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CONTRIBUTION FROM THE WESTINGHOUSE RESEARCH LABORATORIES,
PITTSBURGH 35, PENNSYLVANIA

Electrolytic Preparation of Tellurides

BY ARMAND J. PANSON

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The compounds CuTe, ZnTe, SnTe, PbTe, and Bi_2Te_3 were prepared by electrolysis with tellurium cathodes and metal anodes in ammonium acetate acid buffer solutions. The tellurides were formed by homogeneous reaction between metal cations and telluride ions in the bulk of the solutions. GeTe, Ag_2Te, SnTe, and ZnTe were also prepared by adding metal salt solutions to electrolytically generated telluride solutions. X-Ray measurements indicated that stoichiometric SnTe is formed in contrast to extensive nonstoichiometry possible in compounds prepared at elevated temperatures. Also, GeTe prepared at room temperature was shown to have a somewhat smaller trigonal distortion than observed in GeTe preparations quenched from higher temperatures. In addition, a low temperature CuTe phase was observed which transformed to the previously reported orthorhombic phase on annealing above 250°.

Introduction

Direct union of the elements either by melting or by sintering compacted powders is the most commonly used method of preparing tellurides and other semiconducting compounds. In either case high temperatures are required. As the compounds are cooled, the electronic system comes to equilibrium at room temperature, but the motion of lattice defects and the diffusion of atoms is very slow below about one-half the absolute melting temperature. Thus the lattice defect concentration and the chemical composition of compounds prepared in this way are characteristic of some ill-defined high temperature.

The preparation of such nonstoichiometric compounds by alternate methods at low temperature can give products with equilibrium defect concentrations and can reveal new low temperature structures. The study of such compounds may contribute considerable information to solid state chemistry and, in particular, to the study of semiconductors.

Apart from these considerations there may be practical disadvantages to the direct reaction of the elements. For example, very high temperatures may be necessary to effect reactions, high vapor pressures may be encountered, and peritectic reactions may interfere. In this paper a convenient electrolytic method for preparing tellurides from aqueous solution at room temperature will be described.

Previous Methods.—In the older literature Tibbals[1] reported the preparation of tellurides by allowing solutions of Na_2Te to react with metal acetates; Brukl[2] used hydrogen telluride gas which was prepared by hydrolyzing Al_2Te_3. More recently, Nitsche[3] gave a method in which powdered tellurium was reduced by aluminum powder in aqueous ammonia solutions and allowed to react with Zn, Cd, and Hg ammonia complexes. The preparation of tellurides by reaction between fine particle tellurium and fine particle metals formed by hydrazine reduction of ionic solutions was reported by Kulifay.[4]

Electrolytic Preparation.—In the present study electrolytic reactions were used. Telluride ions were formed by cathodic dissolution of tellurium in acid solution. It was generally possible to introduce the metal ions into solution by simultaneous anodic dissolution of the metal by passing current between a tellurium cathode and a metal anode through an acid electrolyte. The electrodes dissolve cleanly and the tellurides are formed by ionic reaction in the bulk of the solution. In cases where metal ions are not conveniently generated by anodic dissolution, they are added as salt solutions to the electrolytically generated telluride ion solutions.

Knowledge of the products formed on cathodic dissolution of tellurium is essential to control the purity of the products. The pH of the electrolyte is a controlling factor since the equilibrium in the reaction

$$Te_2^{2-} = Te + Te^{2-}$$

is maintained and the acid dissociation constants of H_2Te ($K_1 = 2.27 \times 10^{-3}$ and $K_2 = 6.9 \times 10^{-13}$) are smaller than those for H_2Te_2.[5] Although the equilibrium constant for the disproportionation reaction written above is 2×10^{-4}, disproportionation becomes favorable, *i.e.*, hydrogen telluride ion becomes the predominant tellurium species, at pH values less than approximately 9.[5] Metal tellurides formed from solutions containing ditelluride ion are contaminated with tellurium, the net reaction being

$$M^{2+} + Te_2^{2-} = MTe + Te$$

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(1) A. Tibbals, *J. Am. Chem. Soc.*, **31**, 909 (1909).

(2) A. Brukl, *Monatsh. Chem.*, **45**, 471 (1924).

