Crystal structure of rasvumite, KFe$_2$S$_3$

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Abstract

Rasvumite, KFe$_2$S$_3$, isoostructural with BaFe$_2$S$_3$ described by Hong and Steinfink (1972), is orthorhombic, Cmcm, $a = 9.049(6)$, $b = 11.019(7)$, $c = 5.431(4)$Å, $V = 541.5$Å$^3$, $Z = 4$, density (calc) = 3.029 g cm$^{-3}$. Least-squares refinement of 332 single-crystal $hkl$ reduced the conventional residual to 0.081. The structure contains double edge-sharing chains of Fe–S tetrahedra parallel to $c$ and face-sharing pairs of K–S polyhedra that also form double chains parallel to $c$. The average bond distances are: Fe–S = 2.264, Fe–Fe = 2.710, K–S = 3.515Å. By analogy to BaFe$_2$S$_3$, rasvumite has high-spin iron with delocalized electrons such that the average oxidation state is close to the 2.5+ indicated by the formula.

Introduction

Rasvumite was discovered at the Khibina massif, Kola Peninsula, USSR, and described by Sokolova et al. (1970). The chemical formula originally proposed, K$_2$Fe$_4$S$_8$, with $Z = 1$ in the orthorhombic cell, was not compatible with the symmetry. The correct formula, KFe$_2$S$_3$, was assigned by Czamanske et al. (1979) after discovery and study of rasvumite at Coyote Peak, Humboldt County, California.

The Coyote Peak rasvumite has not been found in crystals as excellent as those found in the Khibina massif. Through the courtesy of M. N. Sokolova, Academy of Sciences, Moscow, some of the original crystals were made available to us for study, and one of these was selected for structural analysis.

Comparison of the crystallographic data for rasvumite with those reported for synthetic BaFe$_2$S$_3$, by Hong and Steinfink (1972) left little doubt that the two are isoostructual despite the differences in chemistry and formal valence. The isoostructural relationship is confirmed by the results of our refinement for the rasvumite structure. A brief preliminary description was given by Clark et al. (1979).

Experimental data

Crystallography, collection of data

The crystallographic data for rasvumite given by Czamanske et al. (1979) were confirmed upon examination of the Khibina crystals selected for the structural study. That crystal was a prismatic fragment 0.5 mm long and 0.2 × 0.05 mm in cross-section. It was impossible to obtain a more nearly equant crystal because of its tendency, noted by Sokolova et al. (1970), to split into fine needles when pressed. A least-squares fit of the angular coordinates of 29 automatically centered reflections in the $2\theta$ range 30° to 46° gave the values in Table 1. For comparison, the values reported by Sokolova et al. and by Czamanske et al. (1979) are also listed in Table 1, together with those for the isoostructural synthetics, BaFe$_2$S$_3$ (Hong and Steinfink, 1972) and CsCu$_3$Cl$_5$ (Brink et al., 1954).

A total of 458 reflections in the angular $2\theta$ range of 5° to 60° was measured using an $\omega-2\theta$ scan mode, a scan range of 2°, graphite-monochromatized MoK$\alpha$ radiation, and a solid-state detector system. Two
|   | 15 | 4 | 9 | 27 | 45 | 63 | 81 | 99 | 117 | 135 | 153 | 171 | 189 | 207 | 225 | 243 | 261 | 279 | 297 |
|---|----|---|---|----|----|----|----|----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
|   | 15 | 4 | 9 | 27 | 45 | 63 | 81 | 99 | 117 | 135 | 153 | 171 | 189 | 207 | 225 | 243 | 261 | 279 | 297 |
|   | 15 | 4 | 9 | 27 | 45 | 63 | 81 | 99 | 117 | 135 | 153 | 171 | 189 | 207 | 225 | 243 | 261 | 279 | 297 |
|   | 15 | 4 | 9 | 27 | 45 | 63 | 81 | 99 | 117 | 135 | 153 | 171 | 189 | 207 | 225 | 243 | 261 | 279 | 297 |
|   | 15 | 4 | 9 | 27 | 45 | 63 | 81 | 99 | 117 | 135 | 153 | 171 | 189 | 207 | 225 | 243 | 261 | 279 | 297 |
|   | 15 | 4 | 9 | 27 | 45 | 63 | 81 | 99 | 117 | 135 | 153 | 171 | 189 | 207 | 225 | 243 | 261 | 279 | 297 |

### Table 4 (continued)