

**Na₆Fe(SO₄)₄, THE FERROUS ANALOGUE OF VANTHOFFITE,
A POTENTIAL ION CONDUCTOR: SYNTHESIS AND CRYSTAL STRUCTURE**

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Vanthoffite, Na₆Mg(SO₄)₄, is a rare mineral occasionally occurring in salt deposits. FISCHER & HELLNER (1964) solved its crystal structure from X-ray film data of a synthetic crystal in space group *P2₁/c*. KEESTER & EYSEL (1977) reported lattice parameters derived from X-ray powder data for several synthetic analogues, where Mg was replaced by divalent cations of Mn, Co, Ni, Zn, and also Fe. Later, BARTSCH & HOFFMANN (1986) published a short note on the remarkable Na⁺ ion conductivity of natural and synthetic vanthoffite (in the order of $\sigma = 5 \cdot 10^{-5} \Omega^{-1} \text{ cm}^{-1}$), but no further details were reported subsequently.

In order to provide up-to-date structural and crystal chemical data for the vanthoffite structure type, especially to clarify the details of the three crystallographically different Na⁺ cation environments, single crystals of the Fe²⁺ analogue in sizes up to 0.5 mm were synthesized under low-hydrothermal conditions at ~220° C in Teflon-lined steel autoclaves. The crystal structure was refined on *F*² using CCD single-crystal X-ray diffraction data of the complete Ewald sphere up to $2\theta = 80^\circ$ (Nonius Kappa CCD four-circle diffractometer, graphite monochromatised MoK α radiation). Relevant crystal and refinement data are: Na₆Fe(SO₄)₄, monoclinic, space group *P2₁/c*, *a* = 9.692(1), *b* = 9.267(1), *c* = 8.248(1) Å, β = 113.37(1)°, *V* = 680.0 Å³, *Z* = 2, *R*₁ = 0.024, *wR*₂ = 0.061 for 4213 unique reflections and 125 parameters (*R*_i = 0.030 for merging 15887 total reflections). Our lattice parameters significantly differ (especially *b* and *V*) from those given by KEESTER & EYSEL (1977), irrespective of the fact that their values obviously correspond to the non-reduced cell setting *P2₁/n*.

The structure type of vanthoffite is composed of one octahedral Me²⁺ site, two crystallographically different SO₄ tetrahedra, and three distinct types of Na⁺ positions. The MeO₆ octahedra share all oxygen corners with SO₄ groups, forming rather loose polyhedral layers parallel to (100). One third of the sodium cations (Na3) occupy cavities exclusively within these sheets, while Na1 and Na2 additionally provide linkage between neighbouring sheets.

In Na₆Fe(SO₄)₄, the FeO₆ octahedron is slightly elongated (2.10-2.19 Å) with a typical mean Fe^{[6]2+}-O distance of 2.135 Å. The SO₄ tetrahedra are nearly regularly shaped with <S-O> = 1.474 and 1.476 Å for S1 and S2, respectively. Na1 is clearly six-fold coordinated by oxygen atoms in a strongly distorted octahedral arrangement (2.32-2.49 Å, <Na1-O> = 2.403 Å), Na2 is [5+1] coordinated (2.35-2.47 and 2.82 Å, <Na2-O> = 2.489 Å; two further O atoms follow at ~3.04 Å), and Na3 has seven nearest oxygen neighbours (2.29-2.77 Å, <Na3-O> = 2.519 Å; further Na-O contacts are >3.08 Å). These NaO_x units form a three-dimensional framework of partly edge- and corner-sharing polyhedra. The implications of this structural arrangement for a potential Na⁺ ion conductivity in Na₆Fe(SO₄)₄ will be discussed.

References

- BARTSCH, H.-H. & HOFFMANN, W. (1986): *Z. Kristallogr.*, 174, 5-6.
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