Abnormal thermal expansion and thermal conductivity of $CuIn_7Se_{11}$ single crystals

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Homogeneous $CuIn_7Se_{11}$ single crystals with a diameter of ~ 14 mm and length of ~ 40 mm have been grown from the melt using the Bridgman method. Composition and structure of the obtained single crystals have been defined. It was shown that the obtained single crystals crystallized in a hexagonal structure. The anisotropy of thermal expansion and thermal conductivity in the temperature range of 80−650 K has been investigated on oriented single crystals in parallel and at right angle to the main crystal axis c. Abnormal thermal expansion and thermal conductivity were observed on the single crystals oriented in parallel to the main crystal axis.

Keywords: Bridgman method, single crystals, crystalline structure, thermal expansion, thermal conductivity.

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1. Introduction

$CuIn_7Se_{11}$ crystals are classified as vacancy-ordered defect semiconductors. These crystals are formed in quasi-binary profile $Cu_2Se-In_2Se_3$ at $n = 3$ [1–3] and are advanced materials to be used in high-performance radiation-hardened thin-film solar cells, visible and IR band light emitters and other semiconductor and quantum electronics devices [4–10].

The data on the investigation of the anisotropy of thermal expansion and thermal conductivity of $CuIn_7Se_{11}$ single crystals in the temperature range of 80−650 K has been first discussed herein.

2. Experimental part

$CuIn_7Se_{11}$ single crystals were grown using directional crystallization of the melt in a single-zone vertical oven (Bridgman method). The single crystal growing technique, composition and structure are described in [11].

The composition of the grown single crystals was defined by means of a microprobe X-ray spectrum analysis using „Cameca-SX100“ system.

The structure and parameters of the single crystal lattice cell were found using X-ray methods. The angular positions of the diffraction spectrum lines were recorded using DRON-3M X-ray machine in CuK_α-emission with graphite monochromator.

Thermal expansion of $CuIn_7Se_{11}$ single crystals was measured using a quartz dilatometer in the temperature range of 80−650 K. The system was evacuated before the measurements to prevent the sample oxidation. The temperature was measured using a chromel-alumel thermocouple. The samples were heated at ~ 5 K/min to ensure reproducible results. The measurement error was $\pm 5\%$.

The temperature dependence of relative elongation $(\Delta l/l_0)$ for the specified materials was measured on the single crystal samples with parallel and perpendicular orientation to the main crystal axis with average dimensions $3 \times 3 \times 12$ mm. The thermal expansion coefficient was calculated using a well known equation [12].

Thermal conductivity of $CuIn_7Se_{11}$ single crystals was examined using the absolute steady-state method in the temperature range of 300−650 K [13]. The samples were in the form of parallelepipeds with the dimensions mentioned above. Silver paste was used to ensure the thermal contact between the sample, cooler and heater. The measurement accuracy was $\sim 8\%$.

3. Results and discussion

The microprobe X-ray spectrum analysis has shown that the content of elements in the grown single crystals successfully agreed wit the specified content in the initial charge.

The X-ray examination has shown that the $CuIn_7Se_{11}$ X-ray diffraction images contained reflection indices specific to the hexagonal structure. Lattice cell parameters calculated using the least square method by reflections for which $2\theta > 60^\circ$ are equal to: $a = 4.036$ Å, $c = 32.70$ Å.

Figures 1 and 2 show the temperature dependence and elongation variation $\Delta l/l_0$ measurements for $CuIn_7Se_{11}$ single crystals with perpendicular and parallel orientation relative to the main crystal axis.

Figure 1 shows that there are no irregularities on the dependence $\Delta l/l_0$ of $CuIn_7Se_{11}$ single crystals oriented at right angle to the main crystal axis within the temperature range of interest. The elongation is increased with the temperature growth.

Elongation of $CuIn_7Se_{11}$ single crystals oriented in parallel to the main crystal axis shows an other behavior (Fig. 2). It can be seen that $\Delta l/l_0$ increases with the temperature growth in the range of 90–485 K, than drops sharply in the temperature range of 485–490 K and achieved its minimum after which the elongation is not changed up to 520 K, and then a new growth occurs.

Figures 3 and 4 show the thermal expansion coefficient variations for $CuIn_7Se_{11}$ single crystals oriented at right angle $\alpha_\perp$ and in parallel $\alpha_\parallel$ to the main crystal axis.

Figure 3 shows that in the range of 90–350 K $\alpha_\perp$ increases sharply from $\sim 3.5 \cdot 10^6$ to $9.5 \cdot 10^6\,K^{-1}$, and then the temperature has little effect on the thermal expansion coefficient.

