GROWTH AND PROPERTIES OF $CuGa_3Se_5$ SINGLE CRYSTALS

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Ternary semiconductor compound $CuGa_3Se_5$ appertains to compounds of $I–III_m–VI_n$ type (where m = 3 - 5; n = 5 - 8) and is a promising material for creation on its basis of a number of semiconductor devices, such as infra-red and visible radiation sources, high efficient solar cells and other devices of semiconductor and quantum electronics [1-6]. As it was shown by us in works [7, 8], $I–III_m–VI_n$ compounds are promising materials for creation of wide band converters of solar radiation on their basis.

The growth conditions for $CuGa_3Se_5$ single crystal ternary compounds prepared by the Bridgman-Stockbarger method, investigation of heat expansion anisotropy, structural and optical properties are presented in the given work.

Copper, gallium, and selenium with a purity of > 99.999% were used as starting materials. The metallic components were loaded into a graphitized quartz boat. The boat was mounted at the end of quartz ampoule, and selenium, taken in excess of the stoichiometric amount in order to ensure a selenium vapor pressure of ~ 0.15 MPa over the melt, was placed at the opposite end of the ampoule. After evacuation to a residual pressure of about 10^{-3} Pa and sealing off, the ampoule was mounted in horizontal two – zone furnace so that the metallic components were in the high – temperature zone ~ 1400 K, and the selenium was in the low – temperature zone, which was heated to ~ 850 K at a rate of 100 K/h. These temperatures were then maintained during 2 h for the metals and selenium vapor to react. In order to complete the reaction, the low – temperature zone was heated to ~ 950 K at a rate of 50 K/h. After keeping for 1 h the high – temperature zone was cooled to ~ 900 K at a rate of 50 K/h, and then the furnace was switched off.

The resultant ingots were used for growth of $CuGa_3Se_5$ single crystals by the Bridgman – Stockbarger method. The ingots were transferred to graphitized double-wall quartz ampoules with a slightly conical inner wall terminated with a cylindrical capillary, which ensured the formation of a single crystal seed. The temperature of the melt zone was ~ 1400 - 1420 K and that of the annealing zone was ~ 1100 – 1120 K. After melt homogenization for ~ 24 h, the ampoule was lowered at a rate of 0.18 mm/h through a temperature gradient ~ 40 K/cm.

A single crystal seed has been grown during the initial stage of the process. A ~ 7 mm long portion of the melt was solidified by the ampoule lowering. Next, the solidified material was recrystallized by annealing for 72 h. The single crystal seed thus prepared was used for growth of $CuGa_3Se_5$ single crystal. After the melt was solidified completely, the material was annealed for 150 h. In this way, we obtained $CuGa_3Se_5$ single crystals 14 –16 mm in diameter and up to 50 mm in length.

The elemental composition of the crystals was determined by electron probe X – ray microanalysis using a Cameca – MBX microprobe with a relative accuracy of 5% or better. The content of elements in the grown crystals (Cu : Ga : Se = 10.98 : 33.16 : 55.86 at. %) is in

satisfactory agreement with the specified content in the starting charge (Cu : Ga : Se = 11.11 : 33.33 : 55.56 at. %) and there are no pronounced deviations in various parts of the crystal, this testifying to the uniformity of the grown crystal.

The structure and homogeneity of the single crystals were examined by X-ray diffraction (XRD) analysis using DRON-3M diffractometer (Cu K_α.radiation). The XRD patterns, taken from different parts of the single crystal corresponded to the chalcopyrite structure – space group $P\bar{4}2m$ (Fig. 1, Table 1).

