CdSb Under Pressure:
Compound Decomposition, New Phase Formation and Amorphization

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Introduction

Application of high pressure offers wide possibilities to produce new materials in crystalline and amorphous states.The Cd-Sb alloy system has at ambient pressure one intermediate compound of equiatomic composition, CdSb, orthorhombic, space group *Pbca*, with 16 atoms in the unit cell (Pearson symbol *oP*16). Figure 1 shows the temperature-composition phase diagram for the Cd-Sb alloy system, taken from Ref. [2]. The CdSb compound is semiconducting, and its high-pressure behavior is of fundamental and applied interest.

By "pressure quenching" method it has been found that CdSb transforms under pressure into a new phase with a simple hexagonal structure (*sh*) and a small amount of Cd (Cd-*hcp*) [3]. The sample with the CdSb compound has been exposed at P = 7 GPa and T = 300^{o}C and quenched to liquid nitrogen temperature on decompression. The sample was examined by x-ray diffraction at T = -180^{o}C and a two-phase mixture *sh* + Cd-*hcp* was found. After heating to room temperature an amorphous phase was observed that transformed (after 2 days) into a metastable phase, Cd_3Sb_4, and then into initial compound CdSb.

In a later study [4-5], the CdSb compound was examined *in situ* under pressure with a diamond anvil cell using laboratory x-ray source and scintillation counter. The decomposition of CdSb into *sh* + Cd-*hcp* has been confirmed, however the data obtained in this study were confined in the range of diffraction angle and low precision.

In present work, the CdSb compound is investigated using diamond anvil cells, synchrotron radiation, and imaging plate providing the collection of precise data for detailed structural analysis. The following effects are characterized on compression and decompression:

- the compound decomposition
- new high-pressure phase formation
- amorphization on decompression
- recovering of the initial compound (stable at ambient conditions).

Methods and Materials

CdSb sample was loaded in a symmetric diamond anvil cell with an opening allowing probing up to 22 degrees of 2θ. To determine the pressure, we used *in situ* fluorescence measurements of ruby chips loaded in the sample chamber. Diffraction data were collected at GSECARS beam line at the Advanced Photon Source (APS) in Argonne National Laboratory. Focused, monochromatic beam of wavelength 0.3311 Å was used and the data were recorded on a MAR image plate calibrated with a CeO_2 standard.

Diffraction patterns from the sample were collected on pressure increase up to 15.3 GPa, and on pressure decrease down to ambient temperature. The initial sample revealed a diffraction pattern of the orthorhombic phase (space group *Pbca*), known for the semiconducting CdSb compound at ambient conditions [6]. The refined lattice parameters from our sample at ambient conditions give a = 6.473 Å, b = 8.248 Å, c = 8.531 Å, which are very close to the values given in Ref. [6].

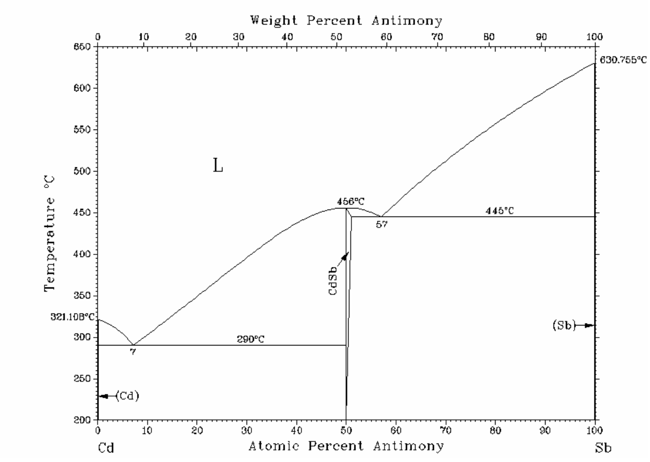

Fig. 1. Temperature-composition phase diagram of the cadmium-antimony alloy system (from Ref. [2]).

Results and Discussion.

On pressure increase to 7.3 GPa, we observed a transition from CdSb orthorhombic phase to a new state that is interpreted as a two-phase mixture of a simple hexagonal Sb-rich phase and a hexagonal close packed phase of (almost pure) Cd (Fig. 2). Any traces of CdSb orthorhombic phase disappear above 8.0 GPa. At 8.4 GPa, the *sh* phase (space group $P6/mmm$) was indexed with lattice parameters a = 3.066(1) Å and c = 2.860(1) Å, and Cd-*hcp* phase (space group $P6_3/mmc$) gave lattice parameters a = 2.93(1) Å and c = 5.165(1) Å, close to those reported in Ref. [7] for pure Cd at this pressure.

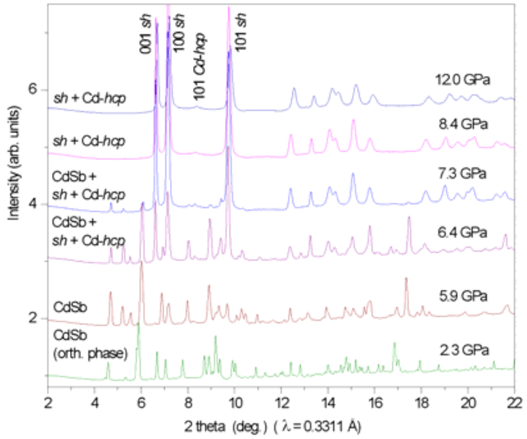

Fig. 2. Integrated diffraction profiles from the CdSb sample on pressure increase, showing a transformation from the ambien pressure orthorhombic phase of CdSb into a two-phase mixture of simple hexagonal phase and Cd-hcp.

