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NOTES

The Stabilization of Tetravalent Iron in Tetrahedral Sulfur Coordination

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We have reported the preparation at high pressure and the crystal structure of the compound Ba_3FeS_5 in which iron has a formal valence of +4 (*1*). The Mössbauer spectrum shows one quadrupole split line with an isomer shift of 0.17 mm/sec (with respect to α–Fe) and a redetermination of the magnetic susceptibility between 77°K and room temperature yields a value for the effective moment of 5.81 B.M. These results are indicative of Fe^{+3}, and we advanced the view that an electron is back-donated from sulfur to iron so that the charge is reduced to +3 (*2*). Many experiments were carried out to see whether pressures near ambient would be sufficient to prepare this compound, but below 20 kilobars $Ba_{15}Fe_7S_{25}$ was always formed. We, therefore, attempted to replace part of the iron by an element which is tetravalent and has a strong preference for tetrahedral coordination, with the hope that the structure would be stabilized and could then be synthesized under ambient pressure conditions. Silicon was used for this purpose, and BaS, Fe, Si, and S were mixed in the proportions $Ba_3Fe_{0.2}Si_{0.8}S_5$, $Ba_3Fe_{0.5}Si_{0.5}S_5$, and $Ba_3Fe_{0.8}Si_{0.2}S_5$. These mixtures were sealed in evacuated quartz ampules, heated at 900°C for several days, and then slowly cooled to room temperature. The X-ray powder diffraction diagrams obtained from these materials were qualitatively very similar to the powder pattern of Ba_3FeS_5, but the diffraction lines were shifted and some changes in relative intensities were observed. It was evident that silicon had stabilized the structure by forming a solid solution $Ba_3(Fe_{1-x}Si_x)S_5$. The powder patterns could be indexed on the basis of small adjustments in the lattice parameters of the Ba_3FeS_5 phase. To determine whether Si indeed replaced Fe by random substitutions in the tetrahedral sites, a single crystal was selected from the product $Ba_3Fe_{0.2}Si_{0.8}S_5$, and a three-dimensional X-ray diffraction structure determination was carried out. The lattice constants were $a = 12.034(2)$Å, $b = 9.493(1)$Å, $c = 8.531(1)$Å, $z = 4$, with space group *Pnma*. The structure was refined by least squares using 1192 structure factors to $R = 0.062$, $wR = 0.057$. The resultant structure was identical to that of Ba_3FeS_5, and the lowest value of R was obtained when the occupancy factors for the atoms in the tetrahedral site were set to 0.2 for iron and 0.8 for silicon, in agreement with the composition of the initial reaction mixtures. Table I shows the Mössbauer isomer shifts and quadrupole splittings for two solid solutions as well as for Ba_3FeS_5.

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TABLE I

ISOMER SHIFT AND QUADRUPOLE SPLITTINGS (REFERRED TO α–Fe)

	δ (mm/sec)	ΔE (mm/sec)
Ba_3FeS_5	0.183	0.518
$Ba_3(Fe_{0.8}Si_{0.2})S_5$	0.152	0.531
$Ba_3(Fe_{0.2}Si_{0.8})S_5$	0.146	0.424
	0.170	1.687

The isomer shift for Ba_3FeS_5 is in agreement with that previously reported (*1*). The isomer shifts for the solid solution phases show a significant decrease from the value for the end member. We interpret the decrease as due to the stabilizing effect of the silicon, whereby a lesser amount of back-donation to the quadrivalent iron occurs, and thus a smaller value of the isomer shift is observed. Two sets of quadrupole split lines were observed in the phase $Ba_3Fe_{0.2}Si_{0.8}S_5$. A very strong absorption pair, with $\delta = 0.146$, is ascribed to the solid solution phase; a very weak pair, corresponding to $\delta = 0.170$, is due to a small amount of an impurity which was not seen in the powder diagram. The substitution of silicon in excess of 0.8 usually showed a second phase in the X-ray powder diffraction patterns, and these lines could be indexed on the basis of the unit cell dimensions for Ba_2SiS_4 (*3*).

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