The Young Modulus and Microhardness Anisotropy in (Pb,Cd)Te Solid Solution Crystallizing in the Rock Salt Structure and Containing 5% of Cd

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A single crystal of (Pb,Cd)Te solid solution with Cd content equal to 5% was grown by self-selecting vapour growth technique and characterized by powder X-ray diffraction using the X'Pert PANalytical diffractometer and Cu K_{α_1} radiation. The X-ray diffraction pattern refinement demonstrated the fcc structure of the rock-salt type of investigated sample, no precipitates or other crystal phases were detected. The sample chemical composition was determined on the basis of measured lattice parameter value. Next, the Young modulus and microhardness were determined by the nanoindentation for carefully prepared, (001), (011) and (111)-oriented single crystal plates. The slight anisotropy of two parameters mentioned above has been found and compared with available literature data.

1. Introduction and motivation

A limited number of IV–VI semiconducting bulk crystals as well as solid solutions containing these compounds serving as a basis of selected devices found commercial applications many years ago. The mechanical properties of these materials (the elastic constants, bulk modulus, hardness, the Young modulus, the Poisson ratio, etc.) have been determined long time ago and they are relatively well-known today. On the contrary, similar properties of several new solid solutions obtained on the basis of IV–VI semiconductors have not yet been a topic for systematic studies and these properties are much less explored.

Among the group of IV–VI semiconductors those which have served for thermoelectric applications or infrared emission or detection are considered particularly interesting. Over the last few years a "renaissance" of topics of studies devoted to the lattice dynamics in these compounds — the phenomenon closely related to mechanical and thermoelectric properties of these materials — could be easily observed [1, 2]. Recently, it was discovered that some among these materials under well selected conditions exhibit the properties of topological crystalline insulators [3, 4]. All studies devoted to new topological states of matter attract a lot of attention. Taking into account all circumstances mentioned above we decided to investigate both the Young modulus (E) and the microhardness (H), as well as their possible anisotropy in a

single crystal of the solid solution based on IV–VI compound. The (Pb,Cd)Te solid solution crystal in which 5% of Pb was replaced by Cd atoms was selected for the present study.

Lead telluride is one of the lead chalcogenides considered as particularly useful on the field of thermoelectricity and infrared detection or emission. The first reports devoted to the hardness determination for this compound appeared almost fifty years ago [5, 6]. In a single n-type PbTe bulk crystal grown by the Bridgman method the microhardness is almost a constant value of $H \approx 300$ MPa for various electron concentration whereas in p-type material this value strongly increases with the hole concentration and can be as high as $H \approx 700$ MPa [7, 8]. Due to the relatively low PbTe microhardness value a layer of this compound is so soft that it can be scratched easily. In order to avoid this problem PbTe can be replaced by a PbTe-based solid solution containing some amount of another compound. A hardening of PbTe crystals by alloying it with CdTe was suggested a long time ago [7]. However, due to very low Cd solubility in PbTe and ultimately a limited in the past access to the (Pb,Cd)Te solid solutions with good structure quality these studies were restrained to samples grown by the Bridgman method only with the nominal Cd content equal at least to 3%.

The successful growth of big, high quality, metastable single (Pb,Cd)Te crystals with Cd content as high as 12% by self-selecting vapour growth (SSVG) method changed this situation [9, 10]. Since 2009 several physical properties of these crystals have been both investigated and reported (see, e.g., [11–14]). Quite recently, we have examined selected mechanical properties of this particular semiconductor. What we have found out is an important

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increase of the H value with an increasing Cd content in (Pb,Cd)Te solid solution [13]. At the same time, determined by us the Young modulus E remains at a constant value, at least within an experimental error.

Despite numerous papers reporting the H and E values for several semiconductors an information on possible anisotropy of these parameters is much more limited. The formula describing dependence of mentioned above values on different crystallographic directions in the crystal lattice were given for cubic crystals a long time ago [15]. The anisotropic hardness predicted from the electronegativity in numerous both tetrahedrally and six-fold coordinated crystals, including several cubic materials with fcc structure of the diamond, zinc blende, or rock salt type, can be found in [16]. However, an experimental information on the anisotropy of the H and E values is not only very limited but also available mostly for a few tetrahedrally coordinated crystals. For example, the measured anisotropy of H was reported in ZnSe [17] and (Cd,Zn)Te [18], while the anisotropy of E in GaAs and Si can be found in [19] and [20], respectively. The only piece of information on predicted anisotropy of H value in a IV–VI compound crystallizing in the rock salt structure (sixfold coordination) concerns PbS [16] but we have not been familiar with any experimental result of this kind corresponding to another IV–VI compound or containing them solid solution.

