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Microhardness and brittle strength of $ZnSe_{(1-x)}Te_x$ crystals grown from melt

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Mechanical properties of $ZnSe_{(1-x)}Te_x$ solid solutions ($0 < C_{Te} < 1.3$ mass %) have been studied using indentation method in two modes (indenting and scratching). The breaking limits for doped and undoped crystals have been measured by uniaxial compression. For the crystals where the dopant concentration $C_{Te} \approx 0.3$ %, the microhardness anisotropy coefficient is equal to unity. This can be explained by disappearance of stacking defects in the crystals at the mentioned tellurium concentration due to favorable conditions for the sphalerite structure in the solid solution. As the Te concentration in the solid solution varies within the 0.2 to 1.3 % range, the crystal microhardness has been shown to increase linearly by 23 %. The fact has been confirmed by measuring the brittle fracture limit for Te doped and undoped ZnSe crystals. The fact can be explained by local distortions of ZnSe lattice due to Te atoms present and by the dislocation mobility decrease associated thereto, the combination of both factors results in the material strengthening. Effect of heat treatment and the block boundaries on the strength limit and cracking resistance of $ZnSe_{(1-x)}Te_x$ crystals has been established that is of importance when the material is subjected to machining.

Изучены механические свойства кристаллов твердых растворов $ZnSe_{(1-x)}Te_x$ ($0 < C_{Te} < 1.3$ мас.%) с помощью методов индентирования в двух его вариантах: вдавливание и царапание, а также измерены пределы разрушения легированных и нелегированных кристаллов методом одноосного сжатия. Установлено, что для кристаллов с концентрацией легирующей примеси $C_{Te} \approx 0.3$ % коэффициент анизотропии микротвердости равен единице. Это можно объяснить исчезновением дефектов упаковки в кристаллах при данной концентрации теллура вследствие благоприятных условий формирования структуры сфалерита в твердом растворе. Показано, что при изменении содержания теллура в твердом растворе в пределах $0.2 \div 1.3$ % величина микротвердости в кристаллах линейно увеличивается на 23 %. Это подтвердили и измерения предела хрупкого разрушения легированных и нелегированных теллуром кристаллов селенида цинка. Данный факт можно объяснить локальными искажениями кристаллической решетки ZnSe атомами теллура и связанным с этим снижением подвижности дислокаций, что в совокупности увеличивает прочность материала. Показано влияние термической обработки и наличия межблочных границ на предел прочности и трещиностойкость кристаллов $ZnSe_{(1-x)}Te_x$, что является важным при механической обработке данного материала.

The hardness and brittleness of solids are among the most important characteristics of construction materials but are of a great importance for optical materials, too. In general, hardness is an integral property that is defined by numerous mechanical characteristics of a crystal, such as plasticity, strength, elasticity limit, etc. For semiconductor zinc selenide crystals, it is just the mechanical strength and crack-

ing resistance that are of importance as the crystal is used in optical elements of IR lasers as well as in ionizing radiation detectors operating in a broad temperature range. The material cracking resistance, or brittleness, influences considerably the crystal machining regime and the yield of non-defective scintillators.

The microhardness, micro-plasticity, and micro-brittleness of $A^{II}B^{VI}$ type semiconducting compounds, including ZnSe, were studied before [1–7]. By analyzing the brittleness rosettes and dislocation rosettes obtained by micro-indentation, the brittle failure and plastic strain features of $A^{II}B^{VI}$ crystals having lattices of wuertzite, sphalerite or sphalerite with stacking faults were studied. ZnSe crystals are known to be able to crystallize in the wuertzite (W) structure as well as in the sphalerite (S) one, depending on the growing conditions. The crystals grown from melt are of the S structure but may include polytypes, twins, and stacking faults [8]. This is connected with the incompleteness of the $W \rightarrow S$ phase transition that the crystals grown from melt are subjected to. The phase transition temperature is 1420°C at heating and 1410°C at cooling [9].

