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Anisotropy of Young's Modulus and Microhardness of PbTe

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Nanoindentation measurements were performed for a single PbTe crystal grown by self-selecting vapour growth method and characterized by X-ray diffraction. The microhardness and Young's modulus were determined for a few loads applied along the [001], [011] and [111] high symmetry directions for carefully oriented, 2 mm thick crystal plates. An anisotropy of two parameters has been suggested and compared with available literature data. The present results qualitatively confirm the theoretical predictions for a rock salt type crystal (PbS). The microhardness anisotropy value is in an agreement with recently determined, relevant value for (Pb,Cd)Te solid solution.

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1. Introduction and motivation

Most of mechanical properties of several IV–VI semiconducting bulk crystals as well as solid solutions containing these compounds (the elastic constants, bulk modulus, hardness, Young's modulus, Poisson's ratio, etc.) have been determined long time ago and they are relatively well-known. However, a possible anisotropy of parameters describing selected mechanical properties (like, e.g., hardness or Young's modulus) have not yet been the topic of systematic studies and their determination needs a further experimental effort.

Among the group of IV–VI materials mentioned above those which have served for thermoelectric applications or infrared emission or detection are considered as particularly interesting. They attracted a lot of attention starting from the second half of 20th century. The best known example of such material is PbTe. Still, a few years ago this semiconductor has been considered as a basis of well-established applications only and not as an object for possible new research.

This situation changed rapidly in 2010. According to a few reports published in prestigious scientific journals like *Science* or *Nature*, the PbTe structure and lattice dynamics still reveals new features and require a much better knowledge than that commonly accepted before this date [1, 2]. Even if not all experimental findings or their interpretation presented in [1, 2] have been confirmed by more recent data (see, e.g., [3, 4]) due to these two seminal papers several research groups focused their activity on properties of IV–VI based semiconductors and numerous publications dedicated to problems of the crystal structure and of the lattice dynamics of these materials appeared in the literature within the last few years (see, e.g., [5–8]).

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In parallel, in the last decade extensive studies of various systems exhibiting properties of topological insulators were conducted. Recently, it was discovered that for some among IV–VI based materials a transition to the topological crystalline insulator state takes place under well selected conditions [9, 10]. The studies of all problems related to properties of topological states of matter are a very hot topic of contemporary solid state physics. Taking into account all circumstances mentioned above (a necessity of detailed characterization of materials serving for a variety of important applications and a clear scientific interest in studies of basic properties of this group of semiconductors) we decided to get a more detailed information on selected mechanical properties of PbTe.

The first reports devoted to the determination of PbTe hardness appeared almost fifty years ago [11, 12]. In a single n-type PbTe bulk crystal grown by the Bridgman method the microhardness has an almost constant value of $H \approx 300$ MPa for various electron concentration, whereas in p-type material its value strongly increases with the hole concentration and can be as high as $H \approx 700$ MPa [13, 14]. These values are relatively low in comparison to reported hardness values not only for Si, but also for GaAs, ZnTe and other semiconducting compounds of III–V or even of II–VI type. One can improve the mechanical properties of a given semiconductor by the crystal doping or alloying with another compound. Several further reports were devoted to the mechanical properties of solid solutions grown on the basis of PbTe, like, e.g., (Pb,Ge)Te or (Pb,Cd)Te (see [13–17] and references therein). However, such basic experimental data as anisotropy of Young's modulus (E) and that of the hardness (H) are not available for such "classical" material as PbTe. This is in a clear contradiction to a wide, detailed knowledge on analogous properties of the elementary semiconductors or of the III–V type materials. The anisotropic hardness predicted form the electronegativity in numerous both tetrahedrally and sixfold coordinated crystals, including several cubic materials with fcc structure of the diamond, zinc blende, or rock salt type,

