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ELECTRIC AND PHOTOELECTRIC PROPERTIES OF SINGLE CRYSTALS OF SELENIDE AND SULFIDE OF ANTIMONY

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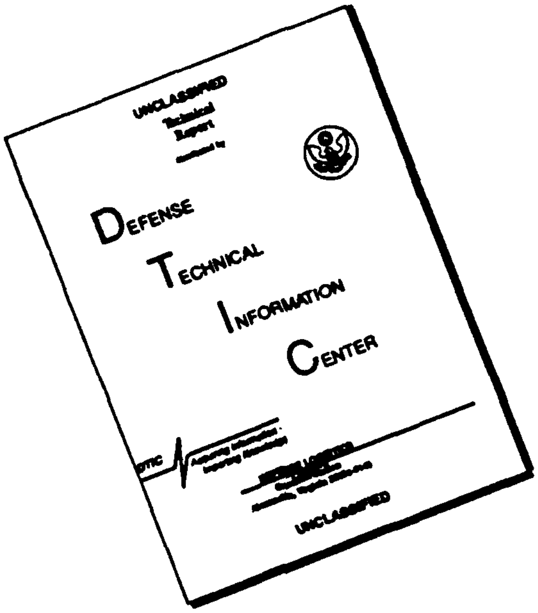

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ELECTRIC AND PHOTOELECTRIC PROPERTIES OF SINGLE CRYSTALS OF SELENIDE AND SULFIDE OF ANTIMONY. I. METHOD OF GROWING SINGLE CRYSTALS OF Sb_2Se_3 AND Sb_2S_3

[Following is the translation of an article by A. F. Skubenko entitled "Elektrychni i fotoelektrychni vlastyvosti monokrystaliv selenidu i sul'fidu surmy. I. Metodyka vyroshchuvannya monokrystaliv Sb_2Se_3 i Sb_2S_3" (English version above), in Ukrayins'kyy Fizychnyy Zhurnal (Ukrainian Journal of Physics), Vol V, No 6, Kiev, Nov-Dec 1960.]

The study of new semiconducting substances presents an important problem both to science as well as engineering. The manufacture of semiconducting equipment is closely associated with a knowledge of the physical properties of semiconducting materials. The limited use of these materials is explained not so much by their scarcity in nature, as by the fact that they have been insufficiently studied.

The group of compounds of antimony with selenium, sulfur and tellurium is one of the groups of semiconducting substances which has been investigated very little. There are several known works on the investigation of the volumetric properties of these compounds, but the study of Sb_2Se_3 and Sb_2S_3 was made on natural crystals (stibnite) or on polycrystalline specimens.

A far greater number of works are dedicated to the investigation of thin films, which is connected with their practical application. There is a complete lack of works on three-component systems of the mSb_2S_3 - nSb_2Se_3 type. Earlier investigations showed that these compounds have good photoelectric properties. They are photosensitive in a wide band of the visible part of the spectrum and in the close infrared. The study of these objects can be of scientific and practical interest.

Important problems of modern metallurgy of semiconductors are: processes of purification of materials, technology of obtaining new substances, and growing of single crystals. One of the first among our articles is dedicated to these problems. In subsequent works we will consider the electric and photoelectric properties of single crystal compounds of Sb_2Se_3 and Sb_2S_3 and of the triple systems of the $nSb_2Se_3 \cdot mSb_2S_3$ type.

1. Introduction

Within the last decade, the zonal or fraction melting /1 - 5/ has been widely used in the technology of preparation of pure elements and compounds commonly used. Zonal melting graduated from the experimental laboratory to become an engineering method of deriving ultrapure materials (1 atom of admixtures per 10^{10} atoms of the substance). In addition, zonal melting is used for growing large uniform single crystals, for homogenization of admixtures in the reverse-progressive motion of the zone, for alloying ingots with a given admixture and concentration, and for reliable p-n conversions. The process of zonal melting is also used as an analytical method of separation of traces of admixtures by means of concentrating them at the ends of the specimen.

