Study of the structure, electrical properties and magnetic susceptibility of $Cu_3Fe_{0.5}Se_2$ crystals

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The $Cu_3Fe_{0.5}Se_2$ crystals are grown by substitution a part of Cu with Fe atoms, structure and cell parameters of this crystal are specified as: Orthorhombic with a=8169; b=8238; c=12052 Å; and V=811.15 $Å^3$, D_x=6,23 g/cm^3, Sp.Gr.Pnma, Z=8. The magnetic succeptibility of this crystal is measred in the temperature range of $100°K<T<400°K$, and H=2 Tesla. It is found that below T=350 °K system changes to antiferromagnetic state. Parameters of α, σ and k are obtained in the temperature range of $80°K<T<400°K$, and is calculated n = $5×10^{19} cm^{-3}$.

1. Introduction

Formation of four types of crystals has been detected by the crystalline I_2-like transporter when Selenium monocrystals analogue chalcopyrite have been grown from the gas phase [1, 2]

1- $CuFeSe_2$ with the structure of chalcopyrite ($I\bar{4}2d$)
2- $CuFeSe_2$ with the structure of the defective
   chalcopyrite-type ($P\bar{4}2c$)
3- Iodide of $Cu_{2-x}I_2$ structure type and Sphalerite
4- Fine lamellar single crystals with Orthorhombic
   structure of unknown composition.

Chemical analysis of these crystals by EDXS, showed that the composition consist of 54.5 ± 3% atomic percent Cu; 10.02 ± 08% Fe and 35.5 ± 4.2% Se. These values correspond to the chemical composition stoichiometry $Cu_3Fe_{0.5}Se_2$. This article is devoted to the study of radiographic, magnetic susceptibility and thermal parameters of the $Cu_3Fe_{0.5}Se_2$ crystals.

2. Experimental

2.1. Synthesis and growth of $Cu_3Fe_{0.5}Se_2$ single crystals

$Cu_3Fe_{0.5}Se_2$ crystals are synthesized by using of stoichiometric ratio of high purity (%99.998) of Cu, Fe and Se blocks as starting materials. Copper and Iron are pre-cleared of oxide film by passing hydrogen through them at 820-880°K temperature range. First the starting materials are placed in a glass crucible with Su-2500 brands and then in the quartz tube. Implementation of the syntheses in a glass crucible prevent the interaction of the metals with quartz tube. Also for prevent of materials oxidation and contamination of resulted crystals a

preliminary evacuuatin is done, ampoule filled with argon, and after again evacuation to 10^{-4} mm.rt.st. finally is seald.

Fore Synthesis of $Cu_3Fe_{0.5}Se_2$, the ampoule is heated in an inclined furnace at a temperature of 1250-1275 °K within 2-2.5 hours. Then the melt is cooled down to 770°K and kept at that temperature for 10 days. Single crystals were grown by the method described [1].

3. Results

3.1. X-ray studies

The powder XRD analysis of grown crystals is carried out by Cuk_α radiation. This is necessary to compare XRD data of investigated $Cu_3Fe_{0.5}Se_2$ (shown in the table 1) with analogical data of Cu-Se compounds [3]. We know that according to the phase diagram of the Cu-Se system, the composition of Cu_3Se_2 is formed along with other phases [4]. Therefore, at first, our sample data is compared with XRD data of Cu_3Se_2 with Umangite structure in sulfides structures group. There are many tetrahedral and octahedral vacancy defects and also additional Fe atoms are free to locate there without upsetting the symmetry of the lattice. However the comparison of the lattice parameters of $Cu_3Fe_{0.5}Se_2$ with Cu_3Se_2 composition did not give positive results. Therefore, the obtained data are compared with Cu_7S_4-anilite[6]. The results showed full agreement between these two structures. Therefore the lattice structure is orthorhombic and the calculated values of lattice parameters are as follow: a=8169; b=8238; c=12052 Å; and V=811.15 $Å_3$, D_x = 6,23 g/cm^3, space group Pnma, Z = 8.

Thus formed compound is a isomorphic structure with Cu_7S_4 and some differences in lattice parameters associated with the replacement of S(1.82Å) atoms with Se (1.93 Å) atoms.

Table 1. X-ray data of $Cu_3Fe_{0.5}Se_2$ crystal.

№	2θ	d_{exp}	I/I_0	hkl	d_{calc}
1	13.018	6.7952	53.0	011	6.7999
2	25.362	3.5090	13.7	211	3.5014
3	26.169	3.4025	34.9	022	3.4000
4	26.492	3.3618	50.8	202	3.3805
5	32.884	2.7215	100.0	213	2.7230
6	38.730	2.3231	5.9	214	2.3253
7	39.716	2.2676	16.7	033	2.2666
8	40.143	2.2445	11.1	231	2.2392
9	42.972	2.1031	4.9	224	2.0890
10	43.943	2.0588	84.1	040	2.0595
11	44.320	2.0422	83.6	400	2.0423
12	49.866	1.8273	48.2	043	1.8325
13	51.716	1.7662	18.3	135	1.7681
14	59.452	1.5535	10.9	217	1.5573
15	60.998	1.5178	12.0	520	1.5187
16	68.856	1.3625	9.8	600	1.3615
17	70.275	1.3384	7.2	062	1.3384
18	80.908	1.1872	4.1	624	1.1879
19	82.486	1.1684	6.4	633	1.1671
20	89.654	1.0927	6.2	266	1.0921
21	91.018	1.0798	7.0	546	1.0793
22	93.721	1.0556	2.8	732	1.0574
23	96.811	1.0300	1.9	080	1.0298
24	98.729	1.0151	1.6	082	1.0150

Fig. 1. Temperature dependence of magnetic susceptibility of $Cu_3Fe_{0.5}Se_2$ single crystals, when H=2Tesla.

