NONELECTRONIC PROPERTIES OF SEMICONDUCTORS
(ATOMIC STRUCTURE, DIFFUSION)

Anisotropy of the Thermal Expansion of $CuIn_5Se_8$ Single Crystals in Two Structural Modifications

I. V. Bodnar

Belarusian State University of Information and Radio Electronics, Minsk, 220013 Belarus
e-mail: chemzav@bsuir.by
Submitted November 10, 2015; accepted for publication November 16, 2015

Abstract—Thermal expansion in the temperature range 80−700 K is studied for two (trigonal and hexagonal) structural modifications of $CuIn_5Se_8$ single crystals grown by planar crystallization of the melt. From the data, the thermal-expansion coefficients are calculated for both modifications. It is established that, in the temperature range under study, the thermal expansion of both modifications is anisotropic. For the trigonal modification, the thermal-expansion coefficient in the direction of the **c** axis (α_c) is larger than that in the direction of the orthogonal **a** axis (α_a). For the hexagonal modification of the $CuIn_5Se_8$ crystal, the thermal-expansion coefficient in the direction of the **c** axis exhibits anomalous behavior: as the temperature is increased, the coefficient α_c increases, after which it decreases to negative values, reaches a minimum, and then increases further. Such behavior of the coefficient α_c is associated with the phase transformation of the hexagonal modification of the $CuIn_5Se_8$ compound into the trigonal modification.

1. INTRODUCTION

$CuIn_5Se_8$ crystals belong to the class of imperfect $A^I B^{III}_{2n+1} C^{VI}_{3n+2}$ semiconductors with ordered vacancies formed on the $Cu_2Se−In_2Se_3$ quasi-binary section at $n = 2$ [1−3]. The $CuIn_5Se_8$ compound exhibits direct interband transitions and is a promising material for the production of new optoelectronic devices of different applications: highly efficient radiation-resistant converters of solar energy, infrared detectors, heterojunctions of various types, etc. [1−5]. The $CuIn_5Se_8$ compound can exist in several structural modifications, but the modification stable at room temperature is hexagonal [6−9].

In this paper, we for the first time report the results of studies on thermal expansion for two modifications of $CuIn_5Se_8$ single crystals in the temperature range 80−700 K.

2. EXPERIMENTAL

$CuIn_5Se_8$ single crystals were grown by planar crystallization of the melt of >99.999%-pure elemental components. The components were loaded into doubled quartz cells with a tapered (cone-shaped) bottom. A quartz bar which served as a holder was soldered to the outer cell and connected to a vibrator. After evacuation of the cell to a residual pressure of ~10^{-3} Pa, it was placed into a vertical single-zone furnace with a specified temperature gradient. Upon heating of the cell in the furnace, the contents of the cells were subjected to vibrational mixing which significantly accelerated compound formation and prevented the cells from exploding.

The furnace temperature was elevated to ~(1000–1020) K at a rate of ~50 K h^{-1}. At these temperatures, the cells were isothermally exposed for ~2 h, with the vibration turned on. Then the temperature was elevated to 1250 K and maintained for another 2 h. Thereafter, we turned off the vibration and conducted planar crystallization of the melt by lowering the furnace temperature to ~1020 K at a rate of ~2 K h^{-1}. At this temperature, we performed homogenizing annealing of the resultant ingots for 150 h. The $CuIn_5Se_8$ single crystals grown under such conditions were ~14 mm in diameter and ~40 mm in length. The crystals were uniform and homogeneous, as established by microprobe X-ray spectral analysis, X-ray diffraction (XRD) analysis, and differential thermal analysis (DTA).

To obtain the trigonal modification, the annealed single crystals were quenched in icy water.

The elemental composition of the single crystals was determined by microprobe X-ray spectral analysis using a Cameca-SX100 setup. The relative error of determining the content of the components was ±5%.

