

05.2-09 PREPARATION OF $Ba_p(Fe_2S_4)_q$: A ONE-DIMENSIONAL TRANSITION METAL CHALCOGENIDE. By J.S. Swinnea and H. Steinfink, Department of Chemical Engineering, Materials Science Laboratories, The University of Texas, Austin, Texas, 78712 U.S.A.

Research in our laboratory has produced many compounds in the Ba-Fe-S system. We have discovered and investigated a group of compounds in this system which has the general formula $Ba_p(Fe_2S_4)_q$, p and q integral, or $Ba_{1+x}Fe_2S_4$.

These compounds comprise a crystallographic series to which the designation "infinitely adaptive" has been given. It was found that the preparation of these compounds required carefully controlled reaction temperature and sulfur pressure. We undertook a systematic investigation of reaction conditions at temperatures of 650°C, 747°C, and 800°C and sulfur fugacities from 1×10^{-4} atm to 6.4 atm. Results from this study show that the phase $BaFe_2S_4$ is not part of the infinitely adaptive

series, but coexists with $Ba_{1.07}Fe_2S_4$ in a biphasic region on the phase diagram. Furthermore, the series only appears to exist in the region $0.07 \leq x \leq 0.142$ with the phase $BaFe_2S_3$ being formed above the highest barium content phase.

$Ba_p(Fe_2S_4)_q$ appears to be a good model of a one-dimensional structure because of its well separated infinite chains of edge sharing FeS_4 tetrahedra. Results from magnetic susceptibility measurements indicate an effective moment of $1.81 \mu_B$ and an exchange coupling, J/K, of $-112^\circ K$. Room temperature electrical conductivities for $x \neq 0$ phases of 2×10^{-1} (ohm cm) $^{-1}$ decrease to 10^{-4} (ohm cm) $^{-1}$ at 50°K. Furthermore, Mössbauer spectroscopy reveals a complex transition at about 265°K.

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05.2-10 COMPOUNDS WITH INTERMEDIATE SPIN: THE CRYSTAL STRUCTURE OF $Fe[S_2CN(C_3H_4N)_2]_3 \cdot \frac{1}{2}CHCl_3$ AT 150 AND 295 K. By J. Albertsson, Å. Oskarsson and K. Ståhl. *Inorganic Chemistry, Chemical Center, University of Lund, P.O.B. 740, S-220 07 Lund, Sweden.*

In connection with investigations of structure-property relations in various solid $Fe(S_2CNR_2)_3$ complexes (Albertsson, Elding & Oskarsson, *Acta Chem. Scand.* (1979) A33, 703), we have synthesized tris(N,N-dipropionitril-dithiocarbamato)iron(III). Single crystals of the hemisolvate were grown from chloroform and three-dimensional X-ray intensities were collected at 150 and 295 K. At both temperatures the compound crystallizes in triclinic space group $P\bar{1}$, $Z = 2$. The cell constants and the effective magnetic moments are: 150 K, $a = 10.676(4)$, $b = 12.038(5)$, $c = 14.034(5)$ Å, $\alpha = 70.35(4)$, $\beta = 74.61(3)$, $\gamma = 67.26(3)^\circ$, $\mu = 2.78$ B.M. (low spin form); 295 K, $a = 10.765(5)$, $b = 12.062(6)$, $c = 14.113(6)$ Å, $\alpha = 70.13(5)$, $\beta = 74.98(3)$, $\gamma = 67.59(4)^\circ$, $\mu = 3.68$ B.M. (intermediate spin form). The non-H atoms were located with MULTAN and difference maps. The analysis of the structure is in progress: the refinements have so far converged to $R = 0.050$ (150 K) and 0.063 (295 K).

The structure comprises mononuclear complexes of pseudo-symmetry D_3 van der Waals packed with statistically distributed chloroform molecules. The average Fe-S distance is 2.307(7) Å at 150 K and 2.321(9) Å at 295 K. The structure and its magnetic properties will be discussed in relation to other solid iron dithiocarbamate complexes.

05.2-11 THE STRUCTURAL BASIS FOR PYROELECTRICITY IN $LiIO_3$. By C. Svensson and J. Albertsson, *Inorganic Chemistry, Chemical Center, University of Lund, P.O.B. 740, S-220 07 Lund, Sweden*; R. Liminga, *Institute of Chemistry, University of Uppsala, Sweden*; and S. C. Abrahams, *Bell Laboratories, Murray Hill, NJ 07974, USA.*

Hexagonal $LiIO_3$ -III, space group $P6_3$, is a well-known dielectric and nonlinear optic material. It has a structure from which those of a range of potentially useful transition metal iodates with different stoichiometries and unit cell metrics may be derived (Svensson, Abrahams and Bernstein, *J. Solid State Chem.* (1981) in press). $LiIO_3$ has been chosen to study the relationship between polarization and structural change as a function of temperature in a simple material. It was previously inferred, on the basis of a simple point charge and dipole model, that the spontaneous polarization of $LiIO_3$ increases with increasing temperature (Liminga and Abrahams, *J. Appl. Crystallogr.* (1976) 9, 42): the atomic displacements have been estimated to be on the order of 0.4×10^{-4} Å K^{-1} (Abrahams, *Mat. Res. Bull.* (1978) 13, 1253).

We have now collected several three-dimensional X-ray diffraction sets of integrated intensity data from room temperature to that of the phase II transition (γ - $LiIO_3$ in the old notation) at about 525 K. Analysis of the experiment is still in progress: the structural refinements indicate significant coordinate changes with temperature. The pyroelectric effect will be discussed in terms of absolute configuration, atomic displacements and iodate ion deformations.