The aim of present studies was to analyze expected anisotropy of the microhardness and the Young modulus values in (Pb,Cd)Te solid solution containing 5% of Cd. The nanoindentation measurements performed on oriented single crystals were selected for such purpose.

2. Experimental details

The single, big (Pb,Cd)Te crystal with the volume exceeding 1 cm^3 and nominal 5% of the Cd content was grown at the Institute of Physics, PAS, by the SSVG method. The crystal structure characterization was performed by powder X-ray diffraction at the same laboratory using Cu K_{α_1} radiation and X'Pert PANalytical diffractometer. The X-ray diffraction pattern was measured in a wide angular range ($20° \leq 2\theta \leq 150°$). The obtained from the XRD data by Le Bail refinement lattice parameter value served for the determination of the chemical composition of investigated crystal using the relation given in [10]. Next, carefully (001), (011), and (111)-oriented, 2 mm thick crystal slices were cut, mechanically polished and etched in 5% bromine methanol solution. The data about microhardness and the Young modulus were determined by the nanoindentation method, the Berkovich form of the indenter was used. For the measurements mentioned above an Ultra Nanohardness Tester CSM UNHT/AFM with the following parameters was used: maximum load 0.2, 0.5, 1.0, 5.0, and 10.0 mN, linear change of the load during application or removal of the load 0.033 mN/s, application time of the maximum load 30 s.

3. Results and discussion

The X-ray diffraction pattern corresponding to the investigated crystal is shown in Fig. 1. The XRD data refinement demonstrated the cubic fcc structure of the rocksalt type of investigated sample. The determined lattice parameter value was very close to the nominal one. All observed Bragg peaks resulted from X-ray diffraction on (Pb,Cd)Te crystal with a fixed chemical composition, containing 5% of Cd, no precipitates or other crystal phases were detected.
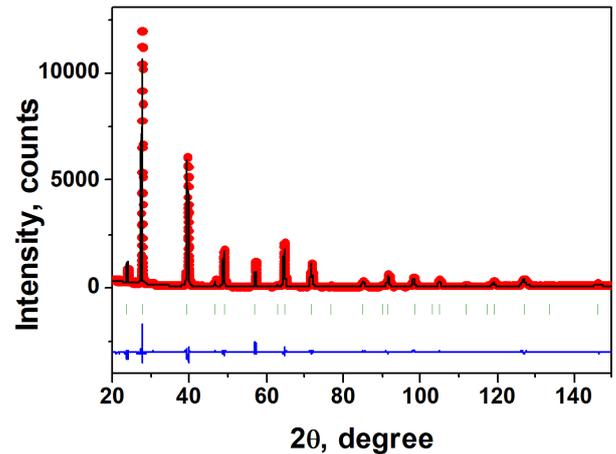

Fig. 1. The result of Le Bail refinement for analyzed (Pb,Cd)Te sample. The experimental XRD data are indicated by dots and the calculated ones by the solid line. The short vertical lines mark the positions of the Bragg reflections corresponding to the (Pb,Cd)Te sample, whereas the lowest curve shows the difference between the observed and calculated powder diffraction patterns.
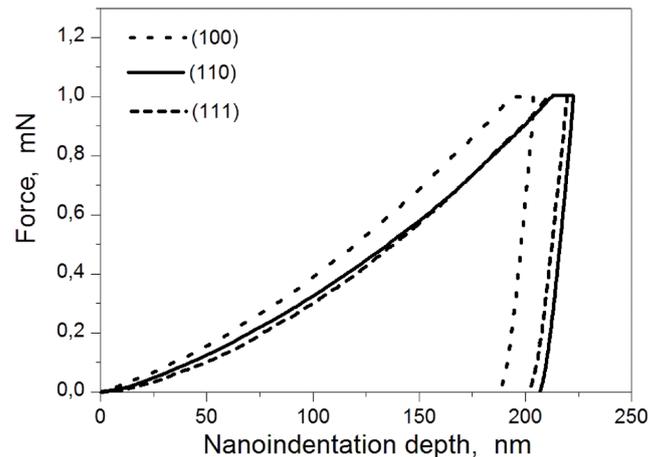

