

## **Spectroscopic and structural properties of synthetic micas on the annite-siderophyllite binary: Synthesis, crystal structure refinement, Mössbauer, and infrared spectroscopy**

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### **ABSTRACT**

The effect of the incorporation of Al-Tschermak's molecule to the trioctahedral potassium mica annite  $\{K\}[Fe_3] < AlSi_3 > O_{10}(OH)_2$  on local and average structure has been investigated by hydrothermal synthesis, structure refinement of X-ray powder diffraction data, Mössbauer and infrared spectroscopy. The various types of brackets indicate different structural sites. Samples with compositions  $\{K\}[Fe_{3-x}Al_x] < Al_{1+x}Si_{3-x} > O_{10}(OH)_2$  were prepared by hydrothermal techniques. The maximum solubility of  $Al^{3+}$  is limited to  $x = 0.92$  at 500 °C and to  $x = 0.82$  at 700 °C. The main factor controlling the substitution limits is the ditrigonal distortion of the tetrahedral rings. Lattice parameters decrease linearly with increasing  $Al^{3+}$  content of the mica. A considerable decrease of M2-O and nearly no change of M1-O bond lengths with increasing  $Al^{3+}$  contents is indicative of preferred occupation of the M2 site by  $[Al^{3+}]$ . Changes in K-O distances are also very pronounced and reflect the ditrigonal distortion of the tetrahedral sheet. The bimodal ferrous quadrupole splitting distribution (QSD) in annite, extracted from Mössbauer spectra, becomes narrower and more centered around 2.60 mm/s with increasing  $Al^{3+}$  contents, and its evolution suggests an increasing deviation from ideal octahedral coordination of Fe by O, illustrated by the increasing octahedral flattening angle  $\psi$ . The population of individual QSD components proves that it is impossible to resolve cis and trans M-sites in micas by Mössbauer spectroscopy. In the hydroxyl stretching region, up to 7 bands are observed in the infra-red spectra which correspond to OH groups adjacent to 3  $Fe^{2+}$  (N-bands), to OH groups coordinated by  $Fe^{2+}$ ,  $Al^{3+}$ , and  $Fe^{3+}$  (I-bands) and to configurations having one octahedral vacancy (V-bands). N- and I-type bands are shifted toward lower wavenumbers with increasing  $Al^{3+}$  content because of increasing  $OH \cdots O_{tet}$  interactions.