(3) R. Nitsche, *Angew. Chem.*, **69**, 333 (1957).

(4) S. M. Kulifay, *J. Am. Chem. Soc.*, **83**, 4916 (1961).

(5) A. J. Panson, *J. Phys. Chem.*, **68**, 1721 (1964).

For this reason electrolytes of pH 4.5 or less were used.

Oxygen, which reacts readily with telluride ions to form tellurium, is another possible source of tellurium contamination which can be avoided by carefully degassing the solutions before electrolysis is started.

The precipitates generally were of quite fine particle size as shown by broadened X-ray powder patterns. Aging the precipitates in boiling water for about 16 hr. increased particle size sufficiently to give sharp X-ray powder patterns.

Experimental

Electrolysis reactions were performed in a three-neck round-bottom flask of about 1-l. capacity. Tellurium cathodes 5 mm. in diameter and about 7 cm. long were cast from 99.999% semiconductor grade material under high vacuum. The high purity anode metals were fashioned into cylinders generally somewhat larger than the cathode. Electrodes were introduced into the flask through ground glass stoppers in each of the side necks, and vacuum seals were made between metal and glass with DeKhotinsky cement. The center neck served for filling the flask and then attachment to a mechanical vacuum pump for evacuation. A Teflon-coated magnetic stirring bar was used for stirring during electrolysis.

The electrolyte most generally used was 500 ml. of 1 M NH_4OH to which sufficient acetic acid was added to give a pH of 4.5. Prior to electrolysis the flask containing the electrolyte with the electrodes in place was evacuated and magnetically stirred for 30 min. to degas the solution. The electrolysis was then performed for a measured time under vacuum with stirring. A constant current was maintained to facilitate calculation of the coulombs passed from which theoretical weight losses were determined and compared with the actual electrode weight losses at the conclusion of the experiment. Also, the corresponding precipitate weights were determined.

Preparations in which metal ions were added as dissolved salts to electrolytically generated telluride solutions were performed in a three-neck 500-ml. round-bottom flask equipped with a 15-mm. diameter side arm sealed horizontally into it and bent up vertically. A platinum anode was introduced through the top of the relatively narrow arm so that mixing of the catholyte and anolyte was minimized. The flask was fitted with a tellurium cathode and a dropping funnel for introduction of metal salt solutions. Connection was made to a mechanical vacuum pump for degassing. The experiment was performed under an atmosphere of purified argon as gaseous products were formed at the anode and electrolysis under vacuum would cause excessive agitation and mixing of the anode and cathode solutions.

To promote particle size growth the fine particle precipitates formed by both preparation methods were boiled in the electrolyte solutions in which they were prepared for about 16 hr. (overnight) under an atmosphere of argon. Care was taken to minimize exposure of the precipitate to air until after boiling as a precautionary measure against oxidation. The precipitates were washed by decantation, centrifuged, and dried in a current of purified argon at 120° for 4 hr. and weighed. X-Ray patterns taken with a 11.54-cm. Debye–Scherer camera showed line broadening due to fine particle size for the precipitates before boiling. After boiling sharp patterns were obtained which were suitable for precision lattice parameter measurements. Parameters were corrected for absorption error by extrapolating to $\theta = 90°$ using the function[6]

$$\frac{1}{2}\left(\frac{\cos^2\theta}{\sin\theta}+\frac{\cos^2\theta}{\theta}\right)$$

Results and Discussion

Electrolytic Method.—The compounds CuTe, ZnTe, SnTe, PbTe, and Bi_2Te_3 were prepared by passing current between tellurium cathodes and metal anodes in ammonium acetate–acid buffer solutions. The choice of pH represents a compromise between a low enough value to prevent hydrolysis of anode products and a value high enough to avoid competitive hydrogen evolution at the tellurium cathode and to suppress the formation of ditelluride ion. Identification of the products was made by X-ray powder patterns and by comparing precipitate weights with those calculated on the basis of the number of faradays passed on electrolysis. The X-ray patterns were sharp after boiling the precipitates and no foreign lines were observed. It should be noted that in several preparations where air was accidentally admitted to the solutions during electrolysis, tellurium lines were found in the X-ray patterns. These preparations were discarded. The yields of the reactions are very high and, considering the transfer manipulations, may be considered almost quantitative. The data are presented in Table I.

