Synthesis and structural characterization of high-pressure AlPO₄ phases

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Because of its quartz like structural behavior at ambient conditions, AlPO₄ is seen as an appropriate analog for SiO₂ also at high temperature - high pressure conditions. The phase relation of AlPO₄ was target in several investigations at high temperatures (e.g. (1) Muraoka Y. & Kihara K. 1997) or high pressures (e.g. (2) Sharma S.M. et al 2000). However, the phase relation of AlPO₄ in the middle temperature-pressure range is poorly known. There is only one study conducted by (3) Seifert K.F. 1968 reporting the observation of two polymorphs of AlPO₄ at 6 GPa and 400-900°C with unsolved structures and one polymorph at 7-10GPa and 900-1000°C with a Cmcm structure containing one octahedrally coordinated aluminum site and one tetrahedrally coordinated phosphorous site. To obtain new information on the pressure-temperature phase relations in this system, this project was carried out.

An USSA-5000 Kawai-type multi-anvil press has been used for high-pressure synthesis. Two samples have been synthesized at 6 GPa and 1000°C, 1500°C respectively using a starting material of AlPO₄ chemical as received. A third sample produced at 6 GPa and 1500°C using a starting material of AlPO₄ chemical dried at 1000°C for 26 hours. The recovered samples have been characterized by a range of advanced NMR techniques, including ¹H, ²⁷Al and ³¹P MAS NMR, ²⁷Al triple-quantum (3Q) MAS NMR, ³¹P double-quantum (DQ) MAS NMR, ¹H↔²⁷Al, ¹H↔³¹P and ²⁷Al↔³¹P cross-polarization (CP) MAS NMR, and ²⁷Al↔³¹P 3QMAS/HETCOR (heteronuclear correlation) NMR, as well as micro-Raman and electron microprobe analyses.

For the system Al₂O₃-P₂O₅-H₂O, two new crystalline AlPO₄ phases have been found to be stable at 6 GPa and 1500°C. Each of them contains multiple six (and five?) coordinated aluminum sites and multiple four coordinated phosphorous sites. For all three samples, minor hydrous phases were also detected. One of them has been confirmed to be trolleite Al₄(PO₄)₃(OH)₃. Trolleite has been previously reported to be stable up to 2.3 GPa at 1000°C (⁴Bass and Sclar 1979). This study has confirmed that its stability field extends to at least 6 GPa.

(1) Muraoka Y. & Kihara K.; The temperature dependence of the crystal structure of berlinite, a quartz-type form of AlPO₄; Physics and Chemistry of Minerals 24 (1997) p.243-25
(3) Seifert K.F.; Zur Druck-Kristallchemie der AX₂-Verbindungen; Fortschritte der Mineralogie 45 (1968) p214-280
(4) Bass J.D. & Sclar C.B.; The stability of trolleite and the Al₂O₃-AlPO₄-H₂O phase diagram; American Mineralogist 64 (1979) p.1175-1183