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LOW TEMPERATURE SYNTHESIS OF $Hg_{1-x}Cd_xTe$, $0 \leq x \leq 1$

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ABSTRACT Solid solutions of $Hg_{1-x}Cd_xTe$ with $0 \leq x \leq 1.0$ were prepared at low temperatures, where Hg pressure is about 1 atm. For the composition $x < 0.7$, complete reaction was observed within 72 h at 420°C. For $x = 0.7$, 0.9 and 1.0, minimum synthesis temperatures of 460°C, 490°C and 760°C, respectively, were needed for complete reaction. Homogeneous solid solutions of $Hg_{1-x}Cd_xTe$, as determined by X-ray and atomic absorption analyses, were obtained after 168 h at 420°C for $x < 0.7$, the temperature increasing for $x \geq 0.7$.

Introduction

Mercury telluride and cadmium telluride form a continuous series of solid solutions, $Hg_{1-x}Cd_xTe$ ($0 < x < 1$), having a cubic zinc blende structure in which the Hg and Cd atoms are randomly distributed over the metal site sub-lattice. $Hg_{1-x}Cd_xTe$ is currently the principal semiconductor material used for high quality medium and far IR detectors (1). Very pure, high quality single crystals or epitaxial layers are used for these optoelectronic applications. The crystals are usually grown from the melt, either from the elements or from CdTe and HgTe binary compounds (1). At the temperatures of homogenization in the melt very high pressures develop: e.g. for $x = 0.2$, 34 atm at 800°C. In all cases, the synthesis of the alloy is part of the crystal growth process. The conditions required for synthesis have not yet been investigated. Our results suggest the feasibility of low temperature synthesis of homogeneous charges of $Hg_{1-x}Cd_xTe$, $0 \leq x \leq 1$.

Experimental

Stoichiometric amounts of high purity Hg (Beth-Lehem Apparatus, >6N), Cd (Cominco American, ~6N) and Te (Cominco American, ~6N) were weighed. Cd

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was etched with 10% HCl/ethanol, rinsed thoroughly with ethanol and dried with anhydrous nitrogen before use. The total weight of each sample was ca. 2g. The elements were sealed under high vacuum (∿10^{-7} torr) in a clean quartz ampoule, which was placed in a cold vertical furnace, with a flat temperature profile (±1°C). The furnace was heated to the required temperature. Special attention was paid to avoid overshooting the desired temperature. The accuracy in temperature determination was ±2°C. The charge was heated for either 72 or 168 h and was cooled slowly by turning off the furnace.

Material identification and homogeneity was checked by powder X-ray diffraction (XRD) and atomic absorption spectrometry (AAS). At least three analyses of randomly chosen samples were carried out for each charge by each technique. XRD data were collected with a horizontal Philips Diffractometer, using CuK_α radiation. The difference between the lattice constants of HgTe (6.462 Å) and CdTe (6.482 Å) (2) is only 0.3%; therefore the accuracy in composition determination is low: $\Delta a_o = \pm 0.001$ Å, yielding $\Delta x = \pm 0.05$. The limit of detection in XRD for free Te in CdTe, HgTe or $Hg_{1-x}Cd_xTe$ is ∿0.5 mol%. Cd residues (1-2 mg) could be easily detected on grinding the reaction mixture. AAS data were collected with a Perkin Elmer 460 spectrometer, the samples having been dissolved in warm aqua regia; the accuracy was ±3%.

Results and Discussion

The compositions studied were x = 0, 0.1, 0.3, 0.5, 0.7, 0.9 and 1.0. On mixing the elements at room temperature, Cd-amalgam was immediately formed for all compositions. After synthesis, the $Hg_{1-x}Cd_xTe$ alloys appeared as polycrystalline lumps, which disintegrated easily. In no case was adhesion to the quartz walls of the ampoule observed. Occasionally, traces of Te showed up in the diffractograms and were attributed to stoichiometric compensation for the loss of Hg to the vapor phase.

