Temperature and composition effects on elastic properties of CdZnSb solid solution single crystals

V.N.Balazyuk, A.I.Eremenko[*], N.D.Raransky

Yu.Fed'kovich National Chernivtsi University, 2 Kotsyubinsky St., 58012 Chernivtsi, Ukraine
[*]National Khmelnitsky University, 11 Institutskaya St., 29016 Khmelnitsky, Ukraine

Temperature dependences of elastic constant tensor components for $Cd_{1-x}Zn_xSb$ solid solutions have been studies in the 80–300 K range using the pulsed ultrasonic method. It has been found that the Zn content increase in the solid solutions results in enhanced elastic stability of the crystal lattice and reduced anisotropy in mechanical properties of the solid solutions.

Импульсным ультразвуковым методом исследованы температурные зависимости компонент тензора упругих постоянных твердых растворов $Cd_{1-x}Zn_xSb$ в интервале 80–300 К. Установлено, что повышение содержания Zn в твердом растворе приводит к повышению упругой устойчивости кристаллической решетки и выравниванию анизотропии механических свойств твердых растворов.

The semiconducting compound CdSb and its solid solutions CdZnSb are materials of good prospects for electronics. The thermoelectric and galvanomagnetic properties thereof were subjected to numerous investigations due to a considerable anisotropy of the material thermo-e.m.f. [1]. The structurally perfect single crystals of those materials that exhibit a high photosensitivity and thus can be used as the IR range receivers, photoresistors, filters, submillimeter receivers, the UHF power measurers, and in other devices [1, 2]. The practical applications thereof requires thorough and comprehensive studies on the behavior of the material physicochemical properties and atomic interactions under various external actions, including the elastic straining.

The elastic properties of cadmium antimonide were studied in [3–6] where the elastic moduli of polycrystalline CdSb have been determined, the elasticity anisotropy has been studied as well as the temperature and pressure effects on the elastic constants of CdSb single crystals. As to CdZnSb solid solutions, essentially no similar study results are reported in literature as far as we know, except for [7]. The purpose of this work was to study the temperature and pressure effects on the elastic properties of the solid solutions of the CdSb–ZnSb system.

The CdSb and ZnSb single crystals have been prepared by the Czochralski technique and the $Cd_{1-x}Zn_xSb$ solid solutions ($x = 3$; 9; 12.5 at. % Zn), by zone melting. The single crystal structure was examined by XRD using a DRON-3 diffractometer in Cu Kα emission. The sample density was measured by hydrostatic weighing in ethane tetrabromide ($C_2H_2Br_4$) at $T = 293$ K and by X-ray technique under correction for thermal expansion. The ultrasonic (US) wave propagation speed was measured using the technique of reflected echo US pulses [8] at

Table 1. Elastic constants $C_{\mu v}$ of $Cd_{1-x}Zn_xSb$ solid solutions at T = 300 K

$C_{\mu v} \cdot 10^{-10}$, Pa	C_{11}	C_{22}	C_{33}	C_{44}	C_{55}	C_{66}	C_{12}	C_{13}	C_{23}
CdSb									
(x = 0 at.% Zn)	7.049	8.232	7.790	1.435	2.858	2.341	3.164	3.035	3.270
(x = 3 at.% Zn)	7.123	8.290	7.830	1.456	2.915	2.377	3.178	3.058	3.265
(x = 9 at.% Zn)	7.218	8.417	7.921	1.498	3.016	2.452	3.204	3.108	3.255
(x = 12.5 at.% Zn	7.382	8.485	7.978	1.522	3.074	2.494	3.220	3.135	3.250
ZnSb									
(x = 100 at.% Zn)	9.240	10.302	9.362	2.158	4.630	3.603	3.292	3.836	3.107

Table 2. Lattice periods and density of $Cd_{1-x}Zn_xSb$ solid solutions

at.% Zn	0	3	9	12.5	100
$a \cdot 10^{10}$, m	6.4743	6.4673	6.4560	6.4480	6.2016
$b \cdot 10^{10}$, m	8.2213	8.2087	8.1843	8.1640	7.7416
$c \cdot 10^{10}$, m	8.5307	8.5203	8.4997	8.4910	8.0995
$\rho \cdot 10^{-3}$, kg/m^3	6.902	6.861	6.820	6.792	6.380

Table 3. Components $S_{\mu v}$ of elastic compliance tensor of $Cd_{1-x}Zn_xSb$ solid solutions

