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Crystal structures of Zn_2GeO_4 spinel and Zn_2SiO_4 modified spinel phases

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High pressure phase relations of Zn_2GeO_4 and Zn_2SiO_4 were studied in 1960s to 1970s (e.g., Syono et al., 1971) in relation to high-pressure mantle minerals, but the crystal structures of high pressure phases discovered have not been determined, except for phase II of Zn_2SiO_4. In last year's JPGU meeting, we reported the structures of phase III and IV of Zn_2SiO_4 (SIT02-24). Here, we report the crystal structures of cubic and tetragonal spinels in Zn_2GeO_4 and phase V of Zn_2SiO_4, and also present new structural insights regarding phase III and IV of Zn_2SiO_4.

All samples were synthesized using 5000ton Kawai-type multianvil press at Misasa. Starting materials were Zn_2GeO_4 and Zn_2SiO_4 phenacite phases synthesized at ambient pressure. Powder X-ray diffraction patterns were obtained at BL19B2 of SPring-8 using a large Debye-Scherrer camera. For refinement, the Rietveld method was used (RIETAN-FP). Details of the procedure are same as those of Kanzaki and Xue (2012). ^{29}Si MAS NMR spectrum of phase V was also obtained.

Cubic and tetragonal spinels of Zn_2GeO_4 were synthesized at 3 GPa and 1600 ^{o}C, and 5 GPa and 1200 ^{o}C, respectively. As expected, these spinels have inverse-type in which the tetrahedral site is occupied by Zn. For tetragonal spinel, the symmetry is lowered as a result of ordering of Zn and Ge in the octahedral sites. The tetragonal spinel phase is isostructural to Zn_2TiO_4. Bond distances calculated by Brown's bond valence agree well with the experimental values from the present study.

For the structures of phase III and IV of Zn_2SiO_4, after last year's presentation (SIT02-24), we noted that phase III is isostructural to the high-temperature phase of $(Zn_{1.1}Li_{0.6}Si_{0.3})SiO_4$(Liu et al., 2013). The latter structure is related to the olivine structure in that metal cations occupy vacant tetrahedral sites, rather than octahedral sites of the olivine structure, and is referred to as "tetrahedral olivine" by Baur (1980). In phase IV, triclusters made of two ZnO_4 and one SiO_4 sharing a common oxygen form columns running along the c-direction. Similar columns also exist in phase II, which explains the similar densities of phases II and IV.

We refined crystal structure of phase V of Zn_2SiO_4, and confirmed that it has a modified spinel structure. Its structural parameters are similar to those of Mg_2SiO_4 wadsleyite. Octahedral sites are occupied by Zn only, and no Zn/Si disorder was detected. This is consistent with the ^{29}Si MAS NMR result that revealed a single peak of tetrahedral Si for phase V.

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