

The crystal structures of two Zn_2SiO_4 high-pressure polymorphs

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Introduction

The M_2SiO_4 group (M: divalent cations e.g. Mg, Fe) includes the most important constituent minerals of the deep Earth, and thus many of them have been extensively studied. However, some systems containing less common cations (e.g. Zn) are not yet fully understood. The Zn_2SiO_4 system is of special interest from the crystal chemical point of view, because Zn is a strongly tetrahedral coordination preferred element. The phase relation of Zn_2SiO_4 has been reported by Syono et al. [1]. Five phases were identified in the pressure range up to 13 GPa (denominated as phase I to V in the order of increasing pressure) [1]. The crystal structures of phases I (willemite), II and V (modified-spinel structure) have been determined. Phase III and IV have been suggested to be non-stoichiometric [1], but their structures remain undetermined. Here, we report the crystal structures of Zn_2SiO_4 III and IV determined via an ab initio structure determination technique from synchrotron powder X-ray diffraction data utilizing local structural information from NMR as constraints.

Experimental

The Zn_2SiO_4 polymorphs (phase III-6.5 GPa and 1273 K, phase IV-8 GPa and 1273 K) have been synthesized employing a Kawai-type double-stage uniaxial split-sphere multi-anvil apparatus at ISEI, using willemite as starting material. The latter was synthesized at ambient pressure and 1523 K from a mixture of $2ZnO + SiO_2$. All the samples have been confirmed to give consistent X-ray diffraction patterns as those reported previously. ²⁹Si MAS NMR spectra have been obtained using a Varian Unity-Inova 9.4T spectrometer at a resonance frequency of 79.5 MHz at ISEI. Synchrotron powder X-ray diffraction data were acquired under ambient condition at the beamline BL19B2 of SPring-8. Chemical analyses have been performed using a JEOL JXA-8800 electron microprobe. The crystal structures were solved using an ab initio structure determination technique by FOX [2] from the synchrotron powder X-ray diffraction data, using the information from ²⁹Si NMR as constraints. The obtained structures were further refined with the Rietveld method using the RIETAN-FP program [3].

Results and Discussion

The ²⁹Si MAS NMR spectra for both phases III and IV contain a single peak for tetrahedral Si. Electron microprobe analyses showed that the Zn/Si ratios are within uncertainty of 2.00 for these two phases, indicating that both of them are stoichiometric, contrary to previous report [1]. The space groups of phase III & IV were determined to be Pnma and Pbcu, respectively. Their cell parameters are consistent with those reported by Syono et al. [1]. Both of them contain tetrahedral Si and Zn, like phases I and II. Phase III shows an approximately hexagonally close-packed structure with Si in tetrahedral sites, closely related to that of olivine. Unlike the latter, Zn cations in phase III occupy tetrahedral, rather than octahedral positions. The volume per unit formula of phase III is somewhat larger than that of 'virtual olivine' for Zn_2SiO_4 [1]. Phase IV contains unique edge-shared Zn-O tetrahedral dimers, in contrast to phases I to III that contain only corner-shared Zn-O tetrahedra. The volumes per unit formula for phases III and IV are somewhat larger than that of the lower-pressure polymorph, phase II [1]. This suggests that phases III and IV could have undergone structural changes during decompression. Further in situ high-pressure high-temperature measurements are necessary to resolve this issue.

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References

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