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On the Preparation of Some Group I—VI Semiconducting Compounds

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A new method for the preparation of cuprous and silver sulphide, selenide and telluride is described. The method provides a stage of purification of the nonmetallic component, which is in most cases a carrier of uncontrolled impurities. The variation of composition by preferential evaporation in vaccum is described and two methods for measurement of stoichiometry are given: measurement by weighing and measurement by electrical conductivity, if the relation composition *vs.* conductivity is known. Single crystals can be easily obtained only in the case of cuprous sulphide and selenide.

INTRODUCTION

In this paper the symbol $(Cu, Ag)_{2\pm x}(S, Se, Te)$ is used to denote a group of non-stoichiometric sulphides, selenides and tellurides of monovalent copper and silver. Owing to their characteristic similarity in many physical properties, these compounds are called the silver sulphide group semiconductors[1], after the best known member of the group. They are also called the ion mobile semiconductors[2] because of their mixed ionic and electronic conductivity.

In the past three years extensive investigations of these substances have been carried out in our laboratory[3-7]. One of the most important problems is the preparation of samples with the highest possible purity, desired composition and crystal state. Generally, two facts should be taken into account in order to solve this problem. All $(Cu, Ag)_{2\pm x}(S, Se, Te)$ compounds have variable stoichiometry and a phase transition at a temperature between 100^0 C and 200^0 C. These facts require that three main problems be considered separately:

(*i*) the synthesis of a compound,
(*ii*) the variation and control of its composition,
(*iii*) the preparation of single crystals.

(*i*) In the majority of published papers about $(Cu, Ag)_{2\pm x}(S, Se, Te)$ compounds a direct synthesis of their components was used, as the most successful method of preparation[8-18]. But a few indirect chemical methods were also published[19-22].

(*ii*) The compounds under consideration belong to the so-called Bertholide compounds. Their composition may be varied within some definite interval depending on the compound itself and on temperature. We have denoted this property by the variable x in the subscript of the general formula. The range of homogeneity may be very wide, as in the case of $Cu_{2-x}Se$ $(0.14 \geqq x \geqq$

$\geqq 0.0025$ at 400^0 C[23]), or close to the stoichiometric composition, as in the case of $Ag_{2+x}Se$ ($0.002 \geqq x \geqq 0$ at 200^0 C[24]). From all investigations of electrical properties completed so far, it seems that $(Cu, Ag)_{2\pm x}(S, Se, Te)$ compounds cannot be prepared with exact stoichiometric composition[9–18].

Two techniques for the variation and control of the composition are known: the extraction of metallic component from a nearly stoichiometric compound by diffusion of Cu or Ag atoms into S, Se or Te bars placed in contact with the sample[25,26], and the extraction or addition of metallic component using proper solid galvanic cells[2,23,24,27–29].

(*iii*) It is well known that substances with phase transformations at a temperature between the melting point and room temperature cannot be easily prepared as single crystals[30]. A deviation from this general rule is observed only on cuprous sulphide and selenide. Owing to special circumstances during phase transformation[3,5,7], these compounds can be prepared in the single crystal form[6,8,15,16]. It has been found that in this case the zone melting technique is the most successful method.

The intention of the present paper is to give some new facts which appeared during investigations of the semiconducting properties of the compounds under consideration. The authors prefer to describe their experience acquired in the preparation of $Cu_{2-x}Se$ and $Ag_{2+x}Se$, but they believe that these results can be applied to other $(Cu, Ag)_{2\pm x}(S, Se, Te)$ compounds.

EXPERIMENTAL

It has been found in our experiments that the impurities introduced into the compounds during synthesis have their origin mainly in impure selenium. In spite of its declared high purity, this material contains a white-gray powder which, being unvolatile, remains if selenium evaporates. The content of this impurity is higher if selenium is used in the form of powder. In some cases encountered in practice the impurity content was as high as 1.5 w%. There is no evidence that impurities of this sort affect the concentration of charge carriers *i. e.* the conductivity of cuprous and silver selenides, but they certainly affect the homogeneity of samples.

In order to avoid these difficulties, we introduced a stage of purification of selenium before synthesis. A piece of selenium was placed in a silica tube and covered with silica wool. The tube was then thinned at one end, precisely weighed (to ± 0.1 mg) and placed in another silica tube with weighed copper or silver scrapings (Fig. 1). Before heating to the reaction temperature the tubes were evacuated to 10^{-5} mm Hg and sealed. During the synthesis, which is rapid at 400—500 °C, selenium evaporated from the inner tube and gradually reacted with copper or

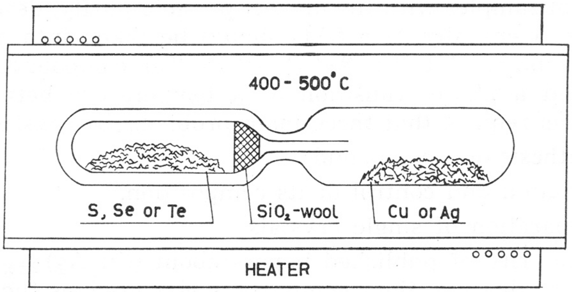

Fig. 1. Double silica tube for the synthesis of $(Cu, Ag)_{2\pm x}(S. Se, Te)$ compounds.

silver in the outer tube. All non-volatile impurities remained at the place of selenium. The reaction of 30 g of material lasted about 3 hours at 500 °C. After completion of the reaction the system was cooled down to room temperature and the tubes opened at the left end. The inner ampulla was carefully taken out and weighed. The Cu/Se or Ag/Se ratio was then calculated from the mass of copper or silver and the difference between the masses of the ampulla before and after synthesis.