$S_{\mu v} \cdot 10^{11}$, Pa^{-1}	S_{11}	S_{22}	S_{33}	S_{44}	S_{55}	S_{66}	S_{12}	S_{13}	S_{23}
CdSb									
(x = 0 at.% Zn)	1.857	1.589	1.670	6.970	3.500	4.271	−0.479	−0.474	−0.482
(x = 3 at.% Zn)	1.850	1.582	1.669	6.868	3.343	4.207	−0.508	−0.511	−0.460
(x = 9 at.% Zn)	1.827	1.548	1.645	6.675	3.315	4.078	−0.497	−0.512	−0.441
(x = 12.5 at.% Zn)	1.767	1.516	1.628	6.570	3.253	4.009	−0.463	−0.506	−0.434
ZnSb									
(x = 100 at.% Zn)	1.382	1.145	1.346	4.634	2.160	2.773	−0.299	−0.466	−0.256

10 MHz frequency. Various lubricants as well as salol were used as acoustic contacts. The thermostat temperature was controlled to within ±0.5 K. From the measured US wave propagation speeds at 300 K, the concentration dependences $C_{ijkl}(x)$ have been determined for all the nine components of the elastic constant tensor in the solid solutions under study. These values $C_{\mu v}$ (in the Foigt's notation) at T = 300 K are presented in Table 1. The maximum relative error of diagonal ($C_{\mu\mu}$) and non-diagonal ($C_{\mu v}$) tensor components was 0.5 and 3 %, respectively.

It follows from Table 1 that the increasing Zn content in the solid solutions results in increasing $C_{\mu v}$ values, except for C_{23}. The $C_{\mu v}(x)$ dependences are linear within the experimental accuracy. The absolute $C_{\mu\mu}$ values for CdSb agree well with the data from [7], while some difference is observed for non-diagonal tensor components

$C_{\mu v}$, perhaps due to differences in accuracy between the acoustic experimental techniques used in [7] and in this work as well as in the perfection of the studied crystals. Table 2 presents the density values and the crystal lattice periods of the solid solutions under study.

It is of interest to study the behavior of the main macroscopic elasticity parameters in the main crystallographic directions, in particular, in comparison with anisotropy of other physical properties. Table 3 presents the components $S_{\mu v}$ of the elastic compliance tensor that are related to the elastic constants according to the relationship

$$S_{\mu v} = \frac{(-1)^{\mu+v}|C_{\mu v}|}{|C|}, \qquad (1)$$

where $|C|$ is the determinant of the elastic constants matrix; $|C_{\mu v}|$, the corresponding algebraic supplements.

Table 4. Elastic characteristics of $Cd_{1-x}Zn_xSb$ solid solutions (E_μ, $\cdot 10^{10}$ Pa; χ_μ, χ_ν, $\cdot 10^{-11}$ Pa^{-1})

Elastic characteristics	E_1	E_2	E_3	χ_1	χ_2	χ_3	χ_ν
CdSb							
($x = 0$ at.% Zn)	5.385	6.293	5.988	0.904	0.628	0.714	2.246
($x = 3$ at.% Zn)	5.405	6.321	5.992	0.886	0.619	0.697	2.201
($x = 9$ at.% Zn)	5.473	6.460	6.079	0.818	0.618	0.692	2.128
($x = 12.5$ at.% Zn)	5.659	6.596	6.142	0.798	0.617	0.680	2.097
ZnSb							
($x = 100$ at.% Zn)	7.246	8.734	7.429	0.616	0.586	0.620	1.822

Table 5. Log derivatives of elastic moduli with respect to temperature

$\dfrac{d\ln C_{\mu\nu}}{dT}$, 10^{-3} К$^{-1}$								
$\mu\nu$	11	22	33	44	55	66	12	13	23
$x = 0$ at.% Zn	−0.343	−0.553	−0.256	−0.422	−0.397	−0.707	0.189	0.864	−0.264
$x = 12.5$ at.% Zn	−0.336	−0.515	−0.242	−0.412	−0.452	−0.627	0.166	0.751	−0.238
$x = 100$ at.% Zn	−0.284	−0.409	−0.170	−0.333	−0.632	−0.396	−0.127	0.261	−0.195

$\dfrac{d\ln S_{\mu\nu}}{dT}$, 10^{-3} К$^{-1}$								
$\mu\nu$	11	22	33	44	55	66	12	13	23
$x =$ at.% Zn	0.675	0.569	0.449	0.346	0.367	0.611	0.674	1.650	0.205
$x = 12.5$ at.% Zn	0.666	0.551	0.461	0.379	0.412	0.551	0.903	1.680	0.207
$x = 100$ at.% Zn	0.441	0.409	0.324	0.249	0.555	0.364	0.486	0.888	0.210

