Pressure–induced phase transitions of Zn$_2$SiO$_4$ III and IV studied using in-situ Raman spectroscopy

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Recent structural study of the high-pressure Zn$_2$SiO$_4$ phases III and IV has suggested that they are retrograde phases formed during decompression. To clarify the stabilities of these phases under pressure, in-situ high-pressure Raman spectroscopic measurements were taken at room temperature. Phase III, having a ‘tetrahedral olivine’ structure, transformed to a new phase at 5.5 GPa during compression and returned to phase III at 1.7 GPa during decompression. Phase IV also exhibited a phase transition at 2.5 GPa with very small hysteresis. Both transitions are first-order. These observations confirmed that phases III and IV are retrograde phases.

Keywords: Zn$_2$SiO$_4$, Raman spectroscopy, High-pressure phase, Phase transition, Unquenchable phase

INTRODUCTION

Although the Zn$^{2+}$ ion has an ionic radius slightly longer than that of Mg$^{2+}$ (0.75 versus 0.72 Å) (Shannon, 1976), Zn$^{2+}$ ions prefer tetrahedral sites over octahedral sites (e.g., Syono et al. 1971). As a result, zinc silicates exhibit quite different crystalline phases and phase relations compared to those of magnesium silicates at ambient pressure. For instance, Zn$_2$SiO$_4$ adopts a phenacite (Be$_2$SiO$_4$) structure at ambient conditions, in which Zn is in a tetrahedral site, rather than the olivine structure M$_2$SiO$_4$ adopts for Mg and most of the divalent transition metal ions (Fe, Ni, Co, and Mn). As coordination number generally increases with pressure by phase transition, one might expect the olivine phase of Zn$_2$SiO$_4$ as a high-pressure phase. High-pressure phase relations of Zn$_2$SiO$_4$ were determined using quench experiments by Ringwood and Major (1967) and Syono et al. (1971). These studies failed to synthesize the olivine or spinel phase; instead, they discovered four high-pressure polymorphs (II, III, IV, and V), in which a phenacite structure (willemite) is assigned as phase I. The pressure-induced phase transition sequence determined by previous quench experiments up to nearly 13 GPa is as follow: I → II → III → IV → V. Phase V then decomposes to the ZnSiO$_3$ ilmenite phase plus ZnO (NaCl structure) at approximately 13 GPa.

(Ito and Matsui 1974). The crystal structure of phase II was solved by Marumo and Syono (1971), and Zn occupies tetrahedral sites in this compact structure. Syono et al. (1971) identified phase V as a modified spinel structure, and recently Kanzaki (2018) refined its crystal structure. This is the only phase to have octahedral Zn sites in known Zn$_2$SiO$_4$ phases thus far.

The crystal structures of phases III and IV were not known for a long time, but Liu et al. (2013) solved their structures using synthesized powder samples recovered to ambient conditions. Phase III has a ‘tetrahedral olivine’ structure (Baur, 1980) in which Zn ions occupy vacant tetrahedral sites of the olivine structure, leaving the octahedral M1 and M2 sites vacant. Phase IV consists of tetrahedrally coordinated Zn and Si and features a unique edge-shared Zn$_2$O$_6$ dimer. The study also shows that these two phases have densities lower than those of phase II, and phase III has a density slightly lower than those of phase I. Although this was already noted in Syono et al. (1971), they suggested that the lower densities could be because of the non-stoichiometric nature of phases III and IV. However, Liu et al. (2013) clearly demonstrated that phase III and IV are stoichiometric based on detailed electron microprobe analysis. Therefore, these phases indeed have lower densities compared to those of phase II and are likely metastable phases transformed from yet unknown high-pressure phases during decompression. This interpretation is also consistent with the broad high-angle diffraction peaks of these phases noted in
Syono et al. (1971) and Liu et al. (2013).

The aforementioned experimental studies were based on quench experiments, and no in-situ high-pressure observation has been conducted for this system to date. If phases III and IV are really retrograde phases, pressure-induced phase transitions to supposed original high-pressure phases might be expected. To explore this possibility, and to obtain insight into the structural information of stable high-pressure phases, an in-situ high-pressure Raman spectroscopic study was conducted.

