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A LOW TEMPERATURE SYNTHESIS FOR POWDER-FORM INTERMETALLICS AND OTHER COMPOUNDS—II

SELENIDES

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Abstract—The work previously reported by KULIFAY has been extended to include selenides, of which nine have been prepared, including CuSe, βAg_aSe , CdSe, PbSe, TlSe, HgSe, NiSe, $Cu_{a-x}Se$ (where $x \sim 0.2$) and CuAgSe. As was the case with intermetallics, antimonides, arsenides and tellurides, the selenide synthesis is quantitative, simple and rapid, and uses a temperature of only 100°C at atmospheric pressure. It consists of the reduction of mixed aqueous solutions containing the elements in the stoicheiometric ratio called for in the product, by addition to aqueous ammoniacal hydrazine solutions. Two copper selenides can be prepared by varying the elemental proportions.

THE writer developed⁽¹⁾ a general method for the synthesis of intermetallics, antimonides, arsenides and tellurides, and it was desired to determine the extent to which the method would apply further, specifically with selenides.

BENZING et al.⁽²⁾ have published work, in which of all selenides prepared but one they first isolated the solid metal selenite before reducing with hydrazine. In preparing zinc and cadmium selenides, they formed first a hydrazinometal selenide complex which was then decomposed with acetic acid before obtaining the normal selenide. The current work extends previous work to the preparation of selenides of silver, thallium, nickel and the ternary CuAgSe, in addition to PbSe, CdSe, CuSe, Cu_{2-x}Se (where $x \sim 0.2$), and HgSe, and provides a simpler method by bypassing the intermediate steps.

EXPERIMENTAL AND RESULTS

Apparatus and procedure. Separate solutions (A) and (B), of the starting metals or compounds indicated in Table 1 were prepared in covered 150 ml beakers. These solutions were then poured together, rinsing to complete the transfer. This mixture was swirled well, resulting in a clear, homogeneous solution of the two metal ions in the exact stoicheiometric ratio desired. The reducing solution indicated was made up in a covered 1 l. beaker and heated to boiling. Just as the boiling temperature was reached, the metals solution was added carefully in a fine stream, with constant stirring and rinsing. The reduction was immediate, and vigourous in the case of the Cu and Hg compounds, where much gas was evolved. The reduction beaker was covered and the contents boiled 1.5 hr, except where otherwise indicated in Table 1, rinsing down occasionally any precipitate which accumulated above the liquid. This was then suction-filtered through an oven-dried, tared, sintered-glass filtering crucible. It was washed well, then drained by suction. This was rinsed with methanol and air-dried at 70°C to constant weight. The products are susceptible to oxidation at higher temperatures.

Materials. All raw materials were B and A Reagent quality or equivalent. Where Hg element was used, its HNO₃ solution was heated after solution was complete, to insure oxidation to Hg (II). This would lessen hydrolytic precipitation at the stage where the metals solutions were rinsed together prior to adding to the reducing solution. Equivalent amounts of HgO may be used instead of Hg, for ease in weighing, and to eliminate the above extra heating.

⁽¹⁾ S. M. KULIFAY, J. Amer. Chem. Soc. 83, 4916-19 (1961).

⁽²⁾ W. C. BENZING, J. B. CONN, J. V. MAGEE and E. J. SHEEHAN, J. Amer. Chem. Soc. 80, 2657–59 (1958).

TABLE 1.

Compound and formula	g A and B in ml solvent	Composition of reducing solution	% Yield and X-ray diffraction analysis
Selenides Cupric selenide (klockmannite) CuSe	(A) 0.6354 g Cu in 4 ml 1:1 HNO ₃ . (B) 0.7896 g Se in 9 ml 2:1 HNO ₃ .	5 g N₂H₄·2HCl 100 ml H₂O 50 ml NH₄OH	99.6%. Agreed quite well with ASTM ⁽³⁾ data for CuSe, with no other detectable crystalline components present.
β silver selenide (naumannite) Ag ₂ Se	(A) $3 \cdot 3979$ g AgNO ₃ in 15 ml H ₂ O, followed by 10 ml NH ₄ OH (B) $0 \cdot 7896$ g Se ir 9 ml 2:1 HNO ₃ , followed by 15 m NH ₄ OH.	15 g N₂H₄·2HCl 150 ml H₂O 50 ml NH₄OH. I. 1	99.5%. The only detectable crystalline component was β Ag ₂ Se, which gave a strong pattern.
Cadmium selenide CdSe	(A) 1.7242 g CdCO ₃ in 6 ml 1:1 HNO ₃ . (B) 0.7896 g Se in 9 ml 2:1 HNO ₃ .	5 g N ₂ H ₄ ·2HCl 100 ml H ₂ O 50 ml NH ₄ OH	99.8%. The major reflexions could be indexed as a FCC structure, with $a_0 \sim$ 6.03 Å, in agreement with HANSEN ⁽⁴⁾ for cubic CdSe. The crystallite size was very small, and there were no detectable free elements.
Lead selenide (clausthalite) Pbse	(A) 2·2321 g PbO in 15 ml 1:2 HNO ₃ . (B) 0·7896 g Se in 9 ml 2:1 HNO ₃	3 g tartaric acid 15 g N ₂ H ₄ ·2HCl 150 ml H ₂ O 50 ml NH ₄ OH	100.7%. The only detectable crystalline component was PbSe, giving a very strong pattern. The pattern was identified by comparison to PbSe data in NBS Circ. 539, Vol. V, p. 38 (1955).
Thallium selenide TISe	(A) 2.3191 g Tl in 25 ml 1:4 HNO ₃ . (B) 0.8940 g Se in 9 ml 2:1 HNO ₃ .	15 g tartaric acid 15 g N ₂ H ₄ ·2HCl 150 ml H ₂ O 65 ml NH ₄ OH	95.9%. The sample gave a strong pattern, body centred tetragonal, with c/a 0.87, which compared favourably with PEAR- son's ⁽⁵⁾ value of 0.873 for TISe. Free elements or TICl were not observed.
Mercuric selenide (tiemannite) HgSe	(A) 2.066 g Hg in 10 ml hot 1:1 HNO ₃ . (B) 0.814 g Se in 9 ml 2:1 HNO ₃ .	15 g N₂H₄·2HCl 150 ml H₂O 50 ml NH₄OH	98.7%. HgSe was the only detectable crystalline matter present. The crystallite size was quite small ($<0.1 \mu$).
Nickel selenide NiSe	(A) 0.5902 g Ni in 4 ml 1:1 HNO ₈ . (B) 0.7930 g Se in 4.5 ml 2:1 HNO ₈ .	5 g N₂H₄ 2HCl 1 g tartaric acid 100 ml H₂O 35 ml NH₄OH†	100.0%. NiSe was the only detectable crystalline component. The crystallite size was extremely small—in the range of a few hundred angstroms.

