

Proton dynamics in letovicite: Part I. Static ^1H and ^{15}N NMR MAS experiments and lineshape simulations

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ABSTRACT

Synthetic letovicite $(\text{NH}_4)_3\text{H}(\text{SO}_4)_2$ has been investigated using ^1H static, low-speed MAS, and ^{15}N MAS NMR spectroscopy. Experiments were carried out in the temperature range of 215–425 K. The ^1H MAS NMR spectra show three different resonances. The resonance assigned to the ammonia protons is broad and spinning sidebands cannot be resolved in the low-speed MAS NMR spectra. On the other hand, the acidic protons in the ferro- and paraphase show narrow signals with sideband patterns that enable a chemical shift anisotropy analysis. The chemical shift parameters of the free protons in the paraphase ($\delta_{\text{iso}} = 13.2$ ppm, $\delta_{\text{aniso}} = 4.5$ ppm, $\eta = 0.0$) differ completely from those of the protons in the ferrophase ($\delta_{\text{iso}} = 14.1$ ppm, $\delta_{\text{aniso}} = 8.5$ ppm, $\eta = 1.0$). The lowering of the chemical shift anisotropy δ_{aniso} by a factor of two and the change of the asymmetry parameter η imply a tetrahedral site jump mechanism of the protons. Three different ammonia tetrahedra can be distinguished by ^{15}N MAS NMR spectroscopy in the $P2/n$ phase below 273 K. Two resonances are prominent for the ferrophase (space group $C2/c$) corresponding to the two different crystallographic sites. Both resonances move together into a single resonance in the high-temperature phase that can be interpreted as fast dynamics of ammonia groups and its local environment so that the two crystallographic sites are locally nearly equal.

Keywords: Letovicite, proton conduction, ferroelastic, ^1H , ^{15}N , chemical shift anisotropy, lineshape analysis, reorientation, MAS, solid state NMR spectroscopy, phase transition