

# The role of Fe and cation order in the crystal chemistry of surinamite, $(\text{Mg}, \text{Fe}^{2+})_3(\text{Al}, \text{Fe}^{3+})_3\text{O}[\text{AlBeSi}_3\text{O}_{15}]$ : A crystal structure, Mössbauer spectroscopic, and optical spectroscopic study

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## ABSTRACT

The crystal structure of surinamite from “Christmas Point,” Enderby Land, Antarctica, has been newly refined by single-crystal X-ray diffraction:  ${}^{\text{VI}}(\text{Mg}_{2.26}\text{Fe}_{0.74}^{2+}\text{Fe}_{0.39}^{3+}\text{Al}_{2.61})\text{O}^{\text{IV}}(\text{Al}_{1.00}\text{Be}_{1.00}\text{Si}_{3.00})\text{O}_{15}$  (simplified formula), space group  $P2/n$ ,  $a = 9.915(2)$ ,  $b = 11.368(2)$ ,  $c = 9.617(2)$ ,  $b = 109.30(2)^\circ$ ,  $Z = 4$ ,  $wR(F^2) = 0.074$  for 4876 independent reflections. The refined site occupancies agree well with the chemical composition determined by electron microprobe analysis and with the  $\text{Fe}^{3+}/\text{Fe}^{2+}$  ratio estimated from stoichiometry. The surinamite structure is characterized by an ordered Al/Be/Si distribution on the tetrahedral sites and by charge ordering with extensive  $\text{Mg}^{2+}\text{-Fe}^{2+}$  and  $\text{Al}^{3+}\text{-Fe}^{3+}$  exchange on the octahedral sites. This cation ordering is distinct from that observed in related phases of the sapphirine series and aenigmatite groups, and the difference is linked to the unique structural topology of the tetrahedral chains in surinamite. Optical and Mössbauer spectra of surinamite have been fully interpreted in terms of an octahedral distribution of  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  cations that agrees very well with the X-ray site populations. Both the X-ray and Mössbauer data establish the absence of significant tetrahedral Fe and the non-uniform distribution of octahedral Fe. Intense and strongly polarized absorption bands caused by IVCT-processes in clusters of  $\text{Fe}^{3+}$  and  $\text{Fe}^{2+}$  iron in edge-sharing octahedral sites produce the unusual color and pleochroism observed in surinamite.