EXPERIMENTAL PROCEDURES

The samples used in this study were from the same run products reported in our previous study (Liu et al., 2013). In short, phases III and IV were synthesized at 6.5 GPa and 1273 K for 2 h, and at approximately 8 GPa and 1273 K for 2 h, respectively, using a 5000-ton, Kawai-type, double-stage uniaxial, split-sphere multi-anvil apparatus installed at the Institute for Planetary Materials, Okayama University.

Unpolarized Raman spectra were acquired using a home-built micro-Raman spectrometer with a 488.123 nm Ar⁺ laser (~ 80 mW). The laser beam was focused onto a fragment of the sample in a diamond anvil cell and with a long working distance 50× objective lens (Mitsutoyo M Plan Apo SL), forming an approximately 1-μm laser spot. Backscattered light was then focused to a pinhole (with a diameter of 200 μm), the passed light was collimated, and then the light passed through a Razor-Edge long-wave pass filter (Semrock Inc.) to reject Rayleigh scattering. It was focused on the entrance slit of the polychromator (Acton Spectra Pro 500i with a focal length of 500 mm and a grating of 1200 gr/mm). The dispersed light was detected using a liquid-N₂-cooled CCD detector (Princeton Instruments, SPEC-10).

For an in-situ high-pressure Raman study, a symmetrical diamond anvil cell was used. The cullet size of the low-fluorescence diamonds was 500 μm. A stainless-steel gasket (SUS301H) of an initial 250-μm thickness was pre-indent to approximately 90 μm, and then an approximately 200-μm-diameter hole was created using a home-built electric discharge machine.

A small fragment of phase III or IV was introduced into the gasket hole along with a few small ruby chips. The pressure medium was a 4:1 methanol-to-ethanol mixture. The exposure time for high-pressure measurements was 60 s, and the spectrum was stacked for 5 times. The pressure was determined using the ruby fluorescence technique (Piermarini et al., 1975) with the same Raman spectrometer. To avoid complications because of Raman scattering from the pressure medium, the laser beam was focused slightly on the inside part of the sample fragment; no Raman peak from the pressure medium was apparent in the reported spectra.

Relative frequencies in the reported spectra were calibrated against Ar⁺ plasma lines of the Ar⁺ ion laser. A Voigt profile function was employed to fit the Raman and ruby fluorescence peaks using the ‘fityxk’ program (Wojdyr, 2010), resulting in a precision of 0.1 cm⁻¹ for the Raman shift reported (for the well-resolved peak), and a precision better than 0.1 GPa for the estimated pressure.

RESULTS AND DISCUSSION

Zn₂SiO₄ phase III

Factor group analysis of Zn₂SiO₄ III with the space group Pnma (D₂h point group) suggested that there are 42 Raman active modes (12A_g + 9B₁g + 12B₂g + 9B₃g). A typical Raman spectrum of phase III under ambient conditions is shown in Figure 1 along with those of other phases for comparison. Up to 14 peaks were identified from the spectrum. The remaining peaks were not observed, possibly because of insufficient intensity or overlap with other peaks.

Selected Raman spectra during compression and decompression are shown in Figure 2. The Raman peaks of phase III were observed up to 5.0 GPa. When the pressure was increased to 5.5 GPa, peaks of phase III were still observed during the initial focusing period, but gradually disappeared, and new peaks emerged within a few minutes, suggesting a first-order transition. The Raman peaks of the new phase were observed up to the highest pressure studied (10.2 GPa). This new phase is designated as phase III-HP hereafter. The positions of the Raman peaks as a function of pressure are summarized in Figure 3 for both the compression and decompression processes. During the decompression process, the Raman peaks of phase III reappeared at 1.3 GPa, showing a large pressure
hysteresis for the transition. A small peak at 413 cm$^{-1}$ did not change its position with pressure and was sharper than other peaks. Thus, it is not a Raman peak of the sample; however, its origin is not clear.

