GROWTH OF TERNARY SEMICONDUCTOR CHALCOGENIDE SINGLE CRYSTALS

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Abstract. In this report the results of experimental investigations on single crystal growth of chalcogenide compounds with spinel \( A^{III}B^{II}C^{VI}; A=\text{Cu},\text{Cd}; B=\text{In},\text{Cr}; C=\text{S},\text{Se} \) and chalcopirite \( A^{II}B^{III}C^{V}; A=\text{Cu}; B=\text{In},\text{Ga},\text{Al}; C=\text{S},\text{Se} \) structure are presented. The polycrystalline starting material was synthesized by the solid state reaction between pure elements in halogen atmosphere. This technique allows to perform the synthesis and crystal growth process in one technological cycle in the same reaction container. Growth at temperatures sufficiently lower than melting or decomposition temperatures was performed by chemical transport reactions and flux method. Single crystals with various habits (bulk, dendrites, whiskers, platelets) and dimensions up to 10 mm were obtained. In order to determine the composition of crystals, X-ray diffraction analysis was performed for some of them.

Key words: chalcogenide, chemical transport reactions, flux method.

1. INTRODUCTION

Ternary semiconductor chalcogenides exhibit a large variety of electrical, photoelectric and photoluminescence properties. The values of the energy gaps of these compounds and their solid solutions lie in the 1.2-4.5 eV interval. The electrical properties of these materials could be easily changed by different doping or thermal treatment. Some chalcogenide compounds possess at the same time semiconductor and magnetic properties with strong interactions of the charged carriers and localized magnetic moments. This is why these materials are prospective for solar cell applications, as laser materials, for integrated circuits, for memory systems and other electronic elements.

In this report the results of experimental investigations on single crystal growth of chalcogenide compounds with spinel \( A^{III}B^{II}C^{VI}; A=\text{Cu},\text{Cd}; B=\text{In},\text{Cr}; C=\text{S},\text{Se} \) and chalcopirite \( A^{II}B^{III}C^{V}; A=\text{Cu}; B=\text{In},\text{Ga},\text{Al}; C=\text{S},\text{Se} \) structure are presented. The ternary semiconductor compounds under consideration have high melting points and they melt incongruently or are peritectically formed. Therefore, we used the chemical transport reactions and flux method for growing single crystals at temperatures sufficiently lower than the melting or decomposition temperatures.
2. EXPERIMENTAL

For a successful realization of crystal growth it was necessary to use polycrystalline compounds as starting materials. We used a synthesis technique that is based on the reaction of the pure elements in halogen atmosphere. This method allows to obtain single phase materials by solid state reaction at relatively low temperature: no more than 650 °C for $A^2B^{III}V_4$ and than 800 °C for $A^2B^{III}V_2$. An additional facility of this method results in the possibility to perform the synthesis and crystal growth process in one technological cycle in the same reaction container.

Single crystal growth by the chemical transport reaction method was performed in evacuated quartz ampoules using iodine as transport agent. The ampoules were placed in a furnace in which a temperature gradient (about 3°C/cm) had been installed. In the hot zone (source zone) the polycrystalline material reacts with iodine to form vapor phase reaction products, which are transported by diffusion in the cold zone where they undergo the reverse reaction resulting in reconstruction of solid stoichiometric material but in a monocrystalline form. This situation is presented in Fig. 1. The influence of the different technological parameters on the growth process was investigated. They include the temperature profile along the furnace, the dimensions of the ampoules, the temperature of the source and growth ends of the ampoules and the temperature difference between them. The temperature of the growth end was established in the interval 670-720°C for CdIn$_2$S$_4$, 630-680 °C for $A^2B^{III}V_4$ (A=Cu, Cd; C=S, Se) and 750-800 °C for $A^2B^{III}V_2$, the temperature of the source end being 50-80 °C higher. In order to decrease the number of crystallization centres a pendulum-like regime of the temperature change is recommended.