The shape of indention dislocation rosette and of the brittleness rosette for ZnS and ZnSe crystals of sphalerite type with twin stacking faults are defined by the fault concentration [1, 10]. However, up to date, no sufficient attention was given in periodic literature to effects of dopants and thermal factors on ZnSe mechanical properties. That is why the aim of this work is to study the mechanical properties of $ZnSe_{(1-x)}Te_x$ solid solution crystals grown from melts and to search for ways to enhance the resistance thereof to mechanical factors. Moreover, an attempt is made to explain the effects associated with the mechanical properties of the material under study.

The $ZnSe_{(1-x)}Te_x$ solid solution crystals grown from melt under inert gas pressure using the Bridgeman-Stockbarger technique. The grown samples were annealed in zinc atmosphere in evacuated quartz ampoules at 1290 K for 24–48 h.

Powdered ZnSe–ZnTe solid solutions containing 0.2 to 3.5 mol.% zinc telluride were used as initial materials. The tellurium concentration (C_{Te}) in the crystals was determined by X-ray fluorescence analysis using a VRA-30 unit providing the lower determination limit of 0.01 % at relative error of maximum 5 %. The local elemental composition was determined using a JSM-820 scanning electron microscope with an X-ray microanalytical system Link AN10185S (EMPA), the analysis sensitivity was about 0.3 to 0.5 %.

To study the effect of tellurium dopant ($0.2 < C_{Te} < 1.3$ mass %) on the crystal mechanical properties, the microhardness (H_μ) and brittle strength (σ) were measured using indentation method in two modes (indenting and scratching) by means of a PMT-3 instrument, a Vickers diamond pyramid being used as the indentor [12]. The error of H_μ measurements did not exceed 5 %. Prior to measurements, the samples were ground and polished mechanically and then polished chemically by $HNO_3/CrO_3/H_2O$ (1/2/3) mixture. The microhardness value was determined by statistical processing of at least 50 indents. The optimum indentor load (P) was found from the $H_\mu(P)$ dependences for ZnSe and $ZnSe_{(1-x)}Te_x$ samples. For those materials, the so-called scale effect was observed, i.e., under conservation of geometric similarity, the H_μ value depended on the load. The limiting load above which the H_μ remained essentially constant was $P \geq 100$ g for ZnSe and $ZnSe_{(1-x)}Te_x$ ($0 < C_{Te} < 1.3$ mass %).

The numerical microhardness values as well as its anisotropy in ZnSe crystals are known to depend to a great extent on the structure perfection and the local phase composition [13, 14]. The undoped ZnSe crystals show a slight microhardness anisotropy of the 1st order, that is, the hardness is different along different direction in the cleavage face (110). If the indentor is arranged so that one indent diagonal (d_c) is directed along [111] while the other one (d_a) is perpendicular thereto, then $d_a > d_c$. For undoped ZnSe, the ratio $(d_a/d_c)^2 = k_1$ where k_1 is the 1st order microhardness anisotropy coefficient [15] amounts 1.02 at the cleavage face (110), that is the indent is slightly distorted (as determined by indenting under $P = 100$ g). As to the closely packed face (111), there is no 1st order H_μ anisotropy at all, the microhardness value being 100 ± 5 kg/mm^2. The scratching method is more sensitive to the microhardness anisotropy due to distinctions in the stressed states and strains. It has been shown in [14] that $k_1 \sim 1.2$ for ZnSe when the scratching method is used.

