$ at about 2 GPa is comparable with the tetragonal α-cristobalite to monoclinic phase transition in SiO$_2$ at 1.6 GPa [8].

The third x-ray diffraction experiment was carried out on the GaPO$_4$+ alcohol to 52 GPa with a relatively large step in each pressure increment. Results thus obtained show that the orthorhombic phase (I) transforms into a monoclinic phase (II) at 2.95 GPa, which in turn changes into the orthorhombic *Cmcm* phase at 7.25 GPa. These findings are consistent with those observed in the first two experiments described above. As can also be seen from figure 3, diffraction patterns collected at pressures between 7.25 and 52 GPa are very similar, indicating that no further phase transformation has taken place in GaPO$_4$. It is therefore concluded that the orthorhombic *Cmcm* phase (III) is thermodynamically stable up to 52 GPa. The predicted stishovite phase based on MD calculations for the SiO$_2$ counterpart (i.e., α-cristobalite phase) [3] was not observed for α-cristobalite GaPO$_4$ in this study.

The effect of volume for phases (I), (II) and (III) is plotted in figure 4. It shows a good agreement between in-house and synchrotron-based experiments, and also between the compression and decompression cycles. The volume change between phases (II) and (III) at 4 GPa is about 17%. Fitting the P–V data of phase (III) using the Murnaghan equation of state yields the zero-pressure bulk modulus $K_0 = 144.1 \pm 6.1$ GPa and its pressure derivative $K_0' = 5.2 \pm 0.4$. These values differ greatly from those ($K_0 = 308$ GPa and $K_0' = 4$) of Badro *et al*, [9]. The discrepancy is very likely due to the fact that only four data points were used for fitting in the latter study. A similar fitting for phase (I) yields $K_0 = 12.08 \pm 2.1$ GPa and $K_0' = 11.5 \pm 3.5$. These values are comparable with the $K_0 = 11.5$ GPa and $K_0' = 9$ for the α-cristobalite phase of silica [10].

Acknowledgments

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