

On the Synthesis, Crystal Chemistry and Magnetic Properties of Rasvumite and Related Compounds.,

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Rasvumite, KFe_2S_3 , belongs to a group of rare iron bearing alkali sulphide minerals together with erdite, bartonite, djerfisherite and others occurring in mafic alkaline rocks on the Kola peninsula (Russia) or Coyote Peak in California (USA) [1]. KFe_2S_3 has been synthesized hydrothermally in microcrystalline appearance at relatively high temperatures of 400 - 500 °C [2]. We succeeded, however, to prepare the compound by solid state synthesis from finely powdered KFeS_2 , Fe, and S at 400 - 500 °C. The lattice parameters of the product (Cmcm, $a = 9.047(4)$, $b = 11.005(6)$, $c = 5.422(2)$ Å) are almost identical with those given for the mineral [1]. By the same method we were able to prepare the new isotypic phases KFe_2Se_3 ($a = 9.357(3)$, $b = 11.551(4)$, $c = 5.627(2)$ Å) and RbFe_2S_3 ($a = 9.218(5)$, $b = 11.203(5)$, $c = 5.443(2)$ Å). These three materials are low temperature phases slowly decomposing above 450 °C into $\text{AFeX}_2 + \text{FeX}$ (A: K, Rb; X: S, Se). On the contrary, isotypic RbFe_2Se_3 melts congruently at ~ 850 °C [3]. Rasvumite belongs to the family of naturally occurring or synthetic fibrous thioferrates having chains of edge-sharing $[\text{FeS}_4]$ tetrahedra. Thus $\text{NaFeS}_2 \cdot x\text{H}_2\text{O}$ (Erdite), KFeS_2 and TiFeS_2 (Raguinite) are composed of single chains, while Rasvumite has double $[\text{Fe}_2\text{S}_3]$ chains. It is interesting to note that KFeS_2 , which has not yet been described as a naturally occurring mineral, appears to be most stable in laboratory experiments, and that $\text{NaFeS}_2 \cdot x\text{H}_2\text{O}$ (Erdite) is not stable in the presence of K^+ ions bearing solutions, forming readily a hydrated phase of KFeS_2 by ion exchange. KFe_2S_3 forms a continuous synthetic series of mixed crystals, $\text{K}_x\text{Ba}_{1-x}\text{Fe}_2\text{S}_3$, with isotypic BaFe_2S_3 . This raises the question of valence change of iron, because formally iron should be in oxidation state +2.5 in KFe_2S_3 and +2 in BaFe_2S_3 . Bond valence calculations and Mössbauer spectra [1, 4, 5], however, suggest an intermediate valence state close to +2.5 in both compounds and the mixed crystals. Below 90 K the Mössbauer spectra show strong magnetic splitting [5], but no magnetic order could be detected yet by neutron powder diffraction.

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