3.3. Electrophysical properties

The polycrystalline samples are used for measuring of the electrophysical properties at the temperature range of $80°K<T<400°K$. Electrical conductivity, termo.e.d.s, and thermal conductivity of the $Cu_3Fe_{0.5}Se_2$ crystal are studied.

Fig. 2. Temperature dependence of electrical conductivity, heat conductivity and termo.e.d.s of $Cu_3Fe_{0.5}Se_2$.

3.2. Magnetic susceptibility

Magnetic susceptibility of obtained $Cu_3Fe_{0.5}Se_2$ monocrystals by sublimation at prolonged annealing at $T=700$ °K was measured by using of SQUIDS magnetometer in a magnetic field H=2Tesla in the temperature range of 80 °K<T<400 °K. In Fig. 1 is presented temperature dependence of magnetic susceptibility of $Cu_3Fe_{0.5}Se_2$. This figure is compared with the corresponding graph for the quasi-one-dimensional antiferromagnetic systems [7]. The temperature dependence of the susceptibility at T=350 °K shows that in the paramagnetic state occurs a paramagnetic type→antiferromagnetic phase transformation, unlike in the ferromagnetic state is observed an antiparallel arrangement of spins.

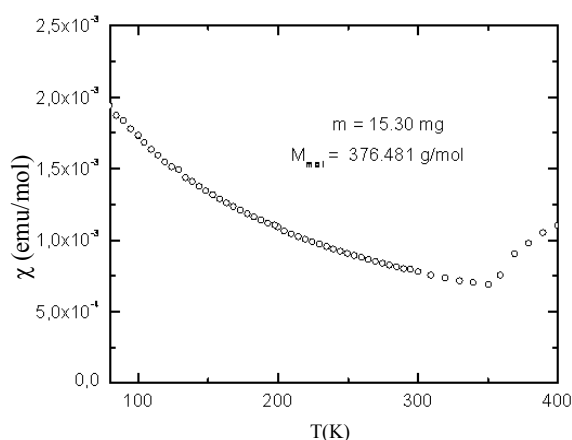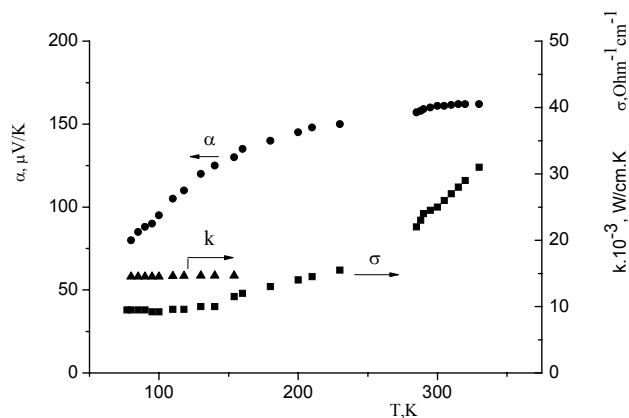The obtained experimental results are presented in Fig. 2. It is based on the temperature dependence of σ, defined by the Hall effect and termo.e.d.s, and the nature of the conductivity corresponds to the electronic type (structure). The concentration of charge carriers, is calculated according to the Hall coefficient, $n = 5\times10^{19}cm^{-3}$.

As shown in Fig. 2, the conductivity improves with increasing temperature. Such a temperature dependence of the electrical conductivity can be explained by assuming that the band gap of $Cu_3Fe_{0.5}Se_2$ has donor levels near the bottom of the conduction band. By increasing temperature, the electrons are generated from these energy levels and added in the valence band and participate in conduction

process. In this case, respectively, the temperature dependence of the coefficient termo.e.d.s slows.

Also Fig. 2 shows the temperature dependence of thermal conductivity k. As it presents, $k_{(T)}$ change slightly in the investigated temperature range. Thermal conductivity of electron that has been determined by Wiedemann-Franz law, is very low in comparison with the overall thermal conductivity. This gave us an opportunity to assess the overall thermal conductivity of the lattice.

4. Conclusion

The $Cu_3Fe_{0.5}Se_2$ crystal is grown and its structure specified as Orthorhombic, a=8169; b=8238; c=12052 Å. This crystal consist of a paramagnit type → anti-ferromagnetic phase transformation at 350 °K. Electrical conductivity increases with increasing temperature. Thermal conductivity is almost constant.

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