Figure 4 shows the thermal expansion coefficient variations for $CuIn_7Se_{11}$ single crystals oriented in parallel to the main crystal axis ($\alpha_\parallel$). It can be seen that in the temperature range of 90–475 K $\alpha_\parallel$ increases sharply from $\sim 2.3 \cdot 10^6$ to $8.65 \cdot 10^6\,K^{-1}$, then decreases sharply to negative values and after that starts growing again. In the temperature range of 504–509 K, $\alpha_\parallel$ is not changed and then new growth begins. Such elongation and thermal expansion coefficient behavior is probably associated with the phase transition of the low-temperature (hexagonal) modification into the high-temperature (rhombohedral) modification.

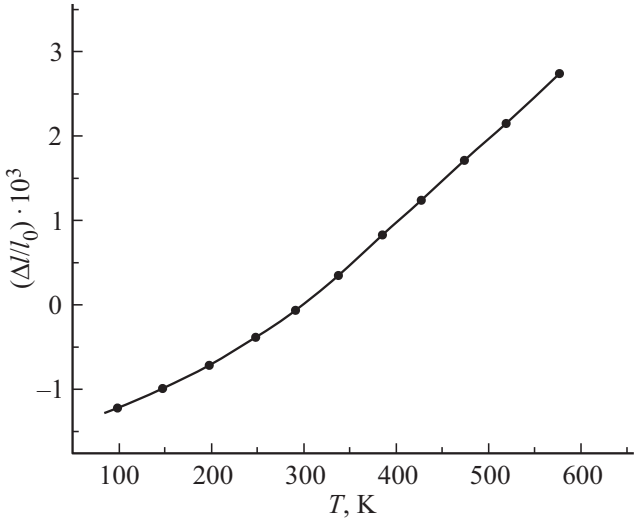

Figure 1. Elongation variation $(\Delta l/l_0)$ for $CuIn_7Se_{11}$ single crystals at right angle to the main crystal axis.

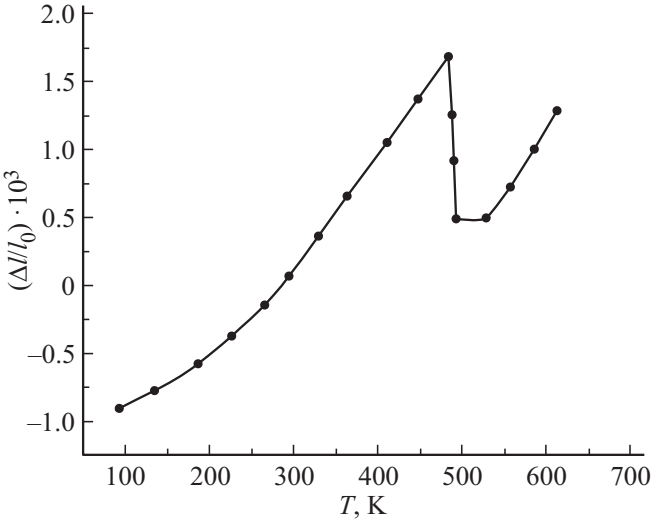

Figure 2. Elongation variation $(\Delta l/l_0)$ for $CuIn_7Se_{11}$ single crystals parallel to the main crystal axis.

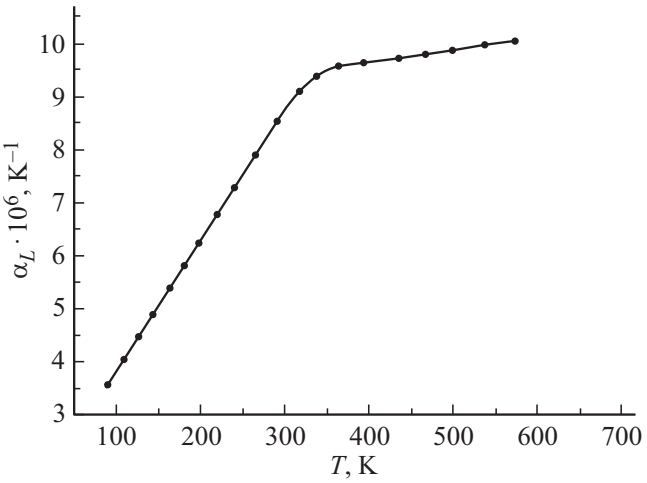

Figure 3. Temperature dependence of thermal expansion coefficient (α_L) for $CuIn_7Se_{11}$ single crystals at right angle to the main crystal axis.