TABLE I

GRAVIMETRIC RESULTS[a]

	Precipitate wt., g.			Corresponding electrode wt. loss, g.		
	Calcd.	Found		Calcd.	Found	pH
CuTe[b]	2.139	1.746	Cu	0.711	0.669	4.5
			Te	1.428	1.120	
					1.789	
ZnTe	0.452	0.447	Zn	0.154	0.154	4.5
			Te	0.298	0.300	
					0.454	
SnTe	0.575	0.552	Sn	0.277	0.274	4.5
			Te	0.298	0.290	
					0.564	
PbTe	0.781	0.778	Pb	0.483	0.498	4.5
			Te	0.298	0.305	
					0.803	
Bi_2Te_3	0.623	0.590	Bi	0.325	0.329	4.0
			Te	0.298	0.297	
					0.626	

[a] Electrolysis conditions: 250 ma. for 30 min. [b] 300 ma. for 120 min.

The electrolytic preparation from solution is particularly suited for the compounds CuTe and ZnTe since these tellurides are difficult to prepare by other techniques. This is because CuTe is reported to suffer a peritectic reaction at 365–367°[7] and thus would be exceedingly difficult or even impossible to prepare in pure form by direct union of the elements.

The preparation of ZnTe by direct reaction of the elements is difficult because of the high (1239°) melting point of the product compared with the 907° boiling point of Zn. High Zn pressures would be encountered by allowing the molten elements to react at temperatures above the melting point of the product. Reaction between the molten components at temperatures below the melting point of ZnTe would be greatly hindered by slow diffusion through a solid product

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(6) A. Taylor and H. Sinclair, *Proc. Phys. Soc.* (London), **57**, 126 (1945).

(7) M. Hansen, "Constitution of Binary Alloys," 2nd Ed., McGraw Hill Book Co., New York, N. Y., 1958.

barrier, so that a complete reaction would not be obtained. Reaction between Zn and Te vapor or the solids using powdered metallurgical techniques would be possible alternatives.

Electrolytically Prepared Telluride and Metal Salt Reactions.—In addition to the compounds prepared by electrolysis between tellurium cathodes and metal anodes, GeTe, Ag_2Te, SnTe, and ZnTe were formed by adding solutions of the metal salts to electrolytically generated telluride solutions.

Germanous solutions[8] were added to electrolytically-generated telluride solutions to prepare GeTe. This method was used rather than electrolysis with a germanium electrode since anodic dissolution of germanium gives the tetravalent ion rather than the divalent ion. The GeTe precipitate was identified by a clear X-ray pattern which showed no impurity lines.

Silver telluride was prepared using silver nitrate solutions, while SnTe and ZnTe were precipitated with chloride solutions. Identification of the products was made by X-ray powder patterns.

Attempts to prepare CrTe and MnTe using chromous acetate solutions and manganous chloride solutions were not successful. These tellurides are not precipitated in acid solution. Slow addition of NH_4OH to cause precipitation resulted in hydrolysis of the metal ions and eventual precipitation of tellurium. Also, a solution containing telluride and manganous ions was added to an excess of isopropyl alcohol in an attempt to precipitate the telluride by lowering the dielectric constant of the medium, but only tellurium was precipitated.

Characterization of Low Temperature Compounds.—While the purpose of this paper is to describe the electrolytic method for preparing tellurides, some observations, however, will now be presented to emphasize the fact that preparation of compounds at room temperature from aqueous solution may yield unique low temperature phases. These phases may not be accessible by the more common high temperature preparation methods.

GeTe.—The structure of GeTe is that of rock salt with a trigonal distortion. The low temperature GeTe preparations have a smaller distortion from cubic symmetry than the higher temperature preparations. The rhombohedral angle reported by Schubert and Fricke[9] for compounds formed at 530° and then annealed at 315° is 88.35°. Measurement of the rhombohedral angle of two electrolytic preparations which were dried at 120° gave the value 88.55 ± 0.02°.[10] To ensure the correctness of this result, one sample was heated to 500° and quenched to compare our high temperature angle measurements with that previously reported. A value of 88.35° was obtained, in exact agreement.