For each composition, a minimum reaction temperature was determined (at 20°C intervals), at which no residue of the elements, except for Te traces, was found. This was defined as the minimal temperature for complete reaction. In the composition range $0 \leq x \leq 0.7$, complete reaction was observed at 420°C (which is below the melting point of Te) within 72 h; for x = 0.9 the temperature needed was 490°C. In the case of x = 1.0 (CdTe) complete reaction was attained (3) only at 760°C. Hence, the addition of a third component, Hg, to the binary mixture of Cd and Te reduces significantly the synthesis temperature of CdTe. For all compositions, at 400°C and 72 h, only a limited surface reaction was observed. For $0 \leq x \leq 0.9$, a thin layer of HgTe covered the Te lumps which retained their original morphology. For x = 1.0, a thin layer of CdTe covered the etched Cd shots. The abrupt change in behavior between 400° and 420°C in the Hg-Te system was explained (3) by the existence of a liquid eutectic composition, which is known to exist at 413°C for 83.3 at% Te (4). This behavior had been found for the Pb-Te and Sn-Te systems as well (3). The fast reaction probably occurs via the liquid phase; the Te dissolves and HgTe precipitates out. The present results indicate the existence of eutectic compositions at $400°C < T < 420°C$ for $0 < x \leq 0.7$, in agreement with Williams (5). For x = 0.9, surface reaction only was observed at 420°C and complete reaction at 490°C. This suggests that at this composition the eutectic temperature is between 420° and 490°C. Recently, the Cd-Te phase diagram was modified to include a eutectic isotherm below the Te melting point, at a Cd content of ∿1% (4,5). However, the Cd-Te system shows a gradual reaction process from 400°C to 760°C (3), rather than an abrupt one. In this, it is similar to the Cd-Se or Sn-Se systems (3), which do not have eutectic compositions.

Samples of composition x ≤ 0.7, heated at 420°C for 72 h showed no residual elements, but were non-homogeneous. Various x values were found for the same weighed composition. Further heating to an overall 168 h yielded homogeneous charges for x < 0.7, with compositions identical to the stoichiometry. In the case of x = 0.7 or 0.9, homogeneous materials were obtained at 460°C and 490°C respectively. The results are summarized in Table 1.

TABLE 1

Required Conditions for Obtaining Homogeneous $Hg_{1-x}Cd_xTe$ Charges

x (by wt.)	T (°C)	t (h)	a_o (Å)	x (AAS)
0.0	420	72	6.462	0.00
0.1	420	168	6.464	0.10
0.3	420	168	6.469	0.31
0.5	420	168	6.472	0.52
0.7	460	168	6.476	0.70_5
0.9	490	72	6.479_5	0.89
1.0	760	72	6.482	1.00

The lattice constants determined are shown, together with previous results (6-9), in Fig. 1. In spite of the comparatively low accuracy in the determination of the lattice constants, they show a linear fit with Vegard's law, and are in very good agreement with the data of Harman (2). Especially significant are the a_o values for x ≥ 0.5, since these compositions are quite difficult to prepare by the usual method because of the high vapor pressures at the melt temperatures. The vapor pressures in the $Hg_{1-x}Cd_xTe$ system produced during homogenization in the melt compared to those produced in the present method are given in Table 2. Liquidus temperatures for the various

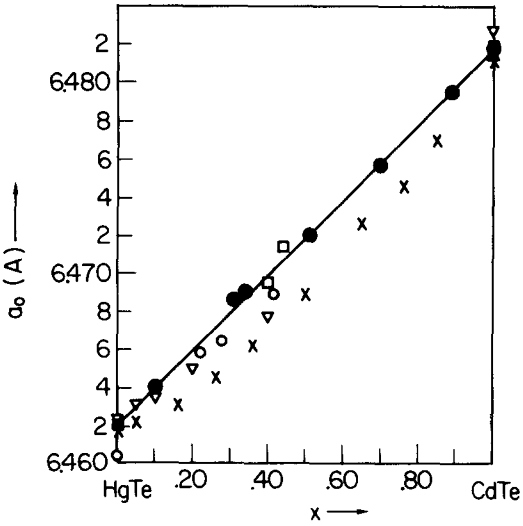

FIG. 1
Lattice constants vs. composition for $Hg_{1-x}Cd_xTe$.
□(2);○(6);×(7);▽(8);△(9);● this study.

TABLE 2

Vapor Pressures in the $Hg_{1-x}Cd_xTe$ System during Homogenization in the Melt and in the Present Method

x	Homogenization in the melt		Present method	
	T (°C)	P (atm)	T (°C)	P (atm)
0	700	17.4	420	0.9
0.1	760	26.7	420	0.9
0.3	865	50.6	420	0.9
0.5	940	74.6	420	0.9
0.7	1025	>100	460	1.6
0.9	1080	>100	490	2.3

compositions were taken from Tung et al. (4). The temperatures of homogenization in the melt were taken as ∿30°C higher than these values. The Hg pressures under these conditions were calculated according to Steininger (10).

The possibility that the Cd-amalgam, formed prior to the reaction with Te, is responsible for the homogenization of the $Hg_{1-x}Cd_xTe$ charges was ruled out because the homogenization was achieved by simply lengthening the duration of the annealing time from 72 to 168 h. It seems that the homogenization proceeds via diffusion in the solid state (11).

The simple procedure outlined in this study for obtaining $Hg_{1-x}Cd_xTe$, $0 \lesssim x \lesssim 1$, at low temperatures avoids high pressures, thus eliminating the need for thick-walled ampoules and appropriate safety measures. Because of the reduced pressures, the quantity of Hg lost from the solid to the vapor phase can be controlled and stoichiometric material obtained.

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