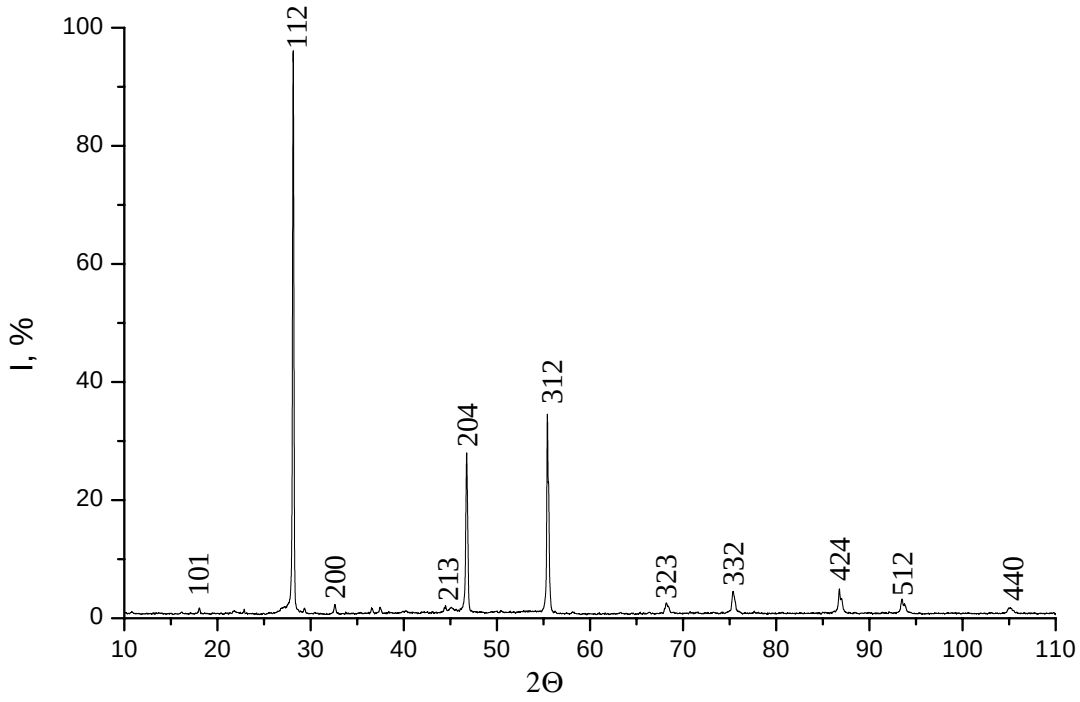

Fig. 1. XRD pattern of $CuGa_3Se_5$ crystal.

Table 1. XRD data for $CuGa_3Se_5$

2θ, град	I/I_0,%	hkl	d,Å		2θ, град	I/I_0,%	hkl	d,Å
18.07	2	101	4.912		58.14	<1	224	1.5853
22.88	1	102.110	3.8827		66.42	<1	323	1.4063
24.27	<1	003.111	3.6640		68.26	3	400	1.3728
28.12	100	112	3.1713		68.46	2	400	1.3727
29.34	2	103	3.0480		75.38	5	332	1.2598
32.62	2	200	2.6649		75.58	<1	332	1.2601
36.59	2	104.202	2.4561		86.79	5	424	1.1211
37.48	2	211	2.3995		87.02	3	424	1.1215
40.17	<1	114	2.2449		93.58	3	512	1.0568
44.45	2	213	2.0398		93.81	2	512	1.0574
46.76	29	204	1.9426		105.02	2	440	0.9707
55.42	35	312	1.6565		105.40	2	440	0.9704
55.56	24	312	1.6566					

The unit cell parameters calculated by the method of least squares from the lines with angles $2\theta > 60^{o}$ are equal to: a = 5.491 ± 0.002 Å and c = 10.993 ± 0.005 Å. The resolution of the high angle lines in the XRD patterns indicates the homogeneity of the grown single crystal.

Phase transition temperatures were determined by differential thermal analysis (DTA) with an accuracy of ~ 2 K. The DTA curves of $CuGa_3Se_5$ are shown in Fig. 2.