Most important is the process of purification of the material from admixtures. It takes place on the boundary of crystallization. Admixtures which lower the melting temperature of the basic substance and which have a coefficient of distribution lower than one, are pushed into the melt and displace in the direction of the motion of the zone. Admixtures which increase the melting temperature of the substance and have a coefficient of distribution greater than one, are pushed in the opposite direction relativ to the motion of the zone.

We used zonal melting to obtain pure single crystals Sb_2Se_3 and Sb_2S_3, as well as uniform triple systems $nSb_2Se_3 - mSb_2S_3$.

2. Description of Equipment

A diagram of the equipment is shown in Fig. 1 a. Four ampoules can simultaneously be processed on this equipment. Oven 3 was made of fireclay (or semifireclay) brick and the method of assembly was as shown in Fig. 1 b.

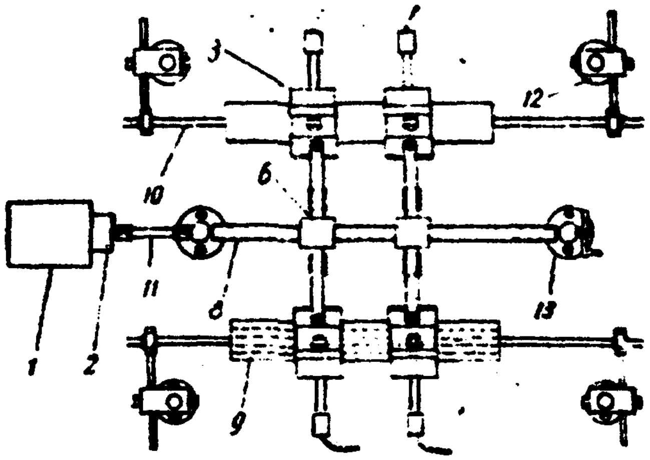

Fig. 1 a.

Diagram of equipment for zonal melting.
1 -- electric motor, 2 -- reducer, 3 -- fireclay brick oven, 6 -- coupling, 8 -- carrying screw, 9 -- additional oven, 10 -- ampoule holders of two tungsten or nickel wires, 11 -- Hooke's joint, 12 -- support for holding the ampoules, 13 -- stand for attaching the screw (height 32 cm).

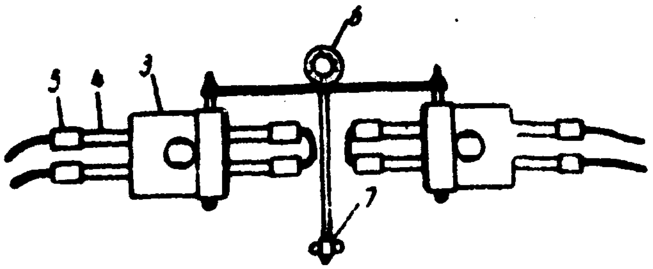

Fig. 1 b.
Assembly diagram of two ovens.
4 -- silite rods, 5 -- aluminum contacts with soldered-in wire, 7 -- wheel with directing rails.

The zone was created by means of silite rods 4 with a diameter of 12 mm (length 28 cm). Conductors were attached to the ends of the resistors by means of soldered aluminum contacts 5. The ovens were assembled in pairs. If the carrying screw 8 is made longer, the number of pairs of ovens can be increased and this makes the equipment more efficient.

Additional ovens 9 of nichrome were wound on an iron housing. They provided the required surrounding temperature at which there was no noticeable transfer of the substance to the cooler walls of the ampoule.

The electric motor 1 and the reduction gear 2 were joined with the screw (pitch 1 mm) by Hooke's joint, on which there were two (or more) couplings 6. Two ovens were mounted on the coupling (Fig. 1, b). A DC electric motor with a reduction gear provided a reverse-progressive motion of the ovens at a speed not exceeding 5 mm/hr. The speed limit can be changed by changing the last gear.

Silite heaters supplied the required temperature within the 6 to 10 mm zone. The temperature distribution in the oven and in the additional ovens is shown in Fig. 2.

