

## PHASE TRANSITIONS AND MECHANICAL PROPERTIES OF TERNARY CHALCOGENIDES

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**Summary** In the present work the mechanical properties of mercury semiconductors in the vicinity of the phase transitions were studied. Under the high hydrostatic pressure treatment the macroscopic bending of samples was observed, that gave the evidence of high plasticity of these materials near the phase transition point. The influences of chemical substitutions in cation and anion sublattices on the properties of ternary chalcogenides were analysed.

### INTRODUCTION

Pressure-induced phase transitions of chalcogenides are known to depend strongly on atom substitution in anion and cation sublattices [1-5]. For example, in ternary chalcogenides the replacement of cations or anions by analogous one shifts the beginning of phase transition from tetrahedral (sphalerite) into octahedral structures (rock salt, cinnabar) as well as corresponding abrupt jumps of resistivity in a wide pressure range [1-5]. In [6] the approach to the lattice stability for diamond-like and sphalerite crystals was suggested, based on the consideration of electron spectrum peculiarities. According to [6] the instability of lattice ought to arise when the indirect overlapping of forbidden gap takes place. The phase diagrams, obtained by using of this approach, gave a good accordance both with experimental data [6] and also with the results of current theoretical models [7]. The pressure shifts of electron bands at  $\Gamma$ ,  $L$  and  $X$ -points of Brillouin zone as well as electron energy gaps for diamond-like and sphalerite compounds are indeed consistent with values of phase transition pressures  $P_t$  [8]. Value of  $P_t$  is connected also with elastic constants of these materials [9], so there has to be a correlation between electrical and mechanical properties at phase transformation, that makes above materials perspective for MEMS (micro-electro-mechanical systems) applications. In contrast to other tetrahedral bonded semiconductors Si, Ge, GaAs, the chalcogenides like HgCdTe possess a bad mechanical properties and so their handling in a technological device process is more difficult [14]. Thus, mechanical properties of ternary chalcogenides are of great interest. The most favourable technique for testing of mechanical properties being the microhardness measurements [14].

### EXPERIMENT

In the present work the influence of various kind of cation and anion substitution at electrical and mechanical properties (microhardness  $H$  before and after pressure treatment, plastic deformation) were investigated. For high pressure measurements a "piston-cylinder" chamber and diamond anvils cell (DAC) were used. Vickers' microhardness was measured before and after high pressure treatment of the samples by PMT-3 apparatus. A surface of the samples was investigated by photo method with assistance of microscope "Neofot". The content of elements in each sample was determined via X-ray spectra method by using of "Superprobe-JCXA-733" spectrometer. Lattice parameters were controlled by standard X-ray diffraction method. For high-pressure study the automated setup was used allowing to measure a several parameters of sample and environment simultaneously [10-13]. For investigations the single crystals of ternary chalcogenides  $\text{HgSe}_{1-x}\text{S}_x$ ,  $\text{HgTe}_{1-x}\text{S}_x$ ,  $\text{Hg}_{1-x}\text{Cd}_x\text{Se}$ ,  $\text{Hg}_{1-x}\text{Mg}_x\text{Te}$  have been taken. The analogous previously published data for other ternary compounds  $\text{HgTe}_{1-x}\text{Se}_x$ ,  $\text{HgGa}_2\text{Se}_3$ ,  $\text{HgIn}_2\text{Te}_3$ ,  $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$ ,  $\text{Cd}_{1-x}\text{Zn}_x\text{Te}$ ,  $\text{Hg}_{1-x}\text{Zn}_x\text{Te}$ ,  $\text{Cd}_{1-x}\text{Mn}_x\text{Te}$  etc. were also analysed.