can be found in [18]. The only prediction of a hardness anisotropy for IV–VI semiconducting compound given in this paper concerns PbS. The predicted value of the H parameter for PbS reaches the maximum for [100] direction, the values corresponding to [110] and [111] directions are much smaller and quite similar. Taking the H value for [100] direction as 100% one obtains about 60% only as H values for two remaining high-symmetry directions. The suggested hardness anisotropy seems to be anomalously high in comparison to other sixfold coordinated compounds, listed in [18]. The anisotropy of both hardness and Young's modulus were directly determined for (Pb,Cd)Te solid solution only using a single crystal containing about 5% of CdTe [17]. The measured anisotropy does not exceed 10% which is in a clear contradiction to theoretical prediction mentioned above. Under these circumstances the question arises: is the theoretical anisotropy for the IV–VI semiconductor overestimated or a relatively low anisotropy observed in the (Pb,Cd)Te solid solution results from PbTe doping with Cd? The last possibility is not excluded because the CdTe solubility in PbTe is very low (about 1%) and the solid solution single crystal employed in the measurements reported in [17] was grown by a particular technique, and has a metastable character.

The aim of present studies was to analyze in a direct manner the anisotropy of the microhardness and Young's modulus in bulk PbTe. The nanoindentation measurements performed on oriented single crystals were selected for such purpose.

2. Experimental details

The single, big PbTe crystal was grown at the Institute of Physics, PAS, by the SSVG method [19, 20]. Its volume exceeded 1 cm^3, the hole concentration was of the order of 5×10^{17} cm^{-3}. The crystal structure characterization was performed by powder X-ray diffraction using Cu K_{α_1} radiation and X'Pert PANalytical diffractometer. Due to a presence of high quality, natural, (100)-oriented crystal surface it was possible to prepare the 2 mm thick PbTe plate corresponding to this orientation. Next, carefully (110) and (111)-oriented, 2 mm thick crystal slices were cut, mechanically polished, and etched in 5% bromine methanol solution in order to get a smooth surface. The data on microhardness and Young's modulus were determined by the nanoindentation method with the use of an Ultra Nanohardness Tester CSM UNHT/AFM at the University of Rzeszów. The following values of parameters were selected for the measurements: maximum load 0.2, 0.5, and 1.0 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. All measurements were performed using the Berkovich form of the indenter.

3. Results and discussion

The experimental curves corresponding to the nanoindentation depth dependence on the applied load, determined for three principal crystallographic directions [100], [110] and [111] and the maximal load equal to 1 mN are presented in Fig. 1. A smaller maximal depth value observed for the nanoindentation corresponding to the force applied along [100] direction in comparison to those determined along two other directions is an evidence of some anisotropy of mechanical properties of investigated crystal. The values of E and H parameters resulting from the nanoindentation measurements are 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. Nevertheless, slightly higher H and E values measured along the [100] direction than those corresponding to [110] and [111] crystal axes were obtained. This finding is in a qualitative agreement with the theoretical predictions given in [18] and confirms our previous results taken for (Pb,Cd)Te solid solution single crystal containing 5% of CdTe [17]. The comparison of the values of E and H determined in PbTe as a result of present studies and those corresponding to (Pb,Cd)Te solid solution, taken from [17], is shown in Fig. 2. A perfect qualitative agreement of results for both semiconductors demonstrates that a presence of CdTe in the investigated sample results in some hardening of material only, and does not modify anisotropy of mechanical properties.

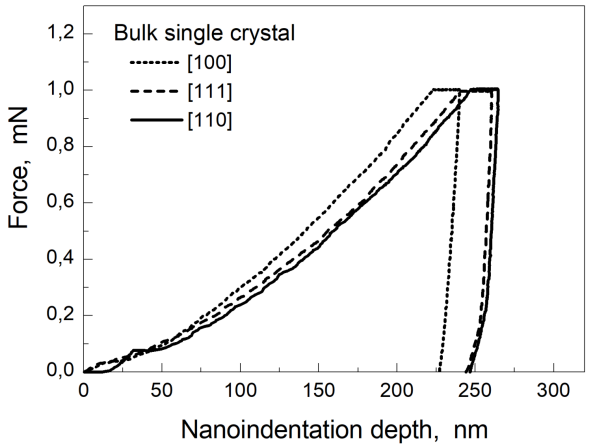

Fig. 1. Comparison of three applied force — nanoindentation depth experimental curves determined for the principal high symmetry directions of PbTe. The [110] direction — solid line, [111] — dashed line, [100] — dotted line, maximum applied load equal to 1 mN.

TABLE I

The microhardness (H) and Young's modulus (E) values for bulk PbTe single crystal determined by the nanoindentation measurements performed along three principal crystal directions for several values of applied maximum load.

