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LOW TEMPERATURE SYNTHESIS OF BINARY CHALCOGENIDES

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ABSTRACT

Synthesis of tellurides and selenides of Hg, Cd, Zn, Ge, Sn and Pb at temperatures considerably below the melting point of the compounds, was studied. The reaction went to completion within a few days.

Tellurides and selenides of groups II and IV are used in optoelectronic devices and nuclear radiation detectors (1-3). For these purposes, high purity ($\geq 99.999\%$) materials in the form of high quality single crystals or epitaxial layers are required. The impurity concentration determines the electrical properties of the material and the device performance.

The stoichiometric compounds are usually obtained from the pure elements, $A + B \rightarrow AB$. The conventional method (4) consists of mixing the elements in a quartz ampoule under high vacuum. The ampoule is heated to a temperature slightly above ($\sim 50^{\circ}$ C) the melting point (MP) of the compound, in a rocking furnace. After several hours (2-24 h) the ampoule is either quenched or slowly cooled to room temperature. This procedure was, and still is, successfully applied in the preparation of PbTe, PbSe, SnTe, SnSe (1,5,6), CdTe (7), HgTe (8,9) and GeTe (10). Usually, annealing in another quartz ampoule under high vacuum, at temperatures slightly below ($\sim 50^{\circ}$ C) the melting point of the compound, for about 1-2 weeks, is required, probably because of the presence of unreacted elements in the quenched charges (see e.g. Ref. 11). The reactions are completed during the annealing by a mechanism which does not require melting of the product.

For high purity material preparation, this conventional synthesis suffers from some major disadvantages. The melting points of the tellurides and selenides used in optoelectronics are quite high (Table I). Heating to above

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	Melting point (^O C)			Eutectic data		
<u>.</u>	М	Х	MX	T(^o C)	atom % X	ref.
РbТе	327	450	904	405	85	12
SnTe	231	450	805	405	84	12
CdTe	321	450	1090	447	99	13,14
HgTe	- 39	450	670	413	83	12
ZnTe	420	450	1239			15,16
GeTe	937	450	725	375	85	12
PbSe	327	217	1065	673	68	12
SnSe	231	217	861	640	61	12
CdSe	321	217	1260?	991	75	16
HgSe	-39	217	749			17

TABLE I

Melting Points and Eutectic Data of the Binary MX Systems Studied

the MP of the compounds involves high temperatures, sometimes dangerously close to or above the softening temperature of the quartz. Not less important is the contamination of the high purity charge by impurity diffusion from the quartz. Diffusion is enhanced with increasing temperature, and seems to become significant at $T \ge 1000^{\circ}$ C. In the case of mercury chalcogenides, very high pressures develop at the syntheses temperatures. With such high pressures, even specially thick walled (d \sim 3mm) ampoules are not always immune to explosions. The mercury chalcogenides obtained are Hg deficient and it is difficult to compensate for the Hg loss during synthesis. A post-annealing procedure for adjusting the material stoichiometry is required.

In the present work, a simple procedure for preparing electronic grade tellurides and selenides of Pb, Sn, Cd, Hg, Zn and Ge is described. Only CdTe had been prepared in a similar way previously (18). Approximately 2 g of stoichiometric amounts of high purity elements were weighed. The elements were sealed under high vacuum ($\sim 10^{-7}$ torr) in a clean quartz ampoule. This was placed in a cold furnace, and the temperature was raised slowly ($\sim 50^{\circ}$ C/h), up to the homogenization temperature. Homogenization time was usually 72 h. After the furnace was turned off, the materials cooled to room temperature in less than 10 h. Material identification and homogeneity were determined by X-ray diffraction analysis on five different samples from the same reaction mixture. The limit of detection for free Te in XRD is ≤ 0.5 atom%. Metal residues ≥ 2 mg (≥ 0.1 %) could be easily detected on grinding the reaction mixture.

The present procedure combines synthesis and annealing in one thermal cycle. No change of ampoule is needed, thereby saving means and time and avoiding potential material contamination. The results shown in Table II indicate complete reaction of the elements within 72 h in all cases studied, at temperatures much below the melting point of the compounds. The homogenization time is shorter than the annealing time reported in the literature. Hence, contamination, if any, of the high purity charge by impurity diffusion from the quartz is minimal. For the mercury chalcogenides, this means that synthesis could be completed at much reduced pressures. In the case of HgTe, the pressure is reduced from P \geq 20 atm at T \sim 700°C to P \sim 0.05 atm at T \sim 450°C.

	Common method	Present method		
		Incomplete reaction	Complete reaction	
PbTe	950-1000	400	>424	
SnTe	850-900	393	≻435	
CdTe	∿1150	672	>760	
HgTe	∿700	409	>419	
ZnTe		801	>847	
GeTe	∿800	580	>637	
PbSe	1100-1150		>308	
SnSe	900-950	490	>529	
CdSe		860*	>945	
HgSe	~800	230	>260	

TABLE II

Synthesis Temperatures for the Binary Compounds, °C, t = 72 h

In all cases studied, the reaction was found to start at temperatures below the homogenization temperature: the more volatile element diffused and was deposited on the surface of the less volatile one. Surface reaction occurred and diffusion into the bulk material followed, forming a layer of the binary product. HgSe was found to be an extreme case: Hg diffused into the solid Se spherules forming HgSe. Although homogenization was achieved at 260°C, no indication of Se melting (MP=217°C) was observed: the resulting HgSe kept the original Se shape, however, the spherules were "swollen".