Fig. 2. Comparison of three applied force — nanoindentation depth experimental curves determined for principal (Pb,Cd)Te crystal high symmetry directions (maximum load of 1 mN). [011] direction — solid line, [111] — dashed line, [001] — dotted line.
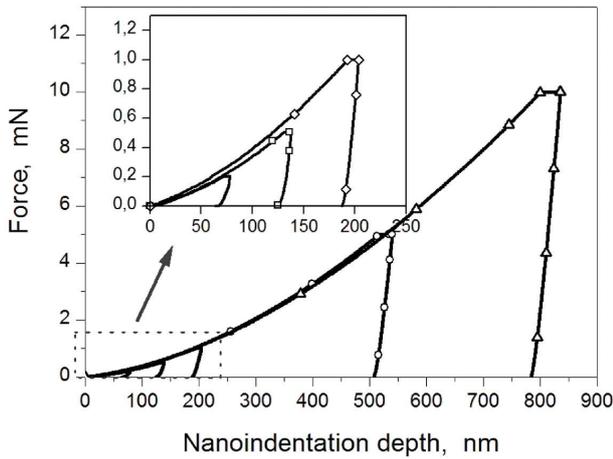
Fig. 3. Nanoindentation depth dependence on the force applied along the [001]-type direction for investigated solid solution. The maximum load 0.2 mN — solid line, 0.5 mN — solid line with squares, 1.0 mN — solid line with diamonds, 5.0 mN — solid line with circles, 10.0 mN — solid line with triangles.

Figure 2 presents the comparison of three experimental curves corresponding to the nanoindentation depth dependence on the applied load, determined for three principal crystallographic directions [001], [011] and [111] and the maximal load equal to 1 mN. A noticeable smaller maximal depth value observed for the nanoindentation along [111] in comparison to those determined along two other directions suggests an anisotropy of the H and/or E parameters.

The evolution of the form of a nanoindentation depth — applied load curve for the force applied along [001] direction is presented in Fig. 3. The parts of all curves, corresponding to an uploading are smooth, no evidence of "pop-in" effects (the discontinuity of the relevant curve resulting from a plastic deformation) are found. The summary of the results of nanoindentation measurements is given in Table I. The relatively greater experimental errors of the H and E values for small applied loads result from the less-precise determination of parameters describing experimental curves in the case of a minor indentation depth. The differences between the relevant values of parameters under interest are not very pronounced but nevertheless the general trend is clear: one obtains slightly higher H and E values measured along the [001] direction than those corresponding to [011] and [111] crystal axes. The [001] axis is a direction of chemical bonds in investigated crystal and for the rock salt structure the atom density is the highest one for (001)-oriented plane so this finding is in a qualitative agreement with the predictions given in [16]. However, there is a surprising discrepancy between quantitative predictions and experimental results for tetrahedrally coordinated and six-fold coordinated cubic crystals. In the former case where the bonds are oriented along the [111]-type directions the H and E parameters reach along these directions values higher by 20–40% than those corresponding to [001] and [011] directions (see [17–20]). In the latter case the hardness anisotropy predicted for PbS exceeds 40% whereas our experimental data for (Pb,Cd)Te solid solutions are almost quasi-isotropic and observed differences do not exceed a few percent only independently of applied maximum load. The reason for this discrepancy remains unknown. More experimental data for the rock-salt type crystals is clearly required in order to confirm our finding and to better understand the mechanical properties of this important group of materials.

TABLE I

The microhardness (H [MPa]) and the Young modulus (E [GPa]) values determined by the nanoindentation measurements performed along three principal crystal directions for several values of the maximum load.

Load [mN]	[110] direction		[111] direction		[100] direction	
	H [MPa]	E [GPa]	H [MPa]	E [GPa]	H [MPa]	E [GPa]
0.2	943±77	64±19	951±94	63±3	990±127	67±15
0.5	922±30	63±5	1012±27	62±14	1009±56	77±8
1.0	911±23	65±4	913±65	60±4	1033±46	74±10
5.0	736±21	55±1	741±29	56±2	789±35	64±7
10.0	636±21	48±3	642±3	49±1	673±15	61±6

4. Conclusions

The microhardness H and the Young modulus E values for (Pb,Cd)Te crystal containing 5% of Cd were determined by the nanoindentation for [001], [011] and [111] directions. The highest values of these parameters were found along [001] direction according to theoretical predictions. The slight anisotropy of both H and E, not exceeding a few percent of relevant values were found.