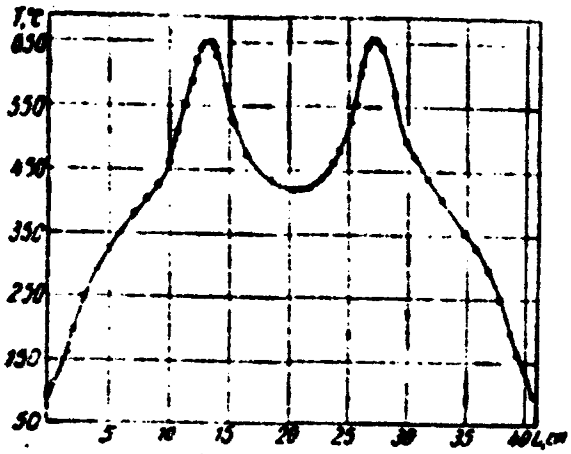

Fig. 2.
Temperature distribution in two ovens for zonal melting, with an additional oven.

It was found possible to maintain a more or less stable zone width by means of ferro-resonant stabilizers and a thermoregulator /8/ developed by the Laboratory. The zone was visually controlled through a porthole in the oven and by means of chromel-alumel thermocouples. The maintenance of a continuous zone width is very important because any change of zone affects both the quality of purification as well as the growth of crystals.

3. The technology of preparing Sb_2S_3 and Sb_2Se_3 compounds and growing single crystals from them.

The initial materials were: selenium (GOST /State Standard/ 6738-53) 99.992% pure, antimony (zonal purification) 99.99% pure and sulfur 99.99% pure.

The individual components were cleansed with aqua regia and washed with distilled water, and were ground to a powdery form in an agate mortar. The components were weighed on an analytical scale with an accuracy up to 10^{4} g. According to the weight of the first component which was put into the ampoule, the necessary weight composition of the second component was determined from the stoichiometric ratio, and the second component was added to the quartz ampoule. Before filling, the latter was heated to a temperature of 650 - 700°C in a vacuum ($1-2 \cdot 10^{-5}$ mm mercury column). The length of the ampoules was 7 - 9 cm and the diameter 8 - 14 mm. The ampoules for growing single crystals had a diameter of 8 - 10 mm and they were made with an oval bottom to improve crystal growth conditions.

The prepared ampoules with substances in a stoichiometric ratio were kept in a high vacuum for some time and were periodically heated to 100 - 120°C. The ampoules were unsoldered in a vacuum ($1.5-3 \cdot 10^{-5}$ mm mercury column) with an oxygen flame.

The amounts of powdery substances of both components should be selected in such a way that in a horizontal position of the ampoule the level of the molten substance would be lower (or even with) than the diameter of the ampoule. Otherwise the ampoules would often burst.

In a synthesis of Sb_2S_3 the components in the unsoldered ampoule were heated at a temperature of 850 - 900°C for 10 to 12 hours. Following this, the oven was turned off and slowly cooled together with the ampoule. With some specimens the process had to be repeated until traces of sulfur disappeared on the walls.

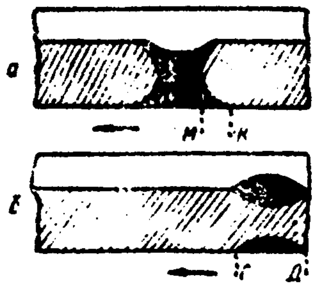

Fig. 3. Diagram representing initial stage of melting of zone (a) and fully melted zone (b).

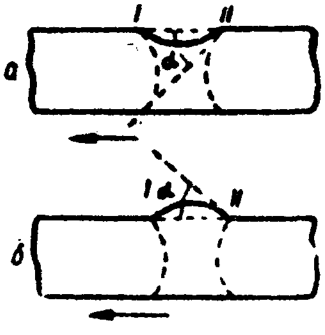

Fig. 4. Diagram showing surface shape of melted zone on ingot Sb_2S_3 (a) and Sb_2Se_3(b).

The synthesis of the compound Sb_2Se_3 proceeded at a faster rate, i.e.: a heating over a period of 6 to 8 hours at a temperature of the order of 900 to 950°C was sufficient.