The compound thus prepared did not have a homogeneous composition and appeared as a great number of small, almost separated crystals. Since such a form is not suitable for electrical measurements, the compound required additional treatment. The outer tube was therefore evacuated again and sealed in the middle, where it had been previously thinned. The sealed ampulla was then heated above the melting point of the compound and after 3—5 hours slowly cooled to room temperature. The compounds prepared in this way were used as the starting material for other stages of the experiment.

Further experience acquired during examinations of copper and silver selenides leads to the conclusion that the composition of the starting material can be easily changed by heating in vacuum. If a compound is saturated with selenium, its dissociation pressure will be relatively high. The gas phase at about 500 °C is almost pure selenium, so that the heating of a compound *in vacuo* causes selenium loss and shifts the composition to the metal-rich side or to the stoichiometric composition, depending on the sort of the compound. Moreover, if only selenium evaporates from a compound, its composition can be easily determined by weighing.

Let us describe an experiment on $Cu_{2-x}Se$, where the assumption that only selenium evaporates seems to be satisfied[7]. In this experiment an electrical property, say electrical conductivity σ *vs.* composition, was measured. A sample of a given shape, chosen for these measurements, was prepared from the starting material with a known index x_1 (starting material was always saturated with selenium, *i. e.* $x_1 \approx 0.15$). After the measurements of $\sigma\ (x_1)$ were completed, the sample was cleaned in benzene and weighed, and the mass m_1 was obtained. In order to change the composition x_1 to another, say $x_2 (x_2 < x_1)$, the sample was placed at the bottom of a long, highly evacuated hardglass tube and heated at 450 °C. During heating a quantity of selenium was evaporated, decreasing the mass of the sample to the lower value m_2 which was obtained by careful weighing after heating. If only selenium evaporates, a new value of index x_2 is given by the formula

$$x_2 = 2 - \left[\frac{m_2}{m_1}\left(\frac{1}{2-x_1} + \frac{M_{Cu}}{M_{Se}}\right) - \frac{M_{Cu}}{M_{Se}}\right]^{-1} \tag{1}$$

where M_{Cu} and M_{Se} are the atomic masses of copper and selenium, respectively. After each process of selenium evaporation, giving samples with new indexes x_3, $x_4 \ldots\ldots x_n$, the measurements of electrical conductivity were carried out, giving the values $\sigma\ (x_3)$, $\sigma\ (x_4), \ldots\ldots \sigma\ (x_n)$. Both processes were repeated several times in order to cover the whole homogeneity range of $Cu_{2-x}Se$. The general formula for the index x_n has the form

$$x_n = 2 - \left[\frac{m_n}{m_{n-1}}\left(\frac{1}{2-x_{n-1}} + 0.805\right) - 0.805\right]^{-1} \tag{2}$$

It should be emphasized that for $Cu_{2-x}Se$ with x near to zero this formula is not quite reliable because the assumption that only selenium evaporates is not quite valid. Besides selenium, cuprous selenide also starts to evaporate, but the evaporation of selenium is predominant. The stoichiometric compound Cu_2Se cannot be obtained by heating in vacuum. Our metallographic examinations showed that before the stoichiometric composition was reached, some quantity of copper in the form of small grains had been precipitated and distributed throughout the whole sample.

There is another possible way to control the composition of $(Cu, Ag)_{2\pm x}$ (S, Se, Te) compounds. It was found that there is a definite, although not sufficiently examined relation between stoichiometric deviations and electrical properties of these compounds. In the high temperature or cubic phases of cuprous and silver sulphides, selenides and tellurides the situation is much simpler than in the low temperature phases. For example, there is a very simple relation between the concentration of charge carriers in cubic phases and their stoichiometric deviations. In the case of cubic $Cu_{2-x}Se$, the electrical neutrality law leads to the conclusion that each excess selenium atom yields two holes in the valence band of the crystal. Since the experiments show that there is no additional effect on the net number of holes, their concentration may be considered equal to the concentration of missing copper atoms. Identical property was found in cubic cuprous sulphide[32]. Thus, every electrical property depending only on the concentration of holes can be used as a measure of stoichiometric deviations.

We measured the electrical conductivity of $Cu_{2-x}Se$ samples with varying x, prepared by the technique described above. All these measurements were performed at 150 °C, where $Cu_{2-x}Se$ is in the high temperature or cubic form. The results are shown in Fig. 2. The straight line shows that the hypothesis about the equality of concentrations of missing copper atoms and holes is justified. Because of the very high concentration of holes (10^{19}—10^{20} cm^{-3}), cuprous selenide in its high temperature phase is a degenerate semiconductor.