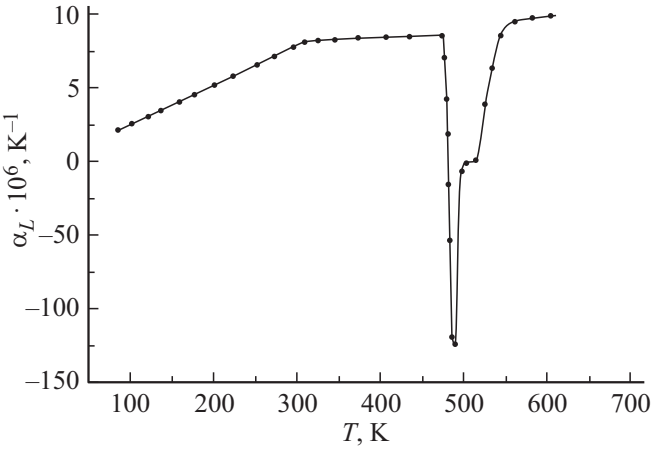

Figure 4. Temperature dependence of thermal expansion coefficient (α_L) for $CuIn_7Se_{11}$ single crystals parallel to the main crystal axis.

The thermal conductivity investigation results for $CuIn_7Se_{11}$ single crystals are shown in Figs. 5 and 6. They are characterized by different nature of temperature dependences of thermal conductivity at right angle $\chi_\perp$ and in parallel $\chi_\parallel$ to the main crystal axis.

Figure 5 shows that there are no irregularities within the temperature range on the thermal conductivity dependence of $CuIn_7Se_{11}$ single crystals oriented at right angle to

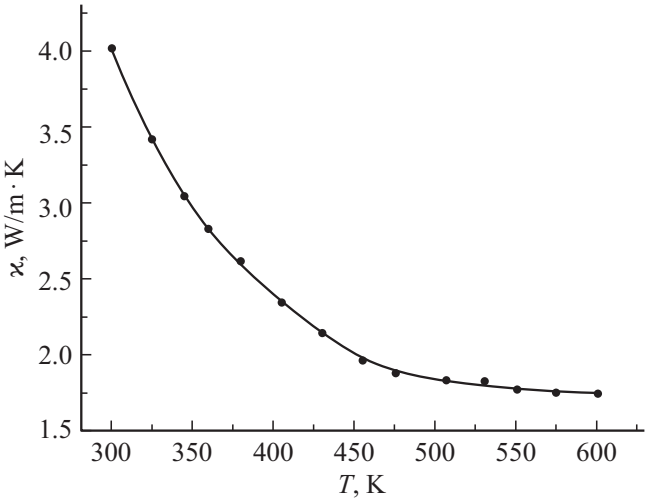

Figure 5. Temperature dependence of thermal conductivity (χ) for $CuIn_7Se_{11}$ single crystals at right angle to the main crystal axis.

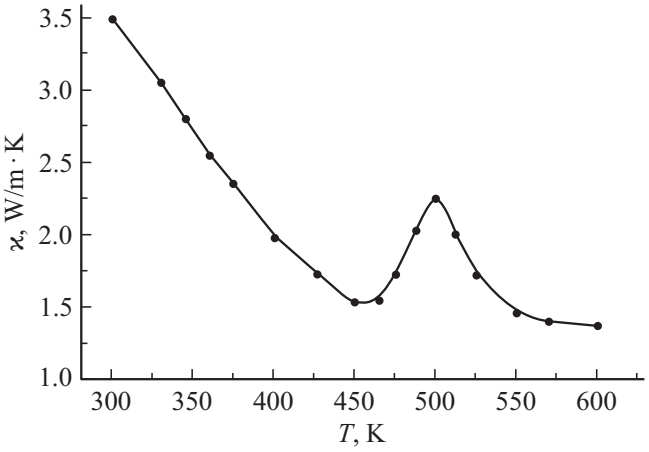

Figure 6. Temperature dependence of thermal conductivity (χ) for $CuIn_7Se_{11}$ single crystals in parallel to the main crystal axis.

the main crystal axis. Thermal conductivity is described by power law T^{-n}, where $0 < n < 1$, which indicates that the scattering processes predominantly take place on the crystalline lattice defects. This results in weak dependence $\chi_\perp$ from the temperature.

Figure 6 shows the temperature dependence of thermal conductivity for $CuIn_7Se_{11}$ single crystals oriented in parallel to the main crystal axis $\chi_\parallel$. The illustrated dependence shows abnormal thermal conductivity in the range of 480−500 K. It is expected that this is due to the phase transition from the low-temperature (hexagonal) modification to the high-temperature (rhombohedral) modification (similar to the thermal expansion described above).

4. Conclusion

Hexagonally structured $CuIn_7Se_{11}$ single crystals grown using the Bridgman method (vertical version) have been first used to investigate the anisotropy of thermal expansion and thermal conductivity in the temperature range of 80−650 K.

No abnormal features were observed on the single crystals oriented at right angle to the main crystal axis c throughout the temperature range. For single crystals oriented in parallel to the main axis, both abnormal thermal expansion and abnormal thermal conductivity are observed which are probably associated with the phase transition of the hexagonal structure into the rhombohedral structure.

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Conflict of interest

The authors declare that they have no conflict of interest.

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