Based on quench experiments by Syono et al. (1971), phase III was observed from 8 to 9.5 GPa at 1273 K. Liu et al. (2013) suggested that the pressure reported by Syono et al. (1971) was somewhat overestimated, as they obtained phase III at 6.5 GPa and 1273 K. Nevertheless, these pressures are higher than the transition pressure of phase III to III–HP observed in the present study. Therefore, at the pressure-temperature conditions of the previous quench experiments for phase III, phase III–HP would be a stable high-pressure phase. Then, phase III–HP transformed to phase III during the decompression process of the previous quench experiments. Unquenchable high-pressure phases are not rare (cf. Yusa, 2017) and are also known in ZnSiO$_3$ pyroxene phases (Arlt and Angel, 2000).

**Zn$_2$SiO$_4$ phase IV**

Factor group analysis of Zn$_2$SiO$_4$ IV with the space group Pbca ($D_{2h}$ point group) implied that there are 84 Raman active modes ($21A_g + 21B_{1g} + 21B_{2g} + 21B_{3g}$). A typical Raman spectrum of phase IV under ambient conditions is shown in Figure 1. Up to 25 peaks were noted from the spectrum.

Selected Raman spectra with pressure are shown in Figure 4. An abrupt change in the pattern and positions of the peaks was noted at 2.7 GPa, suggesting a first-order phase transition. The Raman spectrum of this new phase was different from that of phase III–HP. Thus, this phase is a yet another new phase of Zn$_2$SiO$_4$ and is designated as phase IV–HP hereafter. Raman shifts for compression and decompression processes are shown in Figure 5. The Raman spectrum of IV–HP was observed up to the highest pressure studied (9.7 GPa). During the decompression process, the pattern of phase IV reappeared at 2.4 GPa, suggesting very small pressure hysteresis ($\leq 0.3$ GPa), contrasting with the transition of phase III. Thus, the transition pressure is well constrained.

Phase IV was observed above 9.5 GPa at 1273 K (Syono et al., 1971), whereas Liu et al. (2013) synthesized it at 7 GPa and 1273 K. These pressures are again much higher than the observed transition pressure from phase IV to IV–HP. Thus, phase IV–HP would be a stable high-pressure phase, instead of phase IV, under conditions in which it was synthesized. Phase IV–HP transformed to phase IV during the decompression process of previous quench experiments. The current study was conducted at room temperature, and further in-situ investigation under high-pressure and high-temperature conditions is necessary to fully confirm these results.
Candidate structures of new high-pressure HP phases

Because these new phases cannot be recovered to ambient conditions, no X-ray diffraction study of these phases has been conducted thus far. Raman spectra of phases I to IV as shown in Figure 1 show several intense peaks within a range of 800–1000 cm$^{-1}$, and they are well separated from the lower frequency peaks. These peaks are a result of the Si–O stretching modes of the SiO$_4$ units with low polymerization (Q$^0$). Phases III–HP and IV–HP also have prominent peaks within this range; thus, structures of these phases are also based on SiO$_4$ units of a similar local structure. Although identification of crystal structures solely from Raman data is difficult, crystal structures of new phases might be predicted from proposed structures for A$_2$BX$_4$ compounds. Nalbandyan and Novikova (2012) used the packing density of A$_2$BX$_4$ (X = O, F) compounds to understand and predict high-pressure HP structures. Therefore, possible candidates for the high-pressure phases can be narrowed down to olivine (space group: Pnma), thenardite (Fddd), Na$_2$CrO$_4$ (Cmcm), and Ag$_2$CrO$_4$ (Pnma). Among them, the thenardite structure has a tetrahedral Zn site (Hawthorne and Ferguson, 1975), whereas the Na$_2$CrO$_4$ and Ag$_2$CrO$_4$ structures have both tetrahedral and octahedral Zn sites (Nimmo, 1981; Jacobson and Hackert, 1971). Therefore, thenardite is a less likely candidate as a high-pressure phase. However, the olivine structure is a favorable candidate for phase III–HP because phase III has an olivine-related structure (tetrahedral olivine) as previously mentioned. Notably, phase III–HP has two prominent peaks in the 800–900 cm$^{-1}$ range of the Raman spectra (Figure 2), which is similar to olivine which characteristically has two intense peaks in the region of 800–900 cm$^{-1}$. In conclusion, the possible candidate structures for phases III–HP and IV–HP are olivine, Na$_2$CrO$_4$ and Ag$_2$CrO$_4$.