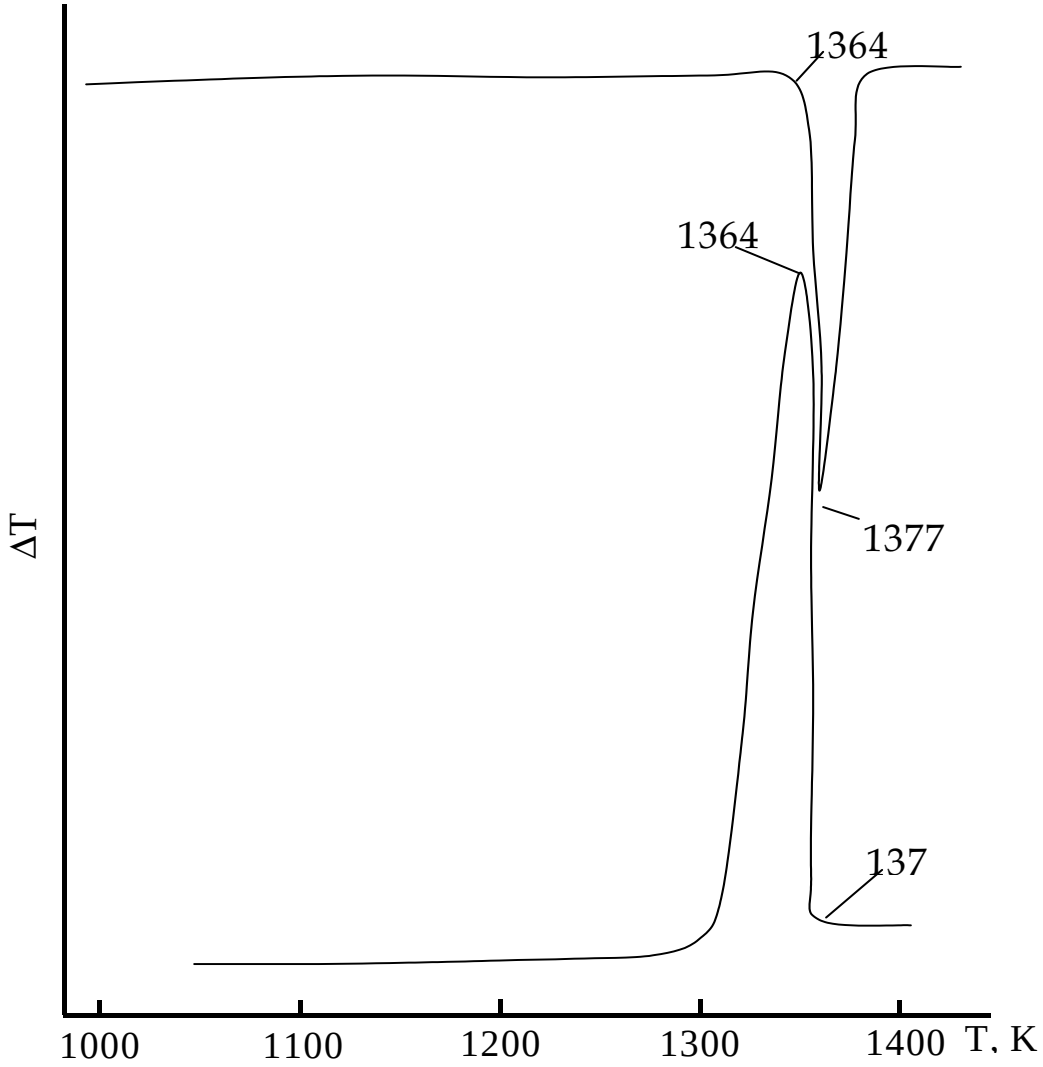

Fig. 2. Thermogram of $CuGa_3Se_5$ crystal.

Both the heating and cooling curves reveal only one peak due to melting, which occurs in the range of 1364 ÷ 1377 K. These results agree well with the data reported by Palatnik and Belova [9] but differ from those reported by Mikkelsen [10]. The likely reason is that the melting point and melting behavior of $CuGa_3Se_5$ compound depend on the preparation conditions and the homogeneity of the samples.

The thermal expansion coefficient (α_L) of $CuGa_3Se_5$ single crystals was measured relative to quartz using a quartz dilatometer. The heating rate was of 3 - 5 K/min, which allowed us to obtain reproducible results. The measurements were carried out for single crystal samp-

les of average dimensions 3 x 3 x 8 mm, oriented parallel ($\alpha_{\parallel}$) and perpendicular ($\alpha_{\perp}$) to the tetragonal axis.

The temperature–dependent thermal expansion data for $CuGa_3Se_5$ are shown in Fig. 3.