We have found that for $ZnSe_{(1-x)}Te_x$ crystals at $C_{Te} \approx 0.3$ %, $d_a = d_c$, i.e., $k_1 = 1$ (indenting mode). This can be explained by the fact that at such a tellurium concentration, the stacking faults disappear and the

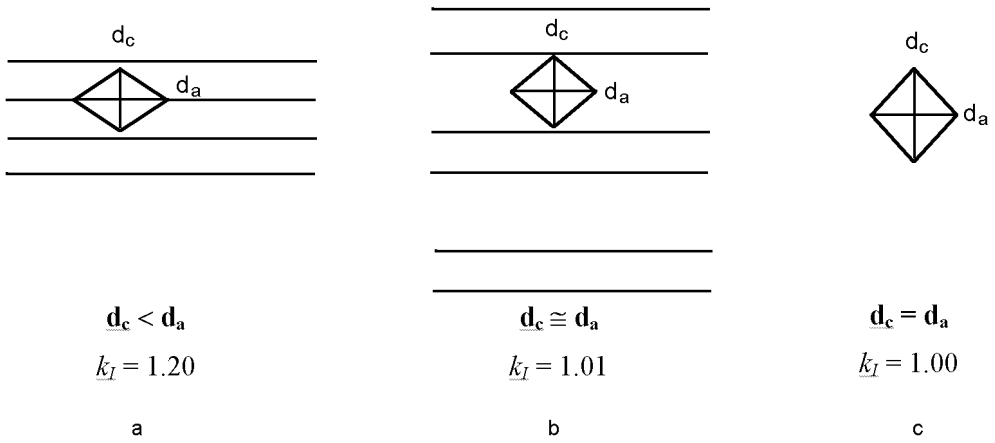

Fig. 1. Dependence of the microhardness anisotropy on the structure perfection for ZnSe and $ZnSe_{(1-x)}Te_x$ crystals: (a) for undoped ZnSe (2 % of stacking faults) with closely arranged stacking fault boundaries; (b) for $ZnSe_{(1-x)}Te_x$ at $C_{Te} < 0.3$ %, the stacking fault boundaries are seldom; (c) for $ZnSe_{(1-x)}Te_x$ at $C_{Te} \geq 0.3$ %, no stacking faults.

sphalerite structure becomes stabilized. Fig. 1, shows schematically the indent variation trend on the (110) plane and thus that of the 1st order microhardness anisotropy coefficient as depending on the structure perfection of ZnSe and $ZnSe_{(1-x)}Te_x$ crystals. The stacking faults are distortions of the crystal structure at which the d_c indent diagonal is compressed between the layers of stacking faults as compared to d_a (Fig. 1a).

The completeness of the phase transition can be assumed to define the physico-mechanical parameters of the material under study due to the fact that it is just the change in the atomic electron state under external factors that is the basis of the polymorphic transformations in covalent crystals. When passing from the hexagonal wuertzite structure to the cubic sphalerite one, the number of valence bonds in ZnSe crystal remains unchanged ($K = 4$) as well as the covalent binding type, but what is changed is just the energy state of orbitals (sp^3) fully hybridized in the S lattice while in the W one, the s- and p-states are non-hybridized in part (one of four bonds is longer than three others). Such a transition resu ts in changed microhardness of the material.

The $ZnSe_{(1-x)}Te_x$ crystals grown from melt are large-block ones, the blocks being oriented predominantly along the growth axis. Therefore, the microhardness studies (at $P = 100$ g) and brittle strength (at $P = 200$ g) of those crystals containing various tellurium concentrations were carried out on the mechanically and chemically treated surfaces of cuts perpendicular to the growth direction, within the central region of each single crystal block. The microhardness measurements evidence an increase of H_μ by about 23 % as the tellurium content in the crystals rises, as is shown in Fig. 2. Deviations are clearly seen from the assumed linear microhardness dependence shown in Fig. 2 as a solid line. This can be explained by variations in the above-mentioned strain-stress states in the crystal, the presence of thermoelastic stresses being formed during the growth in non-equilibrium conditions as well as differences in the defectness of the crystal regions being studied. These deviations are known to be eliminable by a high-temperature annealing with a smooth temperature lowering. In this case, a temperature near 2/3 of the crystal melting point should be attained. We have annealed the samples at 1300 K for 2 days followed by the temperature scaling-down at a rate of 50 K/h. The microhardness measurements on the annealed samples (Fig. 2) show a decreased scatter in H_μ values, thus evidencing the stress relaxation in the crystal. This confirms our suggestion on thermoelastic stresses as the cause of the microhardness dispersion in non-annealed samples. Thus, the high-temperature annealing in the selected conditions provides a substantially enhanced homogeneity of the $ZnSe_{(1-x)}Te_x$ crystals.