$\dfrac{d\ln M}{dT}$, 10^{-3} К$^{-1}$					
M	E_1	E_2	E_3	χ_1	χ_2	χ_3
$x =$ at.% Zn	−0.793	−0.651	−0.499	0.169	0.767	−0.197
$x = 12.5$ at.% Zn	−0.781	−0.740	−0.513	0.148	0.683	−0.191
$x = 100$ at.% Zn	−0.488	−0.499	−0.349	0.080	0.458	−0.051

Using the $S_{\mu\nu}$ values, the Young moduli E_μ, linear compressibility χ_μ values and volume ones χ_ν have been calculated; the results are summarized in Table 4 where the indices $\mu = 1, 2, 3$ correspond to the main crystallographic directions [100], [010], [001], respectively. It follows from Tables 1, 3, and 4 that the $Cd_{1-x}Zn_xSb$ solid solutions exhibit a pronounced anisotropy of elastic properties. For all the compositions, the following inequalities are valid:

$$C_{11} < C_{33} < C_{22}, \quad S_{11} > S_{33} > S_{22}$$

$$C_{44} < C_{66} < C_{55}, \quad S_{44} > S_{66} > S_{55} \quad (2)$$
$$E_1 < E_3 < E_2, \quad \chi_1 > \chi_3 > \chi_2,$$

which confirm that the elasticity anisotropy and the binding force character are manifested in the same manner along the main directions in the crystals under study.

The consideration of deviations from the Cauchy relationships

$$g_{kk} = C_{\mu\nu} - C_{9-\mu-\nu,9-\mu-\nu}, \quad (3)$$
$$(\mu, \nu, k = 1,2,3; \ \mu \neq \nu \neq k)$$

taking into account the signs and absolute values of the g_{kk} tensor components [10] has shown that as the Zn content in the solid solutions rises, the ionic binding fraction in the [100] direction decreases. In fact, according to (3), the value $g_{11} = 0.949 \cdot 10^{10}$ Pa for ZnSb ($x = 100$ at. % Zn) is almost half of $g_{11} = 1.835 \cdot 10^{10}$ Pa for

CdSb ($x = 0$ at % Zn). These estimations are in agreement with the data from [11] where the alloying of CdSb with zinc has been shown to be accompanied by the electron density redistribution on hybrid orbitals of Cd and Zn atoms resulting in a decrease of ionicity in the specified direction.

From the experimental temperature dependences of the US propagation speed, all the nine independent components $C_{\mu\nu}(T)$ of the elastic constant tensor for the studied solid solutions within the 80 to 300 K range. All the $C_{\mu\nu}(T)$ values depend slightly on T and decrease monotonously, except for $C_{12}(T)$ and $C_{13}(T)$ that increase linearly. The linearity in $C_{\mu\nu}(T)$ dependences made it possible to determine the log derivatives of the main elastic parameters with respect to temperature; the data obtained are presented in Table 5. The temperature variation is seen to affect most considerably the elastic constants C_{22}, C_{44}, C_{66}, C_{13}, with relatively large derivative values. Therefore, the temperature gradients will influence considerably the weakening of atomic interaction forces under tensile (compressing) strains in the [010] direction, shear strains in the [100] and [001] ones and transversal counteraction in the [010] one. It is also seen that as the Zn content in the solid solutions rises, the $d\ln C_{\mu\nu}/dT$ values decrease for all the $C_{\mu\nu}$ values, except for C_{55}, while the $d\ln C_{12}/dT$ value that shows an anomaly reverses its sign for ZnSb.

Thus, during the cadmium antimonide alloying with zinc, the electron density is redistributed between the structure orbitals in such a manner that the solid solution crystal lattice takes an enhanced elastic stability. Moreover, it can be concluded from the comparison and consideration of the results obtained that as the Zn content in the $Cd_{1-x}Zn_xSb$ solid solutions rises, those become more isotropic in the mechanical properties as compared to CdSb. The latter fact is to account for when designing anisotropic thermoelements being operated under temperature gradients.

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Вплив температури та складу на пружні властивості монокристалів твердих розчинів CdZnSb

В.Н.Балазюк, А.І.Єременко, Н.Д.Раранський

Імпульсним ультразвуковим методом досліджено температурні залежності компонент тензора пружних постійних твердих розчинів $Cd_{1-x}Zn_xSb$ в інтервалі 80–300 К. Встановлено, що збільшення вмісту Zn у твердому розчині призводить до підвищення пружної стійкості кристалічної гратки і вирівнювання анізотропії механічних властивостей твердих розчинів.