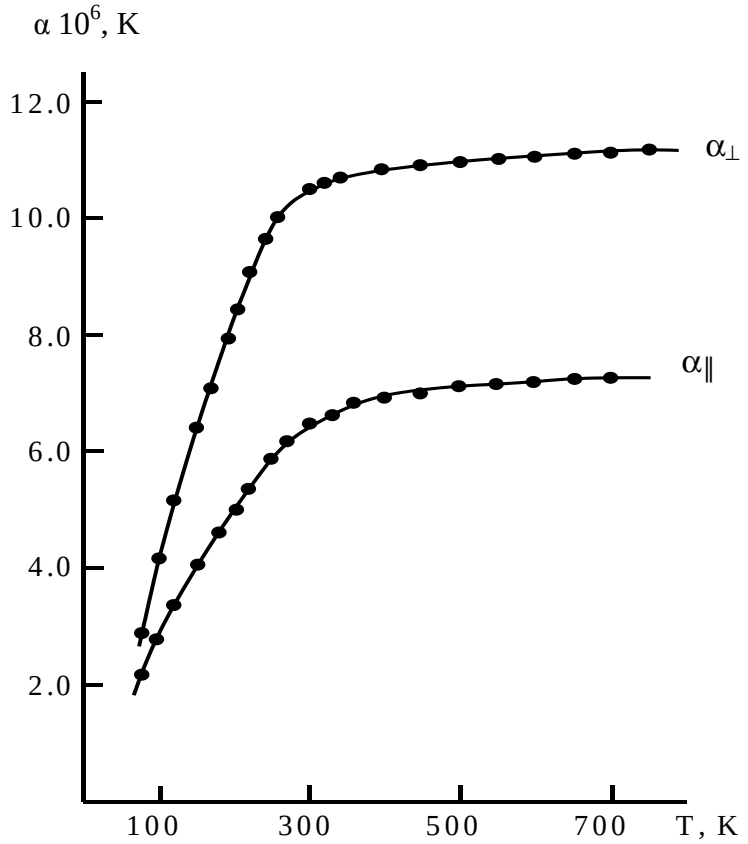

Fig. 3. Thermal expansion of $CuGa_3Se_5$ crystal

The thermal expansion of $CuGa_3Se_5$ crystals is seen to be anisotropic, with no anomalies in the temperature range studied. Both $\alpha_{\parallel}$ and $\alpha_{\perp}$ vary most rapidly in the range of 80-290 K. Above 320 K, the thermal expansion shows only a gradual increase. This behavior is related to changes in the anharmonicity of thermal vibrations in $CuGa_3Se_5$ crystals. The present thermal expansion results differ from the data reported in [11], where thermal expansion of $CuGa_3Se_5$ was determined by XRD. It is well known that XRD results differ from dilatometic ones in physical interpretation [11]: XRD provides data on the thermal expansion of the crystal lattice, while dilatometric measures - the thermal expansion of the bulk material.

The measured thermal expansion coefficients and melting point of $CuGa_3Se_5$ were used to calculate the Debye characteristic temperature (Θ) and mean-root-square dynamic atomic displacements ($\sqrt{U^2}$) by the formulas [12]:

$$\theta^{\alpha} = 14.3/\alpha^{1/2}\bar{A}^{1/2}V^{1/3}, \quad (1)$$

$$\theta^{Tm} = 137\cdot T_m^{1/2}/\bar{A}^{1/2}V^{1/3}, \quad (2)$$

$$\bar{u}^2 = 4.3\cdot 10^{-14}[D(\theta/T)/\theta/T + ¼]/\bar{A}\theta, \quad (3)$$

where $\bar{A}$ is the average atomic mass, V is the average atomic volume, T_m is the melting temperature and $D(\theta/T)$ is the Debye function.

Table 2. Thermal expansion coefficient ($\alpha_\perp$ and $\alpha_\parallel$), Debye temperature (Θ), and mean-root-square dynamic atomic displacements ($\sqrt{U^2}$) of $CuGa_3Se_5$

T. K	$\alpha_\perp \cdot 10^6$, K^{-1}	θ, K	$\sqrt{U^2}$, Å		T, K	$\alpha_\parallel \cdot 10^6$, K^{-1}	θ, K	$\sqrt{U^2}$, Å
80	2.9	420	0.065		85	2.0	506	0.056
100	4.2	349	0.079		100	2.8	428	0.068
120	5.2	314	0.091		120	3.4	388	0.077
150	6.5	281	0.110		150	4.1	354	0.089
170	7.1	269	0.121		180	4.6	334	0.101
190	8.0	253	0.134		200	5.0	320	0.110
200	8.4	247	0.141		220	5.4	308	0.119
220	9.1	237	0.154		250	5.9	295	0.133
240	9.7	230	0.165		270	6.2	288	0.140
260	10.0	226	0.175		300	6.5	281	0.151
280	10.3	223	0.185		330	6.6	279	0.160
300	10.5	221	0.192		360	6.8	275	0.170
320	10.6	220	0.198		400	6.9	273	0.179
400	10.8	218	0.222		450	7.0	271	0.190
450	10.9	217	0.237		500	7.05	270	0.200
500	10.95	216	0.250		550	7.1	269	0.211
550	11.0	216	0.253		600	7.2	267	0.233
650	11.1	215	0.286					

It follows from the calculation results (Table 2) that, at increase of temperature the Debye temperature of CuGa3Se5 crystals decreases and the mean-root-square dynamic atomic displacements increase, indicating that the chemical bonds in $CuGa_3Se_5$ become weaker.

Acknowledgement

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