In summary, two new unquenchable high-pressure phases of Zn$_2$SiO$_4$ (III–HP and IV–HP) were found using phases III and IV as starting materials by in-situ high-pressure Raman spectroscopic study. The two new phases found in this study are stable high-pressure phases, while phases III and IV are retrograde phases during decompression from phases III–HP and IV–HP, respectively. The crystal structures of these new phases have not yet been identified. Therefore, an in-situ high-pressure X-ray diffraction study is necessary to clarify their structures.

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REFERENCES

Arlt, T. and Angel, R.J. (2000) Displacive phase transitions in C-centered clinopyroxenes: spodumene, Li$_2$Si$_2$O$_6$ and ZnSiO$_3$. Physics and Chemistry of Minerals, 27, 719–731.

Baur, W.H. (1980) Solid-Solutions between Octahedral and Tetrahedral Olivine Types in Li–Zn–Germanates. Inorganic and Nuclear Chemistry Letters, 16, 525–527.

Hawthorne, F.C. and Ferguson, R.B. (1975) Anhydrous sulphates. I: Refinement of the crystal structure of celestite with an appendix on the structure of thenardite. The Canadian Mineralogist, 13, 181–187.

Ito, E. and Matsui, Y. (1974) High-pressure synthesis of ZnSiO$_3$...
ilmenite. Physics of the Earth and Planetary Interiors, 9, 344-352.  
Jacobson, R.A. and Hackert, M.L. (1971) The crystal structure of silver chromate. Journal of Solid State Chemistry, 3, 364-368.  
Kanzaki, M. (2018) Crystal structures of Zn$_2$GeO$_4$ cubic/tetragonal spinel and Zn$_2$SiO$_4$ modified spinel phases. Journal of Mineralogical and Petrological Sciences, 113, 41-46.  
Kanzhavanov, S.Zh., Ravindran, P., Vajeeston, P., Ulyashin, A.G., Fjellvåg, H. and Svensson, B.G. (2009) Phase stability and pressure-induced structural transitions at zero temperature in ZnSiO$_3$ and Zn$_2$SiO$_4$. Journal of Physics: Condensed Matter, 21, 485801.  
Liu, X., Kanzaki, M. and Xue, X. (2013) Crystal structures of Zn$_2$SiO$_4$ III and IV synthesized at 6.5-8 GPa and 1,273 K. Physics and Chemistry of Minerals, 40, 467-478.  
Marumo, F. and Syono, Y. (1971) The crystal structure of Zn$_2$SiO$_4$ II, a high-pressure phase of willemite. Acta Crystallographica B, 27, 1868-1870.  
Nalbandyan, V. and Novikova, A. (2012) Structural chemistry of A$_2$MX$_4$ compounds (X = O, F) with isolated tetrahedral anions: search for the densest structure types. Acta Crystallographica B, 68, 227-239.  
Nimmo, J.K. (1981) Sodium chromate (VI) at 296 K. Acta Crystallographica B, 37, 431-433.  
Pierrmarini, G.J., Block, S., Barnett, J.D. and Forman, R.A. (1975) Calibration of the pressure dependence of the R1 ruby fluorescence line to 195 kbar. Journal of Applied Physics, 46, 2774-2780.  
Ringwood, A.E. and Major, A. (1967) High pressure transformation in zinc germanates and silicates. Nature, 215, 1367-1368.  
Shannon, R. (1976) Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides. Acta Crystallographica A, 32, 751-767.  
Syono, Y., Akimoto, S. and Matsui, Y. (1971) High pressure transformation in zinc silicates. Journal of Solid State Chemistry, 3, 369-380.  
Wojdyr, M. (2010) Fityk: a general-purpose peak fitting program. Journal of Applied Crystallography, 43, 1126-1128.  
Yusa, H. (2017) Structural relaxation of oxide compounds from the high-pressure phase. In Nanoinformatics (Tanaka, I. Ed.). Springer Nature, Singapore, 259-277.