The structure and unit-cell parameters of the single crystals were determined by the XRD technique. The XRD patterns were recorded using an automatic computer-controlled DRON-3M X-ray instrument oper-

Table 1. XRD data for the hexagonal modification of $CuIn_5Se_8$ crystals

2θ, deg	d, Å	2θ, deg	d, Å	hkl	I, %
experiment		calculation			
16.24	5.458	16.21	5.462	006	18
18.90	4.691	18.93	4.684	007	4
21.67	4.100	21.67	4.100	008	100
26.79	3.3249	26.76	3.3285	103	3
27.20	3.2757	27.18	3.2780	0.0.10	30
27.66	3.2225	27.70	3.2177	104	4
32.77	2.7308	32.76	2.7315	0.0.12	18
35.57	2.5217	35.56	2.5224	109	2
37.58	2.3914	37.58	2.3914	1.0.10	2
39.70	2.2684	39.70	2.2684	1.0.11	3
41.92	2.1532	41.93	2.1528	1.0.12	5
44.15	2.0495	44.17	2.0486	0.0.16	3
44.85	2.0191	44.85	2.0191	110	3
46.64	1.9457	46.64	1.9457	1.0.14	1
47.09	1.9282	47.09	1.9282	0.0.17	2
49.12	1.8532	49.12	1.8532	1.0.15	5
50.04	1.8212	50.04	1.8212	0.0.18	4
51.72	1.7659	51.72	1.7659	119	2
56.06	1.6391	56.06	1.6391	0.0.20	3
62.26	1.4901	62.26	1.4901	0.0.22	2
68.64	1.3661	68.66	1.3658	0.0.24	10
71.95	1.3112	71.95	1.3112	0.0.25	2
75.29	1.2611	75.31	1.2608	0.0.26	3
78.74	1.2143	78.75	1.2142	0.0.27	2
82.30	1.1705	82.29	1.1707	0.0.28	2
85.90	1.1305	85.91	1.1304	0.0.29	2
89.64	1.0927	89.65	1.0926	0.0.30	3
97.49	1.0246	97.52	1.0243	0.0.32	1
106.06	0.9641	106.05	0.9642	0.0.34	1

Table 2. XRD data for the trigonal modification of $CuIn_5Se_8$ crystals

2θ, deg	d, Å	2θ, deg	d, Å	hkl	I, %
experiment		calculation			
11.49	7.695	11.52	7.675	006	18
13.48	6.563	13.45	6.577	007	4
15.40	5.749	15.38	5.756	008	100
17.36	5.1038	17.33	5.1126	009	3
19.28	4.5996	19.26	4.6044	0.0.10	30
21.20	4.1873	21.21	4.1853	0.0.11	1
23.15	3.8388	23.16	3.8372	0.0.12	100
25.14	3.5392	25.12	3.5420	0.0.13	5
25.52	3.4874	25.50	3.4901	301	1
27.12	3.2852	27.11	3.2864	0.0.14	3
27.47	3.2412	27.49	3.2418	1.1.12	5
29.10	3.0661	29.08	3.0680	0.0.15	3
31.08	2.8751	31.05	2.8777	0.0.16	3
35.06	2.5573	35.05	2.5579	0.0.18	1
37.10	2.4211	37.08	2.4224	0.0.19	2
38.52	2.3351	38.54	2.3340	409	5
39.54	2.2772	39.50	2.2794	4.0.10/412	4
41.64	2.1671	41.65	2.1666	4.0.12	3
42.73	2.1143	42.76	2.1129	2.0.20	2
43.25	2.0902	43.22	2.0914	3.3.15	2
44.78	2.0222	44.80	2.0214	2.2.17	1
45.27	2.0014	45.26	2.0018	0.0.23	3
46.12	1.9665	46.13	1.9661	4.1.12	7
47.68	1.9057	47.68	1.9057	3.3.18	2
48.38	1.8797	48.38	1.8797	4.1.14	3
51.59	1.7701	51.57	1.7707	0.0.26	2
51.97	1.7580	51.98	1.7577	3.3.13	2
53.35	1.7161	53.36	1.7155	3.3.14	2

ating with CuK_α radiation and equipped with a graphite monochromator.

Thermograms were recorded with a system that allowed the recording of the dependence $\Delta T = f(T)$, where T is the temperature and ΔT is the temperature difference between the sample under study and the reference sample.

The thermal expansion of the single crystals was studied in the temperature range 80−600 K, with the use of a quartz dilatometer. Before the measurements, the system was evacuated, which inhibited oxidation of the sample. The temperature was measured with a chromel−alumel thermocouple. The samples were heated with a rate of ~5 K min^{-1}, which made it possi-ble to obtain reproducible results. The measurement error was ±5%.

