

Influence of F content on the composition of Al-rich synthetic phlogopite: Part II. Probing the structural arrangement of aluminum in tetrahedral and octahedral layers by ^{27}Al MQMAS and $^1\text{H}/^{19}\text{F}$ - ^{27}Al HETCOR and REDOR experiments

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ABSTRACT

The influence of F substitution on the local structure of Al in the tetrahedral and octahedral sheets of synthetic Al-rich phlogopite samples with nominal gel compositions of $\text{K}(\text{Mg}_{3-x}\text{Al}_x)[\text{Al}_{1+y}\text{Si}_{3-y}\text{O}_{10}](\text{OH})_y(\text{F})_{2-y}$ between $0.0 \leq x \leq 0.8$ and $0.5 \leq y \leq 1.8$, was studied by ^{27}Al MAS, MQMAS, $\{^1\text{H}/^{19}\text{F}\} \rightarrow ^{27}\text{Al}$ 2D CPMAS (HETCOR) and $\{^1\text{H}/^{19}\text{F}\} ^{27}\text{Al}$ REDOR solid-state NMR and by IR spectroscopy. Changes in intensity of the absorption bands in the OH-stretching region of the IR spectra clearly indicate the incorporation of octahedral Al. Signals from the different phases can be separated in the ^{27}Al MQMAS NMR spectra by generation of an isotropic dimension in F1. The ^{27}Al quadrupolar parameters of the four phases were estimated from ^{27}Al MAS NMR spectra obtained at 104.26 and 208.42 MHz. The quadrupolar coupling constant and isotropic chemical shift increases with increasing Al content for the ^{IV}Al site in phlogopite. The ^{VI}Al site shows a clear increase of the asymmetry parameter and C_Q with increasing F content. The estimated ^{27}Al signal areas show the lowest amount of impurity phases at high OH contents and a stabilization of ^{VI}Al sites by hydroxyl groups. The $\{^1\text{H}\} \rightarrow ^{27}\text{Al}$ 2D CPMAS (HETCOR) NMR experiment at short contact times provides information about site neighborhoods of tetrahedral Al sites and Mg_3OH as well as Mg_2AlOH sites, whereas magnetization is only transferred to the octahedral Al sites from hydroxyl groups in Mg_2AlOH sites. The $\{^{19}\text{F}\} \rightarrow ^{27}\text{Al}$ 2D CPMAS (HETCOR) NMR spectrum is dominated by ^{IV}Al sites coupled to the Mg_3F complex in phlogopite. Resonances from Mg_2AlF complexes are not observed. Finally, the $\{^1\text{H}/^{19}\text{F}\} ^{27}\text{Al}$ REDOR experiments support the results of the 2D CPMAS (HETCOR) experiments.