American Mineralogist, Volume 92, pages 34–43, 2007

^{27}Al and ^{23}Na NMR spectroscopy and structural modeling of aluminofluoride minerals

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Abstract

Simulations of high-resolution ^{19}F-decoupled ^{27}Al and ^{23}Na magic-angle spinning nuclear magnetic resonance (MAS NMR) spectra of the aluminofluoride minerals, cryolite, cryolithionite, thomsenolite, weberite, chiolite, prosopite, and ralstonite combined with theoretical modeling have given accurate values of chemical shift (δ_{iso}), and quadrupolar interaction parameters (C_q and η), thereby eliminating ambiguities incurred by the complex nuclear interactions. These NMR data have been correlated with local electronic environments in the minerals, which were calculated using Full Potential Linearized Augmented Plane Wave (FP LAPW) modeling based on the structures from X-ray diffraction (XRD) data. This combination of NMR, XRD, and modeling techniques allowed the analysis and optimization of the crystal structures.

The electronegativities and distances of neighboring ions, represented here by an environmental parameter χ, are shown to control δ_{iso} of both ^{23}Na and ^{27}Al. The calculations using χ, also show that the ions beyond the nearest neighbor play an important role in determining δ_{iso} of ^{27}Al and ^{23}Na in these aluminofluoride minerals, and the substitution of OH for F significantly affects the shielding around ^{27}Al in prosopite and ralstonite. There is a positive correlation between the site distortion at the Na and Al sites and the values of C_q in these aluminofluoride minerals.

Keywords: Cryolite, cryolithionite, elpasolite, weberite, thomsenolite, prosopite, chiolite, ralstonite, aluminofluoride minerals, ^{23}Na, ^{27}Al MAS NMR, FP LAPW calculations