SnTe.—Tin telluride is a rock salt structure with a defect tin lattice. The formula may be thus represented by $Sn_{1-x}Te$. Measurements of the lattice parameter of tin telluride which was dried at 127° indicate that its composition is very close to stoichiometric, *i.e.*, $x = 0$. The parameter obtained is 6.326 Å. and is close to 6.328 Å. reported by Mazelsky and Lubell[11] for $x = 0$ preparations which were quenched from 500°. A solubility limit of $x = 0.029$ was indicated for the tellurium-rich phase boundary by these authors from lattice parameter and Seebeck coefficient data. The parameter obtained for these compositions was 6.301 Å. A sample of electrolytically prepared material which was annealed at 500° gave a lattice parameter of 6.301 Å., which is in agreement with the previously published parameter and thus supports our low temperature result. This result also may indicate that the SnTe compounds prepared have small amounts of excess tellurium present as an additional phase although no tellurium lines were seen in the X-ray patterns. The absence of tellurium lines shows that the amount of excess free crystalline tellurium is less than about 5% of the total weight. Excess tellurium may be indicated since the composition $Sn_{1-x}Te$, $x = 0.029$, was formed merely by annealing the stoichiometric sample without adding tellurium. Also, differential thermal analysis measurements on one of these compounds showed an endothermic peak at 404° which is identified with the 405° reported[7] eutectic halt line for excess tellurium compositions.

Ag_2Te.—The presence of tellurium in the preparations is not general. This is shown by the differential thermal analysis experiments on electrolytially prepared Ag_2Te. These results indicate that the compounds prepared are in the silver-rich part of the homogeneity range of Ag_2Te. This compound has a low temperature form, α, which transforms to a β form stable to high temperature. The structure change occurs at 145° in the presence of excess silver and at 132° in the presence of excess tellurium. This is evidence for a homogeneity range for Ag_2Te.[7] A sharp differential thermal analysis (DTA) endothermic peak was observed at 148° for the compounds prepared electrolytically. This result indicates that the compounds prepared are silver-rich. In addition, no other DTA peaks were observed up to 500° for these com-

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[8] The germanous solution was prepared by dissolving 2 g. of GeO_2 in 5 ml. of HF. The solution was then reduced by adding 24 g. of NaH_2PO_2 [L. S. Foster, *Inorg. Syn.*, **2**, 103 (1946)] dissolved in 100 ml. of water and heating for 30 min. in a water bath.

[9] K. Schubert and H. Fricke, *Z. Metallkunde*, **44**, 457 (1953).

[10] Rhombohedral angles, α, were measured using the split reflections (220), $(\bar{2}20)$ and also (311), $(31\bar{1})$ for each film. The magnitude of the indices, h, k, l, is the same for each pair of split lines and α is close to 90° so that $\cos^2 \alpha$ terms may neglected. The rhombohedral indexing equation

$$d_{hkl} = a\left[\frac{1 + 2\cos^3\alpha - 3\cos^2\alpha}{(h^2 + k^2 + l^2)\sin^2\alpha + 2(hk + kl + lh)(\cos^2\alpha - \cos\alpha)}\right]^{1/2}$$

may, for such reflections, be simplified and solved for $\cos \alpha$ to give

$$\cos\alpha = \frac{(\sin^2\theta_1 - \sin^2\theta_2)S_1}{2(P_1\sin^2\theta_1 - P_2\sin^2\theta_2)}$$

$$S_1 = h_1^2 + k_1^2 + l_1^2$$

$$P_1 = h_1k_1 + k_1l_1 + l_1k_1$$

[11] R. Mazelsky and M. S. Lubell in "Nonstoichiometric Compounds," Advances in Chemistry Series, No. 39, American Chemical Society, Washington, D. C., 1963, p. 210.

pounds. For the tellurium-rich composition, the phase diagram[7] indicates, in addition to the 132° α to β transformation temperature, structural transformations at 286, 425, and 465°. Also, a eutectic halt line at 351° is shown for Te compositions greater than Ag_3Te_2. As a check on our DTA data for Ag_2Te, a preparation was made with excess tellurium and a DTA curve was obtained for it. A strong endothermic peak was observed at 351° with weaker endothermic peaks also observed at 425 and 458°. Failure to observe the 132° peak and observation of the 351° eutectic halt line indicates that the composition was richer in tellurium than Ag_3Te_2. The observation of these DTA peaks on the tellurium-rich compositions supports the DTA observations made on the clean electrolytic preparation and confirms the result that the composition of these compounds is in the silver-rich portion of the homogeneity range.