The ZnSe microhardness enhancement due to tellurium doping evidences the crystal lattice strengthening. The isovalent tellurium admixture atoms, as it was mentioned above, cause local distortions of the lattice and thus are sources of elastic

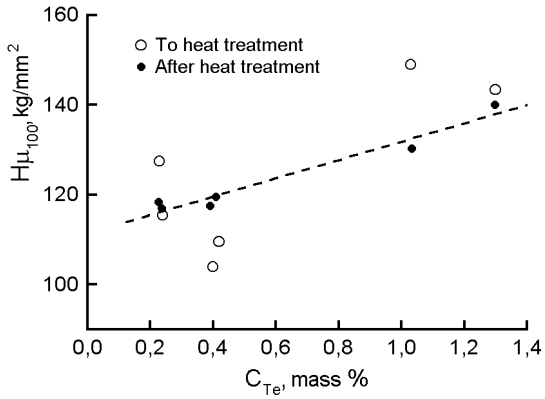

Fig. 2. Microhardness of $ZnSe_{(1-x)}Te_x$ crystals as a function of Te concentration measured on cuts perpendicular to the growth direction under $P = 100$ g.

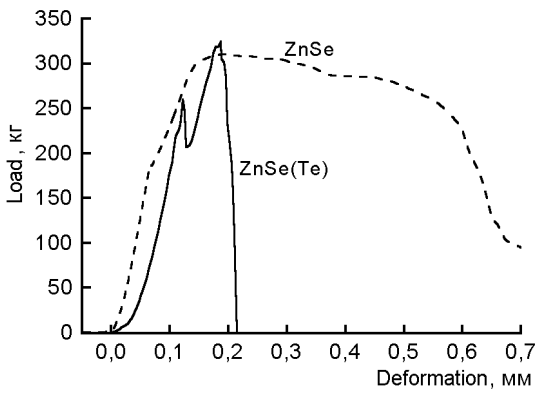

Fig. 3. Straining curve for ZnSe and $ZnSe_{(1-x)}Te_x$ crystals under uniaxial compression.

stresses that decrease in proportion to $1/r^3$ [16] where r is the distance to the impurity atom. The appreciable displacements of atoms arise at a distance of one or two interatomic spacings, thus, the elastic strain field can be considered as a short-range action one. The effect of such defects on H_μ is associated with the elastic interaction of strain fields with the dislocation fields, that results in a decreased dislocation mobility [17] Since the crystal mechanical properties are defined to a great extent just by the dislocation mobility, its decrease causes enhanced strength characteristics of the material. The increase in H_μ is connected with the fact that the strain fields generated by individual defects are not overlapped and contribute additively to the crystal microhardness change [17]:

$$\Delta H = \Delta H_0 N_0,$$

where ΔH is the microhardness change; ΔH_0, the microhardness change due to a single defect; N_0, the defect concentration.

The fact of $ZnSe_{(1-x)}Te_x$ crystal strengthening as compared to ZnSe was checked additionally by measuring the failure limit of the crystals using $5\times5\times20$ mm^3 samples. The doped crystals have been found to fail under higher loads than undoped ones (see Fig. 3). However, those are more easily crumbled into small fragments.

The brittle strength was characterized by the number of cracks and cleavages arising on the crystal plane under indentation. In this case, the brittle strength of $ZnSe_{(1-x)}Te_x$ crystals was measured on the (110) cleavage plane under $P = 200$ g. At C_{Te} about 0.1mass % , $\sigma = 4.02$ kg/mm^2 while it is about 8.33 kg/mm^2 at $C_{Te} = 1.0$ mass %. This means that the (110) face becomes strengthened about twice within the studied dopant content range. The data obtained confirm the fact that introduction of an isovalent impurity into ZnSe crystals enhances the material strength properties. This makes it possible to treat the crystals and to prepare scintillation elements therefrom under higher mechanical loads, thus providing higher machining speeds without deterioration of the surface quality.