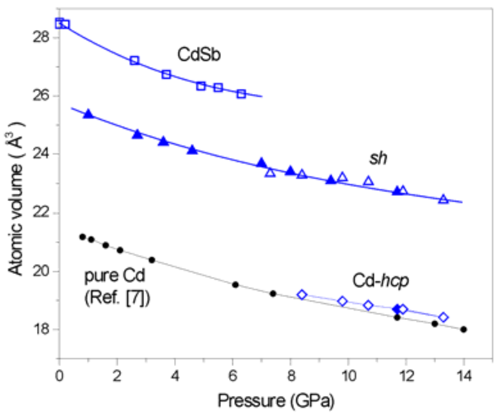

Fig. 3. Pressure-volume data for the CdSb sample. Open symbols show data obtained on pressure increase, solid symbols show data obtained on pressure decrease.The data fot pure Cd from Ref. [7] are shown for comparison.

On pressure decrease, the two phase mixture state of Cd-Sb sample is observed down to 1 GPa. The pressure dependence of volume for the phases observed in this study is shown in Fig. 3. The atomic volume change between the CdSb orthorhombic phase and the simple hexagonal phase is 9.2% at 6.8 GPa.

In a binary system, two phases (of different compositions) are allowed to exist in equilibrium at a certain temperature and pressure. Thus, we analyze the composition of *sh* phase which is expected to be different from 50/50. Figure 4 shows a Rietveld refinement of the CdSb sample on the basis of simple hexagonal phase and Cd-*hcp* phase. The refinement yields the following atomic fractions of the phases: 98.7(1)% for *sh* and 1.3(1)% for Cd-*hcp*. From this we conclude, that we observe a 50/50 compound decomposition into a Sb-rich metallic phase with simple hexagonal structure (~51-55%) and (almost pure) Cd with *hcp* structure.

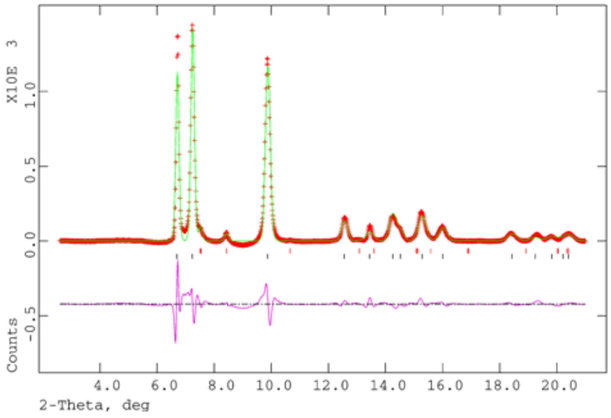

Fig. 4. Rietveld refinement of the CdSb sample at 13.3 GPa on the basis of the two-phase mixture of an Sb-rich sh phase and Cd-hcp phase. Red crosses, green solid lines, and purple line represent experimental, modeled and difference spectra. The upper and lower ticks below the profile indicate the predicted peak positions for Cd-hcp and sh phases, respectively.

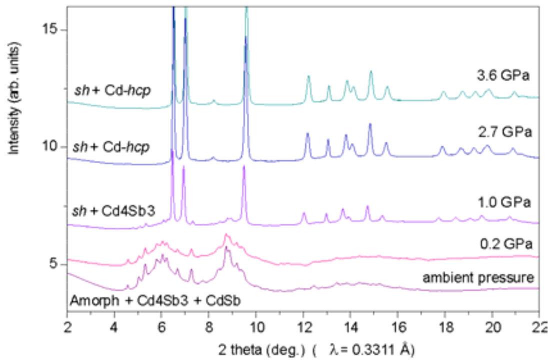

Fig 5. Integrated diffraction profiles of the CdSb sample on pressure decrease, showing amorphization of the simple hexagonal phase.

On pressure decrease below 1 GPa, an amorphous phase is observed (Fig. 5). After several minute, crystalline peaks start to become visible on top of the broad amorphous reflections, originating from a phase mixture of a metastable Cd_4Sb_3 phase with a rhombohedral structure (space group $R\bar{3}c$, lattice parameters a = 13.01 Å and c = 13.01 Å in hexagonal axes [6]) and the stable ambient pressure CdSb phase.

At 0.2 GPa, the halos of the amorphous phase of CdSb sample correspond to the following d-spacings: $d_1 = 3.094(1)$ Å, $d_2 = 2.137(1)$ Å. The full width at half maximum of the halos is $\Delta d_1 = 1.01(1)$ Å and $\Delta d_2 = 0.40(1)$ Å.

After annealing the amorphous sample at ambient pressure and 150°C for 30 min, we observed a diffraction pattern from an entirely crystalline phase without any traces of an amorhpous phase. The indexing shows that the sample transformed back to the orthorhombic CdSb phase. The values of lattice parameters are very close the staring values. Thus, on heating the sample has returned to its initial state.

Summarising our study on the semiconducting CdSb compound, on pressure increase we observed a stoihiometric compound decomposition and a formation of a new intermediate metallic phase of a different composition (Sb-rich) with an excess of Cd. On pressure decrease, the metallic phase (with a simple hexagonal structure) is observed down to a low pressure of 1 GPa in its metastable state, as the high kinetic barrier and a very narrow stability range with respect to composition of the initial compound prevents the back transition to CdSb. As a result, the intermediate phase transforms to an amorphous phase.

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