s5.m15.o5 **On the Synthesis, Crystal Chemistry and Magnetic Properties of Rasvumite and Related Compounds.** Herbert Boller, *Institut für Allgemeine und Anorganische Chemie, Universität Linz, Austria. E-mail: herbert.boller@jku.at*

**Keywords: Rasvumite; Intermediate Valence Compound; Solid State Synthesis**

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 $AFeX_2$ + 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 $[FeS_4]$ tetrahedra. Thus $NaFeS_2 \cdot xH_2O$ (Erdite), $KFeS_2$ and $TlFeS_2$ (Raguinite) are composed of single chains, while Rasvumite has double $[Fe_2S_3]$ 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 $NaFeS_2 \cdot xH_2O$ (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, $K_xBa_{1-x}Fe_2S_3$, 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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s5.m16.o1 **Phase Diagrams of Minerals from Density-Functional Perturbation Theory.** Oganov A.R.[1] and Jung D.Y.[1], G.D. Price[2] and M.J. Gillan[2], [1]*Laboratory of Crystallography, ETH Zurich, Zurich CH-8092, Switzerland. E-mail: a.oganov@mat.ethz.ch,* [2]*University College London, Gower St., London WC1E 6BT, U.K. E-mail: a.oganov@mat.ethz.ch*

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Typical mineralogical models of the Earth's lower mantle are very simple: e.g., 70 vol.% $(Mg,Fe)SiO_3$ perovskite, 20 vol.% (Mg,Fe)O, 5 vol.% $CaSiO_3$ perovskite [1]. However, these models have been challenged by several groups: e.g., decomposition of $MgSiO_3$ [2] and $CaSiO_3$ [3] perovskites has been proposed. Consequently, CsCl-structured CaO and various phases of $SiO_2$ would have to be considered as possible mantle-forming minerals.

Using density-functional perturbation theory [4] we have studied lattice dynamics and high-pressure phase diagrams of MgO [5], $SiO_2$ [6], and $MgSiO_3$ [7]. We find [5] that MgO remains in the NaCl-type structure at all conditions within the Earth. The calculated phase diagram of $SiO_2$ [6] allowed us to predict the depths of seismic discontinuities that would appear within the lower mantle if $SiO_2$ phases were present in significant amounts. However, these depths (1410 and 2210 km) do not correspond to any observed discontinuities, suggesting that $SiO_2$ polymorphs are not present, at least as major phases, in the lower mantle. $MgSiO_3$ perovskite is found [7] to be stable with respect to decomposition into oxides; pressure and temperature only increase its stability. For $CaSiO_3$ perovskite the tetragonal and orthorhombic structures are energetically very similar and slightly more favourable than the idealised cubic structure. The calculated [8] enthalpy of decomposition of this mineral into the oxides is so high (1.21 eV at 40 GPa, 1.76 eV at 120 GPa) that its decomposition within the lower mantle can be effectively ruled out.

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