The relative expansion ($\Delta l/l_0$) of the materials as a function of temperature was measured for the single-crystal samples oriented perpendicularly and parallel to the principal axis of the crystals. The samples were $3 \times 3 \times 12$ mm in average dimensions. The thermal-expansion coefficient was calculated by the well-known formula [10].

3. RESULTS

The results of microprobe X-ray spectral measurements show that the content of components in the single crystals is in satisfactory agreement with the specified composition in the initial mixture.
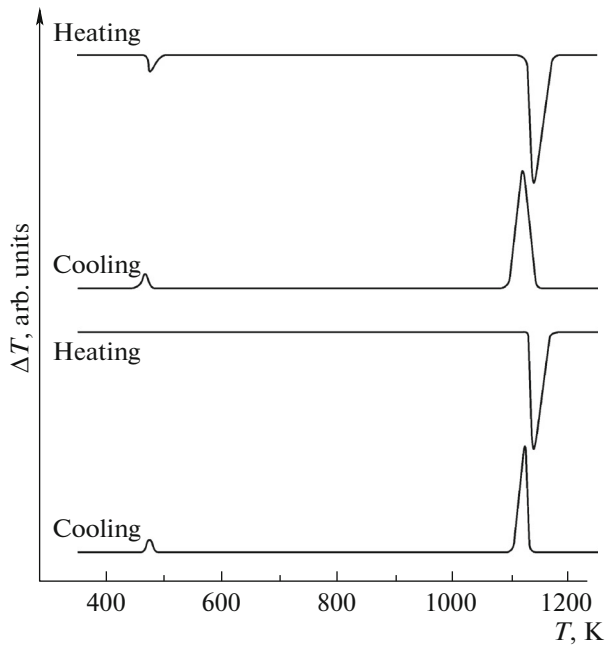
Fig. 1. Thermograms of (upper curves) the hexagonal and (lower curves) trigonal modifications of the $CuIn_5Se_8$ compound.

The angles of reflection (2θ), the interplanar spacings (d), the relative intensities of the reflections (I), and the Miller indices of planes (hkl) in the $CuIn_5Se_8$ compound are listed in Tables 1 and 2. In addition, Tables 1 and 2 give calculated values of the above quantities. As can be seen from Tables 1 and 2, the experimental data and the calculated values are in good agreement. From Tables 1 and 2, it also follows that, depending on the method of cooling, $CuIn_5Se_8$ single crystals can be produced in two structural modifications, the hexagonal modification (upon slow cooling to room temperature) and the trigonal modification (upon quenching of the single crystals).

The unit-cell parameters calculated by the least-squares method are $a = 4.038$ Å and $c = 32.78$ Å for the hexagonal modification and $a = 12.125$ Å and $c = 46.04$ Å for the trigonal modification. The results obtained here are in satisfactory agreement with the data known from publications [1−3].