For large-block $ZnSe_{(1-x)}Te_x$ crystals, it is the inter-crystallite boundaries that effect mainly the micro-brittleness and microhardness. We have studied the microhardness and brittle strength within limits of a single crystal block as functions of distance to the block boundaries (x). Near the boundaries, an increased dispersion in the H_μ values has been found, that dispersion increasing as the x decreases (Fig. 4a). From $x\approx60$ μm on, H_μ increases at approaching the boundary; perhaps this fact could be explained by dislocation beam braking at the barriers. Near the inter-crystallite boundary in a $ZnSe_{(1-x)}Te_x$ crystal, the k_1 value increases considerably attaining 1.2 at $x = 0$, as is seen in Fig. 4b. As in the case of $H_\mu(x)$ dependence (Fig. 4a), the k_1 value approaches that typical of the crystal matrix (~ 1.0) at the distance of about 60 μm from the boundary.

The block boundaries are also efficient stoppers for micro-cracks. Fig. 4c shows the dependence of the crack length (l_c) on x for a $ZnSe_{(1-x)}Te_x$ crystal. At the ordinate axis, there is the ratio l_c/l_{cm} that characterizes the brittle strength, l_{cm} being the crack length at $P = 200$ g typical of structurally homogeneous matrix. It follows from Fig. 4c that at x ~ 15 μm, the average crack

length becomes about halved. Immediately at the twin boundary, $l_c \approx 0.6 l_{cm}$. At $x \approx 35$ to 40 μm, $l_c / l_{cm} = 1$, that is, the block boundary influences no more the crystal microbrittleness.

As mentioned above, since the crystals under study are grown under axial and radial temperature gradients, residual internal stresses are present therein. It is known [18] that after the final cooling of a crystalline ingot, residual compressive stresses arise at its surface, while tensile ones (most favorable for cracking) exist inside the ingot. As a result, fissuration is rather often a typical microstructure defect. This defect effects in general negatively in the course of the material machining as well as the workpiece structure-sensitive properties. In this case, a set of micro-cracks is revealed in the crystal by microscopy. The cracks arise mostly along the block and twin boundaries in the ingot central zone and cause a considerable deterioration of the material mechanical strength. When studying the effect of micro-cracks on the mechanical characteristics of $ZnSe_{(1-x)}Te_x$ crystals, the brittle strength has been found to drop by about 25 % and H_μ by about 14 % in the central crystal region as compared to the peripheral one.

The post-growing heat treatment (HT) of $ZnSe_{(1-x)}Te_x$ crystals is an important stage in technology of semiconducting scintillators on the basis of those crystals making it possible to control the physicochemical, optical, and luminescence properties of the material. We have found that the tensile and compressing residual stresses that are present in the crystals immediately after the growing and resulting in cracking and decreased mechanical strength include up to 50 % of the crystal ingot volume. Moreover, impurities may be localized as adsorbed substances and foreign phase precipitates in the cracks if the cracks are formed prior to decomposition and chemical sorption of COSe, CSe, and CSe_2. After annealing of such crystals in evacuates quartz ampoules at 1300°C, the mechanical properties thereof have been found to be homogenized to a great extent, the values of relative brittle strength and microhardness in the central ingot region being increased up to those in peripheral region, i.e., equalized. Thus, the reduction of residual internal stress level takes place and cracks are cured.