CuTe.—The X-ray patterns obtained for the CuTe preparation which was dried at 120° and for compounds annealed at 200° were very complex and did not correspond to the orthorhombic pattern reported by Anderko and Schubert.[12] Heating the compounds above 250°, however, resulted in a structure change and the orthorhombic pattern reported by Anderko and Schubert was obtained. In addition, careful weighing indicated no weight change attendant with the structure change. These results give evidence for the existence of a low temperature CuTe phase below 250°.

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[12] K. Anderko and K. Schubert, *Z. Metallkunde*, **45**, 371 (1954).

CONTRIBUTION FROM MONSANTO COMPANY,
CENTRAL RESEARCH DEPARTMENT, ST. LOUIS, MISSOURI

Halogen-Terminated Polydimethyltin Sulfides

BY KURT MOEDRITZER AND JOHN R. VAN WAZER

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Mixtures of dimethyltin dihalide with trimeric dimethyltin sulfide were found by proton nuclear magnetic resonance (n.m.r.) to exhibit rapid interchange of halogen atoms for sulfur bridges. The rate was most rapid when the halogen atom was chlorine (average lifetime = *ca.* 10^{-4} sec.) and was slowest for iodine (average lifetime = *ca.* 10^{-2} sec.) in 1 *M* carbon tetrachloride solutions at room temperature. Because of slower rate of exchange for iodine, the equilibrium between the simple dihalide molecule and the end and middle units making up the complicated molecules based on Sn–S–Sn chains terminated with halogen atoms was determined for the case where the halogen is iodine and found to be close to that predicted for statistically random sorting of the iodine with bridging sulfur atoms on the dimethyltin moiety.

In other studies[1] carried out in this laboratory, it has been found that heating of mixtures of dihalodimethylsilanes with either cyclic dimethylsiloxanes or dimethylsilthians gives an equilibrium between the starting materials and the halogen-terminated dimethylsiloxane or dimethylsilthian chain molecules. In the case of the oxygen-bridged compounds, the chain–ring equilibrium is shifted completely to the chain species, within experimental error. On the other hand, in the case of the sulfur-bridged compounds, the rings predominate. In both cases, the time needed for equilibration was found to be in the order of magnitude of days at 200°.

In the study reported here, tin analogs were investigated by proton nuclear magnetic resonance (n.m.r.) in order to demonstrate the existence of the tin-based families of compounds and to obtain a measure of the physical parameters whereby they may be characterized (rate of equilibration, equilibrium constants, etc.).

Experimental

Reagents.—Dimethyltin dichloride, m.p. 105°, and dimethyltin dibromide, m.p. 75°, were obtained from Orgmet, Hampstead, N. H., and dimethyltin diiodide was prepared from dimethyltin dichloride and sodium iodide in acetone[2] and recrystallized from hexane, m.p. 45°. Dimethyltin oxide[3] and trimeric dimethyltin sulfide,[4] m.p. 149°, were prepared according to methods in the literature.

N.m.r. Measurements.—Proton n.m.r. spectra were obtained[1] on a Varian A-60 analytical spectrometer, with the samples being contained in precision 5-mm. o.d. tubes.

Equilibration.—Upon mixing and brief heating (*ca.* 1–2 min. above the melting point of the eutectic), the trimeric dimethyltin sulfide dissolved in the dimethyltin dihalide to give clear liquids, the viscosity of which decreased with increase in the composition parameter $R \equiv X/Sn$, where X = Cl, Br, or I.

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[1] K. Moedritzer and J. R. Van Wazer, *J. Am. Chem. Soc.*, **86**, 802 (1964). Also data being prepared for publication.

[2] D. Seyferth and E. G. Rochow, *ibid.*, **77**, 1302 (1955).

[3] E. Krause and A. von Grosse, "Die Chemie der Metall-organischen Verbindungen," Verlag Bornträger, Berlin, 1937, p. 329.

[4] W. T. Reichle, *J. Org. Chem.*, **26**, 4634 (1961).