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Crystal structure determination of orthorhombic variscite*2O* and its derivative $AlPO_4$ structure at high temperature

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Abstract

Variscite [$Al(PO_4)\cdot 2H_2O$] is an uncommon secondary phosphate mineral but is important in a variety of environmental and technological applications. It exists in at least one monoclinic (metavariscite) and two orthorhombic polymorphs ("Lucin-type" and "Messbach-type"), but the fine-grained nature of the "Messbach-type" variscite has hampered the determination of its crystal structure. The crystal structure of the latter from Tooele County, Utah, was solved and refined using laboratory powder X-ray diffraction (XRD) data, charge-flipping, and the Rietveld method. Both variscite modifications belong to the family of framework 3D MT structures in which octahedra (M) and tetrahedra (T) are linked by bridging O atoms. Topological analysis reveals that the two structures are polytypes. Based on our results and our structural interpretations, we refer to "Lucin-type" variscite as variscite*1O* and the "Messbach-type" as variscite*2O*, to be consistent with modern polytype terminology. The similarity of these two structures suggests that *1O*-*2O* interstratifications may exist in nature, which is consistent with observed broadening of diffraction peaks of the Tooele material. ^{31}P and ^{27}Al MAS/NMR measurements are consistent with the XRD-determined crystal structure, and they show distinct signals for each of the two independent P and Al positions in variscite*2O*.

High-temperature XRD, thermal analyses, and NMR measurements were applied to study the nature of the transformation of variscite*2O* to a derivative $AlPO_4$ structure above 473 K. Charge-flipping analysis showed that the crystal structure of the new anhydrous $AlPO_4$ phase ($AlPO_4$-var*2O* in analogy to its parent structure) can be described as a 3D framework of alternating AlO_4 and PO_4 tetrahedra linked by bridging O atoms. Thermogravimetric analyses revealed almost complete dehydration above ~450 K, and NMR results were consistent with tetrahedral Al and P atoms.

Keywords: Variscite, X-ray powder diffraction, charge-flipping, nuclear magnetic resonance, polytypism, $AlPO_4$