For several binary systems, the reaction proceeded gradually with increasing temperature (mechanism A). For example, in the case of CdTe, after 72 h at 400°C the lumps were covered with a thin layer of CdTe. This reaction probably took place in the solid state. Increasing the temperature above the MP of the elements (Table I), but below the homogenization temperature, resulted in a mixture of Cd, Te and CdTe. The amount of residual elements in the charge decreased with increasing temperature. At the homogenization temperature, 760°C, residual elements were eliminated, probably by sublimation and further reaction. Similar behavior was found for CdSe, SnTe, ZnTe and GeTe. A different behavior was found for PbTe, SnTe and HgTe (mechanism B). Limited reaction was observed at 400°C. However, complete reaction was observed at the homogenization temperatures of 425°C for PbTe and 435°C for Sn_{Tc} , which are below the MP of Te. For HgTe, at 409°C only a thin layer of HgTe was observed on the Te surface but at 417°C complete reaction was found. It seems that in these cases the faster reaction occurs via the liquid eutectic phase (Table I); the Te dissolves into solution and the compound precipitates out. The similar behavior of the PbTe, SnTe and HgTe systems indicates that the vapor pressure (under the present working conditions) has no effect on the reaction, since the vapor pressures in these three systems vary significantly (Table III). It should be noted that the presence of a eutectic composition at low temperature does not ensure a low temperature synthesis in such systems. Although eutectic compositions are known for GeTe and CdTe (Table I) the synthesis proceeds gradually with increasing temperature, via mechanism A.

TABLE III

	Homogenization temperature (°C)	Metal	Tellurium	Compound
PbTe	425	~10 ^{−6}	1.5×10^{-1}	2.4×10^{-6}
SnTe	440	<10 ⁻¹¹	3×10^{-1}	3.1x10 ⁻⁶
CdTe	760	∿300	∿30	∿0.4
HgTe	420	1.6x10 ³	$v8 \times 10^{-2}$	∿40

Vapor Pressures (torr) of Various Tellurides Studied at the Homogenization Temperature

Large, single crystals of CdTe were grown by the vertical unseeded vapor growth technique (19) from growth charges prepared by the present method. The high degree of purity of the CdTe crystals obtained permitted nuclear radiation detection, with performance equal to that of commercial CdTe detectors, indicating the applicability of the low temperature synthesis for electronic materials.

References

- R.K. Willardson and A.C. Beer, eds., Semiconductors and Semimetals, Academic Press, N.Y., vol. 5: Infrared Detectors (1970).
- 2. ibid. vol. 13: Cadmium Telluride (1978).
- 3. ibid. vol. 18: Mercury Cadmium Telluride (1981).
- 4. B. Ray, II-VI Compounds, p. 25, Pergamon Press, Oxford (1969).
- 5. N. Tamari and H. Shtrikman, J. Electron. Mater. 8, 269 (1979).
- 6. H. Maier and D.R. Daniel, J. Electron. Mater. 6, 693 (1977).
- M.R. Lorenz, in: Physics and Chemistry of II-VI Compounds, (M. Aven and J.S. Prener, eds.) p. 107, North-Holland, Amsterdam (1967).
- B.A. Lombos, E.Y.M. Lee, A.L. Kipling and R.W. Krawczyniuk, J. Phys. Chem. Solids <u>36</u>, 1193 (1975).
- 9. A. Groswami and A.B. Mandale, Thin Solid Films 62, 145 (1979).
- 10. N. Yellin and G. Gafni, J. Cryst. Growth 53, 409 (1981).
- 11. S.G. Parker, J.E. Pinell and R.E. Johnson, J. Electron. Mater. 3, 371 (1974)
- M. Hansen, Constitution of Binary Alloys, Metallurgy and Metallurgical Engineering Series, McGraw-Hill, N.Y. (1958).
- 13. T. Tung, C.H. Su, P.K. Liao and R.F. Brebrick, J. Vac. Sci. Technol. 21,

117 (1982).

- 14. D.J. Williams, J. Cryst, Growth 58, 657 (1982).
- 15. R.A. Reynolds, D.G. Stroud and D.A. Stevenson, J. Electrochem. Soc. 114, 1281 (1967).
- 16. J. Steininger, A.J. Strauss and R.F. Brebrick, J. Electrochem. Soc. 117, 1305 (1970).
- 17. T.C. Harman, in: Physics and Chemistry of II-VI Compounds, (M. Aven and J.S. Prener, eds.), p. 774, North-Holland, Amsterdam (1967).
- 18. P. Buck and R. Nitche, J. Cryst. Growth 48, 29 (1980).
- 19. N. Yellin, D. Eger and A. Shachna, J. Cryst. Growth 60, 343 (1982).