### RESULTS AND DISCUSSION

The results obtained are: observation of macroscopic bending and plastic deformation of the samples undergone a high hydrostatic pressure treatment above the phase transition point  $P_t$ , microhardness dependencies on content of substitution atoms  $x$ , irreversible arising of  $H(x)$  after reversible phase transition sphalerite ( $B3$ )  $\rightarrow$  cinnabar ( $B9$ ) controlled by resistivity measurements. The dependencies of  $P_t(x)$  and  $H(x)$  obtained were explained quantitatively by modern theoretical approaches [6-8,14] taking into account the recent neutron and synchrotron data of lattice transformation under variation of  $x$  and  $P$  [15-17].

The value of hardness is known to be inversely proportional to the compressibility  $\beta$  [18]:

$$H = \frac{M}{\rho \cdot q \cdot \beta} \quad (1),$$

where  $M$  the molecular weight,  $\rho$  the density,  $q$  the number of atoms in a formula unit. Eq.1 was confirmed by experimental data for elemental solids and crystalline compounds. For ternary compounds  $H$  is also function of  $x$  [14]:

$$\frac{dH}{d(x)^{0.5}} = 0.48 \cdot G \cdot |\varepsilon_G - 6 \cdot \gamma \cdot \varepsilon_a| \quad (2),$$

with  $\varepsilon_G=(dG/dx)/G$ ,  $\varepsilon_a=(da/dx)/a$ ,  $G$  the bulk shear modulus,  $a$  the lattice constant,  $\gamma$  the Grüneisen constant. The contribution in  $H$  of stress field around solute atoms, caused by different size and modulus (elastic interaction) [14] has been taken into account in Eq. 2. The hardening effect is due to above elastic interaction between solute atoms and screw dislocations, being rate-controlling [14]. Using the HgTeS, HgSeS lattice parameters determined at structural testing to obtain  $\varepsilon_a$  values the fitting of our  $H(x)$  data have been performed. Grüneisen constant was supposed to be 0.5 [14]. The compressibility of HgSe and HgTe have been taken the paper [19]. Eq.2 described well the experimental data obtained in the present and previous work.

Theoretical models [6-7] predict the decreasing of  $P_f(x)$  in HgSe<sub>1-x</sub>S<sub>x</sub>, HgTe<sub>1-x</sub>S<sub>x</sub> compounds and increasing of it for Hg<sub>1-x</sub>Cd<sub>x</sub>Se system, that in a good accordance with experimental data. The about two-fold increase of  $H$  established for samples undergone the phase transitions under hydrostatic  $P$  as well as the increase of electrical resistance after the pressure treatment may be explained by defects of crystal structure. The plastic bending of initially brittle samples suggested high plasticity arising in the vicinity of phase transformation which was accomplished by large hysteresis volumetric effect [1,2,15,16]. The previously studied electrical resistance  $R(P)$ ,  $P_f(x)$  and  $H(x)$  data for ternary compounds HgTe<sub>1-x</sub>Se<sub>x</sub>, HgGa<sub>2</sub>Se<sub>3</sub>, HgIn<sub>2</sub>Te<sub>3</sub>, Hg<sub>1-x</sub>Cd<sub>x</sub>Te, Cd<sub>1-x</sub>Zn<sub>x</sub>Te, Hg<sub>1-x</sub>Zn<sub>x</sub>Te, Cd<sub>1-x</sub>Mn<sub>x</sub>Te have the same features that indicates the overall tendency in their mechanical properties near phase transition point.



Fig. 1. The scheme of plastic bending of chalcogenides (HgSe, Hg<sub>1-x</sub>Cd<sub>x</sub>Se, HgSe<sub>1-x</sub>S<sub>x</sub>) samples investigated after applying of hydrostatic pressure.

## CONCLUSION

A correlation between electronic and mechanical properties of ternary chalcogenides near the phase transition point has been revealed. High plasticity has been established of materials in the vicinity of phase transition under pressure. The mechanism of phase transitions from tetrahedral bonded to octahedral bonded lattice at Hg, Cd and Zn chalcogenides seems to be similar [14], so the behaviour of mechanical properties at phase transition may be the same for this family of ternary semiconductors [7].

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