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Phase relation of $AlPO_4$and crystal structures of high-pressure phases

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$AlPO_4$takes quartz structure (berlinite) at ambient pressure, and it amorphizes under compression, and reverts to crystal again when pressure was released (Kruger and Jeanloz, Science, 1990). In regard to this peculiar behavior, phase relation of this system has been studied by diamond anvil cell (DAC) high-pressure technique. Based on these studies, berlinite transforms to $CrVO_4$phase (Cmcm) at around 10 GPa, and to rutile-like phase at 60 GPa (Pellicer-Porres et al., Nature Materials, 2007). With these transitions, coordination numbers of Al and P change from all 4 in berlinite, to 6 for Al and 4 for P in $CrVO_4$phase, and all 6 in rutile-like phase. Most of these DAC studies were conducted at room temperature. Therefore, there is some doubt about stabilities of these phases. On the other hand, old studies based on quench experiments suggested several unknown phases at 6-7 GPa in this system (Seifert, 1968). However, there is no structural information available for these phases to date, except $CrVO_4$phase. In this study, we re-investigated this system at 5-7 GPa.
We conducted multi-anvil quench experiments, and recovered samples were characterized by Raman, ^{31}P NMR, ^{27}Al 3Q NMR, EPMA and powder XRD. We found three unknown $AlPO_4$phases during the study. At 5 GPa and 1500 ℃, an orthorhombic phase was obtained. At 6 GPa and below 1250 ℃, a triclinic phase was observed, whereas above 1250 ℃, a monoclinic phase was obtained. Subsequently these phases were confirmed as stable phases by in-situ X-ray diffraction at BL04B1, SPring-8.
Crystal structures of three new phases are solved using ab initio powder diffraction structural analysis technique (FOX) with local structural information of Al and P obtained by NMR. Powder diffraction data for the triclinic and monoclinic phases were obtained using Debye-Scherrer camera in BL19B2 of SPring-8. FOX program (Favre-Nicolin and Cerny, J. Appl. Cryst., 2002) can treat atoms, molecules and cation polyhedra as units for structural model in real space, and search the structure which match the pattern best by simulated annealing technique. From NMR, number of sites, their proportions, and coordination number of Al and P can be obtained. Therefore cation polyhedra (e.g., PO_4) can be used as a model in FOX. This significantly reduce degree of freedom for calculations, and allows us solve structure readily. The structural parameters are then refined using Rietveld technique (RIETAN-FP; Izumi and Momma, Solid State Phenom., 2007).
The orthorhombic phase has 2 Al and 2 P sites, all in tetrahedral coordination. There is 4-membered ring in the structure. The structures of the triclinic and monoclinic phases are similar, and both contain two octahedral Al sites, one penta-coordinated Al sites, and 3 tetrahedral P sites. Structure motif of these phases is S-shaped chains made of 6 edge-shared Al polyhedra. The chains are connected by $PO_4$to form the structures. The difference of two phases is difference in orientation of chains. For the triclinic phase there is single orientation, but for the monoclinic phase, two orientations exist. The short chains and penta-coordinated Al are unique, and not found in other $AlPO_4$phase and analogous ABO_4system.
Present study reveals that there is three phases exist between stability region of berlite and $CrVO_4$ phases. DAC experiments conducted at ambient temperature would not give stable phase relations. Therefore the systems which studied only by DAC at room temperature, should be

reinvestigated to establish true phase relations using high-pressure and high-temperature experiments.
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Keywords: AlPO4, phase relation, high pressure, crystal structure, powder X-ray diffraction, NMR