![Fig. 1 – Typical temperature profile along the furnace for chemical transport reactions crystal growth.](image-url)
For CuCr$_2$Se$_4$ impurified with bromine (CuCr$_2$Se$_{4-x}$Br$_x$) we performed the investigation of obtaining single crystals by the flux method. These crystals have a spinel-type lattice with Se$^{2-}$ anions forming a cubic face centred array, the Cu$^{2+}$ and Cr$^{3+}$ cations residing in the tetrahedral and the octahedral interstices, respectively [3]. CuCr$_2$Se$_4$ is a metallic conductor with magnetic properties, the Curie temperature being the highest from all spinel magnetic chalcogenides [4]. An important feature of this compound is the ability to form complete series of solid solutions in the system CuCr$_2$Se$_{4-x}$Br$_x$ with x between 0 and 1. The substitution of Br$^-$ for Se$^{2-}$ results in a linear change of the lattice parameter, an increase in magnetization and a change from a metallic to semiconducting behaviour (metal-semiconductor transition occurring between x=0.5 and x=0.6) [5]. For that reason these materials are prospective for electronic elements with changeable characteristics depending on the magnetic fields.

For CuCr$_2$Se$_{4-x}$Br$_x$ growth polycrystalline Cu, Cr and Se were used in stoichiometric proportion and for solvent CuBr was chosen. Growing of single crystals was achieved in a vertical furnace in which a quartz ampoule charged with the above-mentioned flux and evacuated at 10$^{-4}$ torr was introduced. The maximum heating temperature was 900°C and for complete dissolution it was necessary to keep this temperature during 40 hours. After this the temperature of the container was lowered at a velocity of 1 °C/hour till the solidification of the flux. The duration of the growth experiment was about 500 hours.

3. RESULTS

By using the above-mentioned techniques we succeeded in obtaining single crystals up to 10 mm. Some of them are presented in Figs. 2 and 3.

![CuGaSe$_2$ single crystals](image)

Fig. 2 – CuGaSe$_2$ single crystals; a) bulk, b) dendrite, c) whiskers.
In order to establish the composition of as-grown crystals X-ray diffraction analysis was performed. For example, in Fig. 4 a and b are presented X-ray patterns for two samples in the CuCr$_2$Se$_{4-x}$Br$_x$ system.

There is a relatively good agreement with the literature [6]. The diffraction line (200) from 31.44° (Fig 4a) belongs, probably, to the $\gamma$-CuBr phase, which is in fact the solution used to grow CuCr$_2$Se$_{4-x}$Br$_x$ monocrystals. Also, there were two lines on the spectrum from Fig. 4a belonging to the CuCr$_2$O$_4$ phase, which is formed by replacing oxygen (proceeding from the air) by selenium. These lines appeared also on the b. spectrum, but with greater intensities, this indicating a greater proportion of CuCr$_2$O$_4$ in the b. samples than in a. In the spectrum from Fig 4b the X-ray lines were more numerous in small angle regions, showing formation of compounds with simple structure. Knowing from the literature data [6] the composition dependence of the lattice parameter for this system (Fig. 5),
we can determine the deviation $x$ from the CuCr$_2$Se$_4$ stoichiometry. In this way we determined the values $a = 10.382$ Å and $a = 10.415$ Å for $a$ and $b$ samples, this leading to $x = 0.6$ and $x = 0.9$, respectively. The latter sample contains more bromine than the former and this accounts for the fact that bromine substitutes selenium in the crystal lattice easier in vapor environment than in solution. Considering the electrical properties, because $x$ is greater than 0.6 for both samples (metal-semiconductor transition occurring between $x = 0.5$ and $x = 0.6$), we may admit that samples exhibit semiconductor behaviour.
4. CONCLUSIONS

Experimental investigations were performed on single crystal growth of semiconductor chalcogenide compounds by the chemical transport reactions and flux method. The polycrystalline starting material was synthesized by solid state reaction between pure elements in halogen atmosphere. Single crystals with various habits (bulk, dendrites, whiskers, platelets) and dimensions up to 10 mm were obtained. In order to determine the composition of crystals X-ray diffraction analysis was performed for some of them. The technological parameters (pressure, temperature, growth environment) strongly influenced crystal composition; starting from the same material, using different growth conditions, we found different crystal compositions.

REFERENCES