The thermograms of both structural modifications of the $CuIn_5Se_8$ compound are shown in Fig. 1. From Fig. 1, it can be seen that the thermograms of heating and cooling of the hexagonal modification of the $CuIn_5Se_8$ crystals (upper curves) exhibit two thermal effects. One thermal effect is observed in the temperature range 487−498 K and corresponds to the transition, at which the hexagonal structure transforms into the trigonal one; the other thermal effect observed at $T = 1145$ K corresponds to melting of the compound. For the trigonal modification (lower curves), the thermogram of heating shows one thermal effect at $T =$
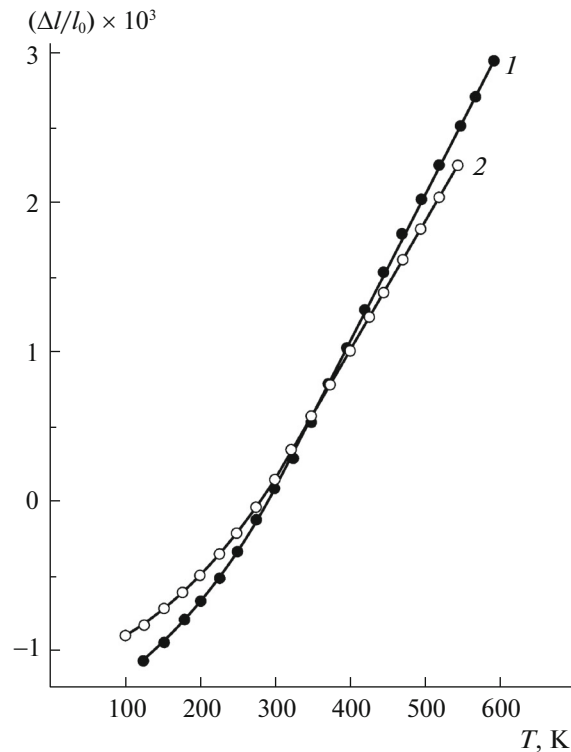
Fig. 2. Temperature variations in the relative expansion ($\Delta l/l_0$) for the trigonal modification of $CuIn_5Se_8$ single crystals along the directions (1) parallel and (2) orthogonal to the principal axis of the crystal.
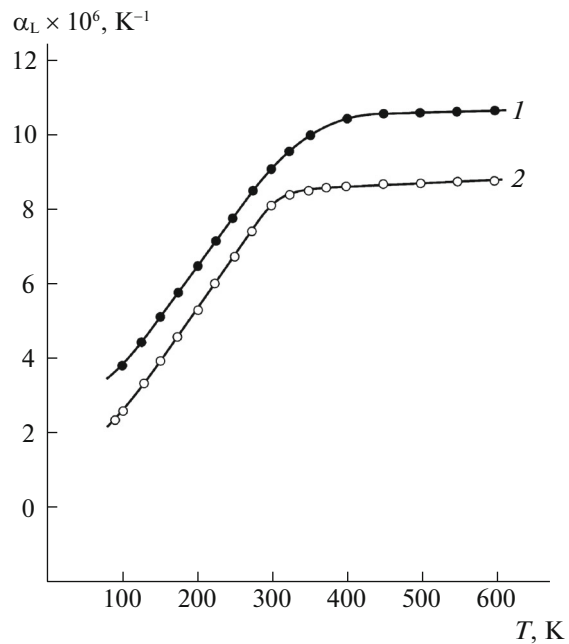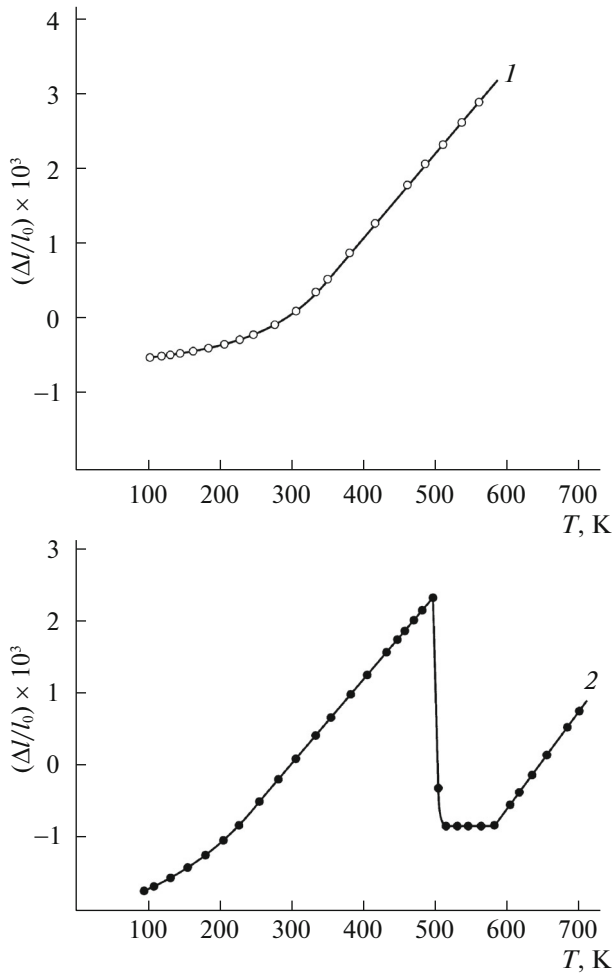
Fig. 3. Temperature dependences of the thermal-expansion coefficient for the trigonal modification of $CuIn_5Se_8$ single crystals along the directions (1) parallel and (2) orthogonal to the principal axis of the crystal.