⁽⁸⁾ J. V. SMITH, Index to the X-ray Powder Data File, ASTM, Philadelphia, Penna., (1959).
⁽⁴⁾ M. HANSEN, Constitution of Binary Alloys McGraw-Hill, New York (1958).
⁽⁵⁾ W. B. PEARSON, A Handbook of Lattice Spacings and Structures of Metals and Alloys. Pergamon Press, New York (1958).

Compound and formula	g A and B in ml solvent	Composition of reducing solution	% Yield and X-ray diffraction analysis
Copper selenide $Cu_{a-x}Se$, where $x \sim 0.2$	(A) 1.1437 g Cu in 8 ml 1:1 HNO ₃ . (B) 0.7896 g Se in 6 ml 2:1 HNO ₃ .	5 g N ₂ H ₄ -2HCl 125 ml H ₂ O 50 ml NH ₄ OH	101.4%. The only component observed was $Cu_{2-x}Se$, where $x \sim 0.2$. No free elements were detected.
Copper silver selenide (eucairite) CuAgSe	(A) 0.6354 g Cu in 6 ml 1:1 HNO ₃ . (B) 1.6989 g AgNO ₃ in 10 ml H ₂ O, then 20 ml NH ₄ · OH. (C) 0.7896 g Se in 6 ml 2:1 HNO ₃ .	10 g N ₂ H ₄ 2HCl 150 ml H ₂ O 40 ml NH ₄ OH	100.2%. The major lines of the sample could be indexed simple tetragonal, with $c/a = 1.543$, in agreement with data in Structure Reports for eucairite.

TABLE 1 (continued)

* The Hg and Se solutions were mixed, without using rinse water, by pouring back and forth, to avoid hydrolysis. Some of the hot reducing liquor was used to rinse the beakers after the addition, and was followed by the water rinses.

 \dagger NH₄OH additions of 17 ml each were made at 15, 30, 45, 75 and 105 min from start of boiling in the NiSe preparation (to prevent hydrolysis of unreacted Ni salts due to loss of NH₃). The boiling period was for 2.5 hr instead of the usual 1.5 hr.

In some cases, the component elements could be dissolved together in the same beaker, but usually faster solution was obtained in separate beakers.

Where dilute acids or bases were used, as in 2:1 HNO₃, the volume of active component is given first, and that of H_2O second.

Experiments. X-ray powder patterns were obtained using a General Electric XRD-3 Diffractometer, equipped with CuK_a radiation filtered through nickel foil ($\lambda = 1.5418$ Å). The instrument settings were: X-ray tube current, 15 mAp; X-ray tube potential, 50 kV; defining slit 1°; Soller slit, wide; detector slit, 0.2°; target-to-beam angle, 4°; scanning rate, 2°/min; recorder range, 2; time constant, B; and recorder chart speed, 0.4 in./ min.

DISCUSSION

It was considered important to add the mixed metals solution to the reducing agent, rather than in the reverse sequence, to avoid contamination of the desired product with possible insoluble hydrolysis products.

BENZING et al. ventured that, since selenium is soluble to some extent in hydrazine, the following reaction takes place:

$$6N_2H_4 + 3H_2O + (2_x + 1)Se \pm 6N_2H_5^+ + 2Se_x^{2-} + SeO_3^{2-}$$

In this case, the Se_x^{2-} would presumably react with the metal ion or free metal, if already reduced, to form the metal selenide. The SeO_3^{2-} would be reduced to free Se to make the reaction go to the right. The formation of an intermediate, soluble selenide ion with hydrazine seems to be reasonable, since one can prepare CdSe and TISe, whereas Cd^{2+} and TI⁺ alone are not reduced to the free metal by hydrazine. However, it is noteworthy that the writer has succeeded in preparing Ag₂Se and HgSe using as a reducing agent acidified solutions of ammonium sulfite; and also Ag₂Se using ammoniacal dextrose or hydroxylamine solutions, none of which contained any hydrazine. Each of these was made in a manner analogous to that described in Table 1, obtained in 99–100 per cent yields, and verified by X-ray diffraction analysis. Further, the writer's earlier publication⁽¹⁾ has shown that many types of compounds, including intermetallics, antimonides, arsenides and tellurides, can be made with this same general method, sometimes in acidic H_3PO_2 solutions, sometimes in alkaline hydrazine. It was suggested there that reaction appears to take place between the reduced elements themselves, while in an intimately mixed, finely-divided and highly active state. It would seem that this type of reaction predominates when acidic sulphite, H_3PO_2 , or ammoniacal dextrose is used in preparing selenides; and that it might figure also when hydrazine is used, in competition with the intermediate soluble selenide reaction.

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