To conclude, the microhardness anisotropy coefficient has been found to be unity

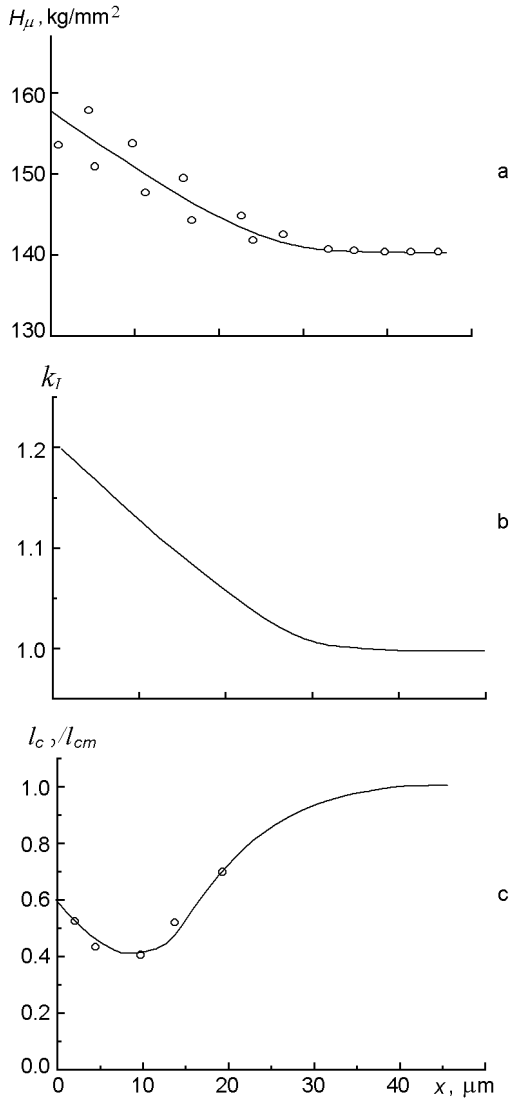

Fig. 4. Dependences of H_μ (a), k_1 on (110) face (b) and relative crack length (c) on distance to the inter-crystallite boundary in $ZnSe_{(1-x)}Te_x$ crystals.

in the crystals where the dopant concentration is about 0.3 %. When the tellurium content in the $ZnSe_{(1-x)}Te_x$ solid solution crystals increases from 0.2 to 1.3 %, the microhardness rises linearly by 23 %. This has been confirmed by the brittle failure limit measurements for Te doped and undoped ZnSe crystals. The annealing has been shown to effect the microhardness dispersion in $ZnSe_{(1-x)}Te_x$ crystals. The heat treatment results in increased strength limit and cracking resistance of $ZnSe_{(1-x)}Te_x$ crystals that is of importance for selection of the material machining regimes and for enhancement of scintillation detector vibration resistance.

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Мікротвердість і крихка міцність кристалів $ZnSe_{(1-x)}Te_x$, що вирощені з розплаву

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Вивчено механічні властивості кристалів твердих розчинів $ZnSe_{(1-x)}Te_x$ ($0 < C_{Te} < 1.3$ мас. %) з використанням методів індентування у двох його варіантах: вдавлення та дряпання, а також виміряно межі руйнування легованих і нелегованих кристалів методом одноосьового стиснення. Встановлено, що для кристалів з концентрацією легуючої домішки $C_{Te} \approx 0.3$ % коефіцієнт анізотропії мікротвердості дорівнює одиниці. Це можна пояснити зникненням дефектів упаковки у кристалах при даній концентрації телуру внаслідок сприятливих умов формування структури сфалериту у твердому розчині. Показано, що при зміні вмісту телуру у твердому розчині у межах $0.2 \div 1.3$ % величина мікротвердості у кристалах лінійно збільшується на 23 %. Це також підтвердили вимірювання краю крихкого руйнування легованих і нелегованих телуром кристалів селеніду цинку. Даний факт можна пояснити локальними викривленнями кристалічної решітки ZnSe атомами телуру й пов'язаним із цим зниженням рухливості дислокацій, що у сукупності підвищує міцність матеріалу. Показано вплив термічної обробки і наявності міжблочних границь на край міцності й тріщиностійкість кристалів $ZnSe_{(1-x)}Te_x$, що є важливим при механічній обробці даного матеріалу.