Fig. 5. Temperature dependence of the thermal-expansion coefficient for the hexagonal modification of $CuIn_5Se_8$ single crystals along the direction orthogonal to the principal axis of the crystal.

Fig. 4. Temperature variations in the relative expansion $\Delta l / l_0$ for the hexagonal modification of $CuIn_5Se_8$ single crystals along the directions (1) orthogonal and (2) parallel to the principal axis of the crystal.

1145 K (melting of the compound), whereas the thermogram of cooling shows two effects, which is indicative of transformation of the crystal into the hexagonal modification upon slow cooling.

Figures 2 and 3 show the temperature dependences of the relative extension ($\Delta l / l_0$) and the linear thermal-expansion coefficient (α_L) measured for the trigonal modification of the $CuIn_5Se_8$ single crystals in the directions parallel (α_c) and orthogonal (α_a) to the principal axis of the crystal. Analysis of the results shows that the characteristic feature of the single crystals under study is that their thermal expansion is substantially anisotropic. The thermal-expansion coefficient measured along the **c** axis, α_c, is larger than that measured along the orthogonal **a** axis, α_a, at all measurement temperatures; i.e., the crystal lattice expands in the [001] direction. The most significant variations in the thermal-expansion coefficients are observed in the temperature range from 80 to 280 K. At higher
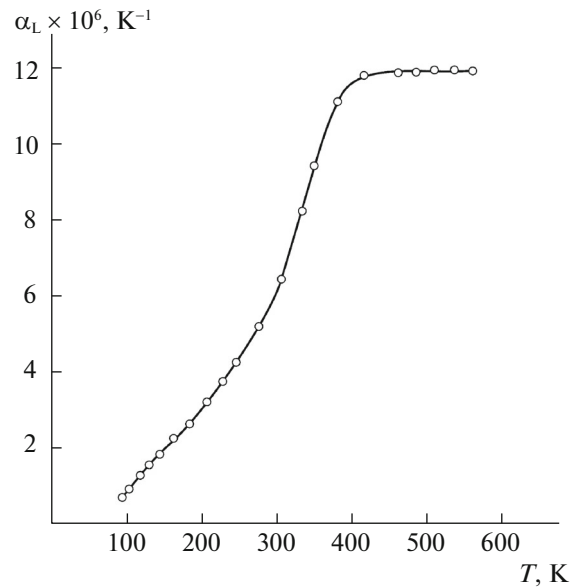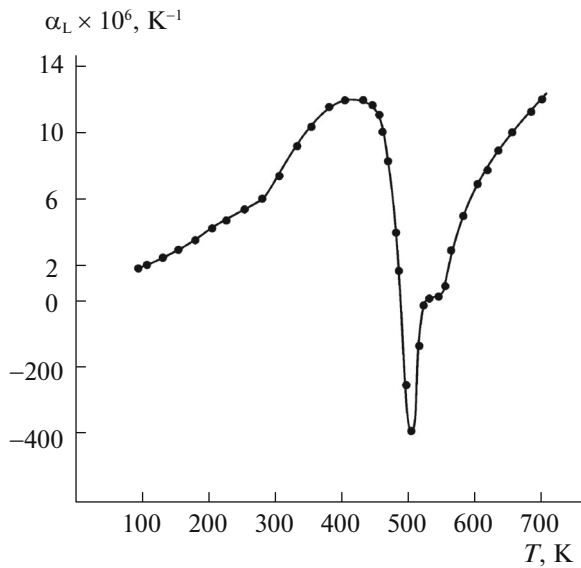
temperatures, the temperature effect becomes noticeably weaker, and at temperature above 300 K, the coefficients vary only slightly. Such character of anisotropy of the thermal expansion of the trigonal modification of $CuIn_5Se_8$ is defined by the specific features of the crystal structure of the compound and indicative of the weaker interaction between atoms along the principal axis of the crystal. The results obtained for the $CuIn_5Se_8$ compound in this study are somewhat different from the data reported in [11]. This is apparently associated with the different methods of thermal-expansion measurements. In [11], thermal expansion was studied by the X-ray technique, and as noted in [10], the X-ray technique and the dilatometry method give results different in physical nature. The X-ray technique serves to determine the thermal-expansion coefficient of the crystal structure, whereas the dilatometry method determines the thermal expansion coefficient of the material as such.