Load	[110] direction		[111] direction		[100] direction	
[mN]	H [MPa]	E [GPa]	H [MPa]	E [GPa]	H [MPa]	E [GPa]
0.2	564 ± 28	57 ± 11	561 ± 36	74 ± 9	594 ± 54	69 ± 5
0.5	547 ± 53	65 ± 9	552 ± 9	75 ± 12	584 ± 99	67 ± 7
1	548 ± 14	65 ± 4	559 ± 5	64 ± 4	592 ± 25	71 ± 6

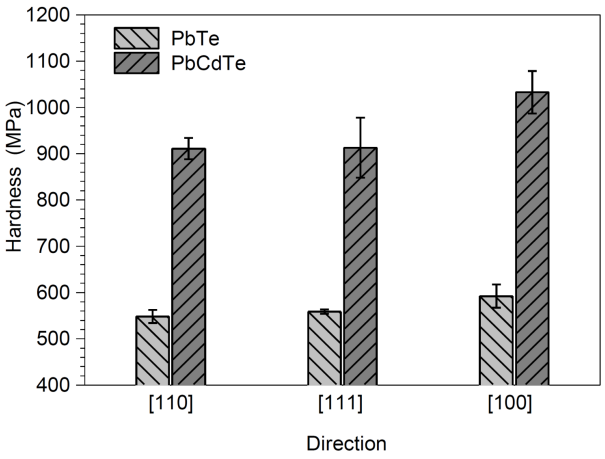

Fig. 2. Comparison of the nanohardness values determined for the bulk PbTe sample with literature data obtained for the bulk (Pb,Cd)Te solid solution containing 5% of CdTe [17]. For the nanoindentation measurements the force was applied along the [001] direction for both investigated samples, the maximum load was equal to 1 mN.

4. Conclusions

The anisotropy of the microhardness H and of Young's modulus E for bulk PbTe single crystal were determined for the first time by the nanoindentation method. The experimental data were obtained for the load applied along the [100], [110] and [111] directions. The highest H value was found for a force applied along [001] direction, which is in a qualitative agreement with the theoretical predictions. The obtained results are in a qualitative agreement with the results obtained previously for (Pb,Cd)Te solid solution and confirm in a direct manner a hardening of this solution with an increasing Cd content.

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References

[1] E.S. Božin, C.D. Malliakas, P. Souvatzis, T. Proffen, N.A. Spaldin, M.G. Kanatzidis, J.L. Billinge, *Science* **330**, 1660 (2010).

[2] 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, *Nature Mater.* **10**, 614 (2011).

[3] K.S. Knight, *J. Phys. Condens. Matter* **26**, 385403 (2014).

[4] K.S. Knight, *Phys. Chem. Miner.* **42**, 235 (2015).

[5] T. Sigha, J. Shiomi, J. Ma, O. Delaire, T. Radzynski, A. Lusakowski, K. Esfarjani, G. Chen, *Phys. Rev. B* **85**, 155203 (2012).

[6] J.M. Skelton, S.C. Parker, A. Togo, I. Tanaka, A. Walsh, *Phys. Rev. B* **89**, 205203 (2014).

[7] N. Shulumba, O. Hellman, A.J. Minnich, *Phys. Rev. B* **95**, 014302 (2017).

[8] G.A.S. Ribeiro, L. Paulatto, R. Bianco, I. Errea, F. Mauri, M. Calandra, *Phys. Rev. B* **97**, 014306 (2018).

[9] 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, *Nature Mater.* **11**, 1023 (2012).

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

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

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

[13] A.J. Crocker, M. Wilson, *J. Mater. Sci.* **13**, 833 (1970).

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

[15] R. Kuna, S. Adamiak, S. Petit, P. Baroni, K. Gas, R. Minikayev, A. Szczerbakow, J. Łazewski, W. Szuszkiewicz, *Acta Phys. Pol. A* **130**, 1245 (2016).

[16] 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).

[17] E. Łusakowska, S. Adamiak, P. Adamski, R. Kuna, R. Minikayev, P. Skupiński, A. Szczerbakow, W, Szuszkiewicz, *Acta Phys. Pol. A* **132**, 343 (2017).

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

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

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