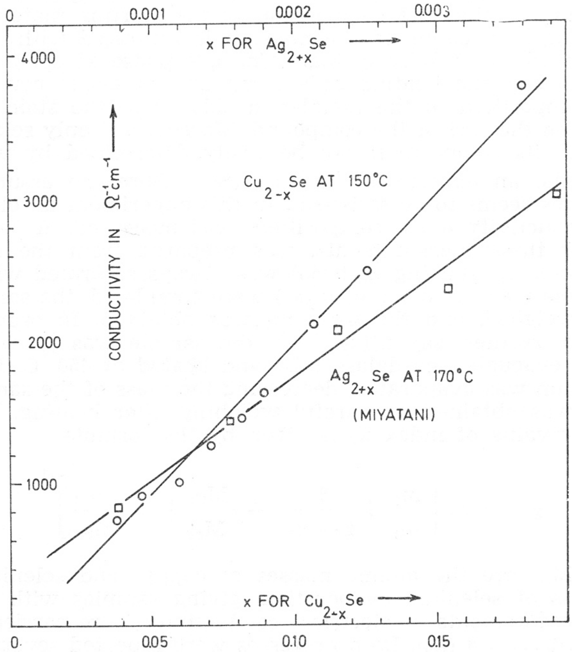

Fig. 2. Plot of electrical conductivity *vs.* composition for cuprous and silver selenides.

Let us briefly consider the case of $Ag_{2+x}Se$. Miyatani[2] has shown that in the cubic phase of this compound each excess silver atom contributes an electron to the conduction band. Thus, there is also a simple relation between stoichiometric irregularities and the concentration of electrons or conductivity. According to Miyatani's results one can plot a similar curve as in the case of $Cu_{2-x}Se$, as shown in Fig. 2. Consequently, electrical conductivity measured at constant temperature can be used as a measure for stoichiometric deviations, especially if there are simple relations between composition and conductivity. In the low temperature phases of $(Cu, Ag)_{2\pm x}$ (S, Se, Te) compounds these relations are not so simple[28,31] and cannot be used easily for the aims treated in the present paper.

In order to prepare single crystals of $Cu_{2-x}Se$ and $Ag_{2+x}Se$, we attempted to apply the simplest form of the Bridgman method. Some quantity of material of desired composition was placed in a silica tube with one cone-shaped end. The tube was then evacuated and sealed reducing the empty space as much as possible. The ampulla thus made was placed in a vertical furnace which had a nearly linear temperature gradient along its length. In the high temperature region of the furnace the material was heated at 10—20 °C above the melting point, and then slowly moved towards the lower temperature region. The speed of the motion was about 1 cm/hour. When the whole material was solidified the sample was cooled to room temperature for about 12 hours.

Such a treatment always gave polycrystalline samples in the case of $Ag_{2+x}Se$. This is in accordance with the findings of Dalven and Gill[12] and with the general principles mentioned in the Introduction. However, single crystals of $Cu_{2-x}Se$ were obtained in almost every experiment. Because of a wide homogeneity range and a wide temperature interval of the phase transition, the rearranging of atoms, giving a new phase, takes place continually and causes formation of single crystals.

The crystalline perfection of the samples was examined by X-ray diffraction[6].

CONCLUSIONS

Some semiconducting $(Cu, Ag)_{2\pm x}$ (S, Se, Te) compounds of various composition were prepared. It was found that the best and simplest method of preparation is the direct synthesis in which a stage of purification of the nonmetallic component is provided, if necessary. In order to attain the conditions for the easiest and most successful method for varying the sample composition, it is desirable that the starting material be saturated with the nonmetallic component.

The evaporation of the nonmetallic component by heating *in vacuo* shifts the composition of the sample to the metal-rich side. If the assumption that only the nonmetallic component evaporates is satisfied, the composition can be found by weighing. It can be also determined by measuring some electrical property at constant temperature, if the relation between the composition and this property is known.

Using the simplest variation of the Bridgman method the single crystals of $Cu_{2-x}Se$ with various composition were obtained.

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IZVOD

Dobivanje nekih poluvodičkih spojeva iz grupe I—VI

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Opisana je nova metoda dobivanja bakar i srebro sulfida, selenida i telurida koja maksimalno vodi računa o sprečavanju onečišćenja. Metoda koristi direktnu sintezu poboljšanu stupnjem predčišćenja nemetalne komponente koja se pokazala kao glavni nosilac neželjenih primjesa. Kako ovi spojevi mogu postojati u užim ili širim područjima homogenosti, istražena je i opisana metoda kontinuiranog mijenjanja njihova sastava, i kontrola stehiometrije pomoću vaganja i mjerenja električne vodljivosti. Opisana je i metoda dobivanja monokristala, primjenljiva na spojeve Cu_xS i Cu_xSe.

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