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THE SYNTHESIS OF IRIDIUM DISULFIDE AND NICKEL DIARSENIDE HAVING THE PYRITE STRUCTURE

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R. A. MUNSON

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The Synthesis of Iridium Disulfide and Nickel Diarsenide Having the Pyrite Structure

BY RONALD A. MUNSON[1]

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The pyrite structure (space group T_h^6[Pa3]) is in general a densely packed arrangement and, therefore, tends to be favored when synthesis is attempted between the transition metals and groups Va and VIa elements at high pressure. The preference of copper disulfide for the pyrite structure when synthesized under pressure allows the realization of the 1:2 cation to anion stoichiometry, which cannot be obtained at all if the synthesis is attempted below 15 kbars pressure.[2] The two syntheses which we wish to report here were performed in the "belt" superpressure apparatus[3] using a cell constructed of sodium chloride with a graphite heater. Both syntheses were carried out at 60 kbars pressure. Pressure and temperature calibration have been described.[2] Compositions have been determined by thermogravimetric analysis.

At 1 atm iridium is known to combine with sulfur to form iridium disulfide having the orthorhombic crystal structure of iridium diselenide,[4,5] in which part of the iridium may be considered to have the +3 oxidation state. If the ratio of sulfur to iridium is increased to nearly 3:1, then a pyrite structure is formed[6] in which the +3 iridium is balanced with cation vacancies. At 60 kbars, a mixture of sulfur and iridium (3:1 mole ratio) will react at 1500° to form the same pyrite structure ($IrS_{2.9}$) observed by Biltz, *et al.*[6] ($a = 5.62$ Å). If, however, sulfur and iridium in a 2:1 mole ratio react at 60 kbars and 1500°, then a new pyrite phase is found ($IrS_{1.9}$) with $a = 5.68$ Å. Powder diffraction patterns obtained from samples having an initial composition with a mole ratio between 2 and 3 which were allowed to react under the same conditions showed the presence of both pyrite phases.

TABLE I
SPACING AND INDEXING OF THE REFLECTIONS OF CUBIC NICKEL DIARSENIDE[a]

d	hkl	Intensity	d	hkl	Intensity
2.86	200	W	1.070	432	M
2.56	210	S	1.051	521	M
2.34	211	S	1.019	440	M
2.03	220	W	0.961	600	W
1.98	221	VW	0.949	610	W
1.73	311	VS	0.936	611	M
1.66	222	W	0.911	620	VW
1.59	230	M	0.880	533	M
1.54	321	S	0.870	622	VW
1.435	400	W	0.860	630	M
1.285	420	W	0.851	631	M
1.255	421	M	0.832	444	VW
1.225	332	W	0.800	640	W
1.174	422	W	0.792	641	S
1.109	511	M	0.785	552	S

[a] Copper $K\alpha_1$ nickel-filtered radiation employed with a Norelco camera of diameter 114.6 mm.

Nickel diarsenide crystallizes in an "anomalous" marcasite structure[7] which differs from the Jahn–Teller marcasite structure by having minimal angular distortion about the cation octahedra. In this sense the "anomalous" marcasites are like the pyrites; however, they differ from the pyrites in that the marcasite structure is a less dense packing arrangement. These factors suggest that materials having the "anomalous" marcasite structure might be induced to form the pyrite structure when synthesized under pressure. An intimate mixture of powdered nickel and arsenic in a 1:2.2 mole ratio after reaction at 60 kbars and 1400° was cooled at pressure to room temperature over a period of 0.5 hr. After the release of the pressure a metallic gray material was obtained which gave the X-ray reflections (Table I) of the cubic pyrite structure, $a = 5.77$ Å. The calculated density, 7.21 g cm^{-3}, may be compared with the pycnometric density of 7.15 ± 0.10 g cm^{-3}. These results suggest that other materials possessing the "anomalous" marcasite structure may also be synthesized in the pyrite arrangement under pressure.

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(1) Bureau of Mines, Metallurgy Research Center, College Park, Md. 20740.

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1-68 (50M)