References

[1] O. Delaire, J. Ma, K. Marty, A.F. May, M.A. McGuire, M.-H. Du, D.J. Singh, A. Podlesnyak, G. Ehlers, M.D. Lumsden, B.C. Sales, *Nat. Mater.* **10**, 614 (2011).

[2] C.W. Li, J. Hong, A.F. May, D. Bansal, S. Chi, T. Hong, G. Ehlers, O. Delaire, *Nat. Phys.* **11**, 1063 (2015).

[3] P. Dziawa, B.J. Kowalski, K. Dybko, R. Buczko, A. Szczerbakow, M. Szot, E. Łusakowska, T. Balasubremanian, B.M. Wojek, M.H. Berntsen, O. Tjernberg, T. Story, *Nat. Mater.* **11**, 1023 (2012).

[4] Y. Tanaka, Z. Ren, T. Sato, K. Nakayama, S. Souma, T. Takahashi, K. Segawa, Y. Ando, *Nat. Phys.* **8**, 800 (2012).

[5] M.S. Ablova, M.N. Vinogradova, M.I. Karklina, *Sov. Phys. Solid State* **10**, 1929 (1969).

[6] M.S. Ablova, M.I. Karklina, M.N. Vinogradova, *Sov. Phys. Solid State* **11**, 2089 (1970).

[7] A.J. Crocker, M. Wilson, *J. Mater. Sci.* **13**, 833 (1978).

[8] Y. Gelbstein, G. Gotesman, Y. Lishzinker, Z. Dashevsky, M.P. Dariel, *J. Appl. Phys.* **104**, 033702 (2008).

[9] A. Szczerbakow, K. Durose, *Prog. Cryst. Growth Charact. Mater.* **51**, 81 (2005).

[10] M. Szot, A. Szczerbakow, K. Dybko, L. Kowalczyk, E. Smajek, V. Domukhovski, E. Lusakowska, P. Dziawa, A. Mycielski, T. Story, M. Bukala, M. Galicka, P. Sankowski, R. Buczko, P. Kacman, *Acta Phys. Pol. A* **116**, 959 (2009).

[11] R. Minikayev, E. Dynowska, E. Kaminska, A. Szczerbakow, D. Trots, T. Story, W. Szuszkiewicz, *Acta Phys. Pol. A* **119**, 699 (2011).

[12] B.A. Orlowski, A. Szczerbakow, B.J. Kowalski, M.A. Pietrzyk, K. Gas, M. Szot, W. Szuszkiewicz, V. Domukhovski, A. Reszka, S. Mickevivius, R.L. Johnson, S. Thiess, W. Drube, *J. Electron. Spectrosc. Relat. Phenom.* **184**, 199 (2011).

[13] R. Kuna, S. Adamiak, S. Petit, P. Baroni, K. Gas, R. Minikayev, A. Szczerbakow, J. Łazewski, W. Szuszkiewicz, *Acta Phys. Pol. A* **130**, 1246 (2016).

[14] R. Kuna, R. Minikayev, M. Trzyna, K. Gas, A. Bosak, A. Szczerbakow, S. Petit, J. Łażewski, W. Szuszkiewicz, *Acta Phys. Pol. A* **130**, 1251 (2016).

[15] W.A. Brantley, *J. Appl. Phys.* **44**, 534 (1973).

[16] K. Li, P. Yang, D. Xue, *Acta Mater.* **60**, 35 (2012).

[17] C. Ascheron, H. Neumann, G. Kuhn, C. Haase, *Cryst. Res. Technol.* **24**, 1275 (1989).

[18] Y. Li, R. Kang, H. Gao, J. Wang, Y. Lang, *Rare Met.* **28**, 570 (2009).

[19] F. Bergner, M. Schaper, R. Hammer, M. Jurisch, A. Kleinwechter, T. Chudoba, *Int. J. Mater. Res.* **98**, 735 (2007).

[20] I.-S. Choi, Y. Gan, *J. Mater. Res.* **27**, 2752 (2012).