

The amblygonite (LiAlPO₄F)-montebrasite (LiAlPO₄OH) solid solution: A combined powder and single-crystal neutron diffraction and solid-state ⁶Li MAS, CP MAS, and REDOR NMR study

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ABSTRACT

The amblygonite-montebrasite series of minerals, common constituents of granitic pegmatites and topaz-bearing granites, show complete solid solution with ideal composition LiAlPO₄(F, OH). These compounds are ideal for studying F ↔ OH solid solution in minerals because natural members of the series generally show little deviation from the ideal composition. In this study, we used powder and single-crystal neutron diffraction and solid-state ⁶Li MAS, CP MAS, and REDOR NMR techniques to study the effect of F ↔ OH substitution on the series.

Lattice parameters refined from single-crystal neutron diffraction data show increasing *b* and decreasing *a*, *c*, and *V* with increasing F/(F + OH). The volume is highest for the OH end-member because of the presence of an additional atom (H). The *a* and *c* parameters decrease with increasing F/(F + OH) because the O-H vector is close to the **a-c** plane and the Al-OH/F vectors are approximately parallel to **c**. Lattice parameters refined from neutron powder diffraction patterns collected at lower *T* show that thermal contraction increases with F/(F + OH), presumably because the F anion takes up less space than the OH molecule.

The results show that the OH/F position is always fully occupied. The H displacement ellipsoid shows little change with occupancy, which obviously corresponds negatively with increasing F/(F + OH). However, the Li displacement ellipsoid becomes extremely large and anisotropic with increasing F fraction. Most of the distortion is associated with the *U*₃ eigenvalue, which lies between the **c** and **c*** directions. *U*_{eq} values corresponding to the Li atom show a greater reduction with decreasing temperature than the other atoms. The temperature dependence of Li is the same regardless of F content. Even when extrapolated to absolute zero the Li displacement ellipsoid is very large, which implies a large static disorder.

At the montebrasite end of the series, there are five short Li-φ (φ = O, OH, F) distances and one very long Li-O4 bond. With increasing F content, the Li-O4 distance decreases and the Li-O3f distance increases, such that at the amblygonite end, the coordination is 4 + 2. The disorder in the Li site is obviously caused by the substitution of F for OH. The driving force is the loss of the hydrogen bond to O4, which causes the Li-O4 bond to strengthen and improves the bond valence to O4. The results show that the H atom position is imbedded *within* the distorted octahedral oxygen coordination of the Li atom.

To represent the disorder better, we used a split Li site model. The results show that Li1 occupancy increases and the Li2 occupancy decreases with increasing F content, and that the Li1-Li2 distance is longer for intermediate compositions than for the end-members.

The ⁶Li MAS NMR experiments provide important structural information complementary to the neutron diffraction results. The spectra of samples in the amblygonite-montebrasite series show two well-resolved peaks, confirming the presence of Li disorder over two distinct sites, and highly resolved ⁶Li MAS NMR spectra are obtained at the very high magnetic field strength of 18.8 T. The peaks at -0.3 ppm and -0.9 ppm were unambiguously assigned to the Li2(OH) and Li1(F) sites found in the neutron diffraction structures. The isotropic chemical shifts are consistent with the coordinations of these Li sites found in the neutron diffraction structures. The relative intensities of the two peaks across the series of samples reflect the varying F/(F + OH). In addition to confirming the assignments of the peaks, it is possible to measure H-Li2 and F-Li1 internuclear distances by

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${}^6\text{Li}\{^1\text{H}\}$ and ${}^6\text{Li}\{^{19}\text{F}\}$ CP and REDOR NMR that are consistent with the corresponding distances from the neutron diffraction structures. The ${}^6\text{Li}\{^1\text{H}\}$ and ${}^6\text{Li}\{^{19}\text{F}\}$ CP and REDOR results indicate that the Li disorder is random throughout the crystals rather than over large domains, a conclusion that cannot be made from diffraction experiments. Variable temperature ${}^6\text{Li}$ MAS NMR spectra confirm that the disorder is static and there is no dynamic exchange involving F, OH, or Li. Each Li ion has access to only one of the two observed sites as determined by the presence of either OH or F in its immediate environment and there is no possibility of a dynamic exchange.