Figure 4 (curves 1, 2) show the relative expansion $\Delta l / l_0$ measured for the hexagonal modification of the $CuIn_5Se_8$ single crystals in the directions orthogonal and parallel to the principal axis of the crystal. It can be seen that no features are observed (Fig. 4, curve 1) and, as the temperature is increased, the relative expansion $\Delta l / l_0$ increases.

The variation in the thermal-expansion coefficient measured for the $CuIn_5Se_8$ single crystal in the direction orthogonal to the principal axis of the crystal **c** (α_a) is shown in Fig. 5. It can be seen that, in the temperature range from 90 to 400 K, the coefficient α_a

4. CONCLUSIONS

The thermal expansion of the trigonal and hexagonal modifications of $CuIn_5Se_8$ single crystals grown by the Bridgman method (vertical version) is for the first time studied by the dilatometric method. The thermal-expansion coefficients are determined, and their temperature dependences are established. It is found that the thermal expansion of both modifications is anisotropic. For the trigonal modification, the thermal-expansion coefficient measured along the **c** axis is larger than that along the perpendicular axis **a**; i.e., the crystal lattice expands mainly in the [001] direction.

Fig. 6. Temperature dependence of the thermal-expansion coefficient for the hexagonal modification of $CuIn_5Se_8$ single crystals along the direction parallel to the principal axis of the crystal.

sharply increases from $\sim0.8 \times 10^6$ to 11.4×10^6 K^{-1}. As the temperature is increased further, it only slightly influences the coefficient of thermal expansion.

The behavior of the relative expansion of the $CuIn_5Se_8$ single crystals in the direction parallel to the principal axis of the crystal **c** (α_c) is quite different. It can be seen that, as the temperature is increased, the relative expansion $\Delta l/l_0$ increases in the range from 90 to 494 K, then sharply drops to negative values in the temperature range from 494 to 508 K and reaches a minimum, after which the expansion remains unchanged up to 600 K. Such behavior of the relative expansion and the coefficient of thermal expansion (Fig. 6) is most likely defined by the phase transition of the low-temperature (hexagonal) modification of the $CuIn_5Se_8$ compound to the high-temperature (trigonal) modification.

REFERENCES

1. W. Hönle, G. Kühn, and U.-C. Boehnke, Cryst. Res. Technol. **23**, 1347 (1988).
2. S. M. Wasim, C. Rincon, and G. Marin, Phys. Status Solidi A **194**, 244 (2002).
3. I. V. Bodnar, V. Yu. Rud, Yu. V. Rud, and M. V. Yakushev, Semiconductors **36**, 1132 (2002).
4. I. V. Bodnar, I. A. Victorov, B. Kh. Bairamov, V. Yu. Rud, Yu. V. Rud, and M. Leon, Thin Solid Films **515**, 5763 (2007).
5. S. M. Wasim, C. Rincon, and G. Marin, Phys. Status Solidi A **194**, 244 (2002).
6. U. C. Boehnke and G. Kuhn, J. Mater. Sci. **22**, 1635 (1987).
7. S. Levchenko, M. Leon, G. Gurieva, R. Serna, J. M. Merino, E. J. Fridriech, E. Arushanov, and I. V. Bodnar, Mater. Chem. Phys. **125**, 77 (2011).
8. G. Marin, R. Marquez, R. Guewara, S. M. Wasim, J. M. Delgado, C. Rincon, and S. Perez, Jpn. J. Appl. Phys. **39**, 44 (2000).
9. J. M. Merino, S. Mahanty, M. Leon, R. Diaz, F. Rueda, and J. L. Martin, Thin Solid Films **361−362**, 70 (2000).
10. S. I. Novikova, *Thermal Expansion of Solids* (Nauka, Moscow, 1974) [in Russian].
11. N. S. Orlova, I. V. Bodnar, T. L. Kushner, and A. M. Koval'chuk, in *Proceedings of the International Conference on Actual Problems of Solid State Physics* (Minsk, 2005), Vol. 2, p. 132.

Translated by E. Smorgonskaya