It was observed that during prolonged heating of the substances at temperatures above 900°C the porosity of the ingot almost completely disappears. In this case the porosity is associated with the emanation of gas which is dissolved in the substance /7/.

During the motion of the zone the rarefied gas diffuses from the crystallization front into the liquid phase. The gas pressure will progressively increase before the boundary of crystallization and this will cause the formation of bubbles in the solid phase. A preceding heating of the substance at a temperature considerably higher than the melting temperature causes an ejection of gas from the substance. Following the synthesis the ampoule was placed in the zonal equipment for multiple passage of the zones.

During melting the substances Sb_2Se_3 and Sb_2S_3 have opposite coefficients of expansion. Sb_2Se_3 increases its volume during melting, while Sb_2S_3 decreases it. During zonal melting the molten zone is displaced along the specimen, expanding from the center of the ingot to the heaters. If the ampoule contains Sb_2S_3, then during the displacement of the zone from right to left, the first to solidify is the sector MK (Fig. 3). The volume of this sector increases, and this causes a rise of the part of the ingot which had earlier solidified and can cause an explosion of the ampoule.

An explosion of an ampoule with Sb_2Se_3 takes place at the beginning of the ingot, when the zone had not as yet completely melted. Here the earlier melted region CD (Fig. 3) expands, which causes either a rise of the whole ingot, if the level is below the diameter, or an explosion of the ampoule, if the level is higher than the diameter.

It was determined by us that ingots of both compounds change their thickness during multiple zone passage (10 to 20 zones). The thickness of Sb_2S_3 changes in the direction of the motion of the zone, and Sb_2Se_3, on the contrary, diminishes its thickness. This fact indicates that there is a transfer of substance in zonal crystallization. The following general rule can be concluded from bibliographical data and our own investigations: all substances which increase in volume during melting (metals, most semiconductors, and particularly Sb_2Se_3) will increase in thickness up to that end of the ingot from which the melting began. The substance will shift in the opposite direction of the motion of the zone. Substances (Sb_2S_3, germanium and others) which decrease in volume during melting, will increase in thickness to the end of the last zone. In these substances the zonal shift is in the direction of the motion of the zone.

There is a continuous and rapid exchange of atoms between the solid and liquid phase during the melting and crystallization of the substance. Two processes of atom exchange take place at the left and right end of the zone. On the left, more atoms leave the solid phase (motion from right to left), and become part of the liquid. On the right, atoms pass from the liquid to the solid phase. In a dynamic equilibrium the zone remains motionless. These processes determine the nature and rate of crystallization (melting) of the substance.

If the substance increases its volume during melting (for example, the case of Sb_2Se_3) then, as can be seen from Fig. 4, b, the conditions of crystallization at boundary II will be different in the volume and in the subsurface layer. During the displacement of the zone from right to left, conditions will appear in the volume favoring crystallization in the direction of the motion. In the surface layer, the presence of the molten substance above the level of the solid phase creates some possibility of crystallization also in the region of angle . As a result of this, the liquid recedes, and this causes a shift of the substance in the opposite direction to the motion of the zone.

In the case of Sb_2S_3 and other similar substances which decrease in volume during melting, the conditions at the crystallization boundary II (Fig. 3, a) are quite different for crystal growth than in the former case. In the subsurface layer crystallization does not freely occur. The atoms extend into the solid phase from below, and not in the direction of the motion of the zone. This causes a certain slowdown of crystallization in this layer. The liquid is pushed to the end of the ingot little by little. During a multiple zone passage there is a noticeable shift of the substance toward the end of the ingot.

Special attention should be paid to the phenomenon of substance displacement in selecting the design of the boat or ampoule and filling them with the substance. If the ingot is passed through a great number of zones, then the above phenomenon produces a considerable contraction of the substance at one end of the ampoule and its explosion.

The displacement of the substance can be almost completely eliminated by tilting the boat or ampoule with with substance or even the entire apparatus in a certain direction. For substances of the Sb_2Se_3 type it is necessary to tilt the work in the direction of the motion of the zone, and for substances of the Sb_2S_3 type -- in the direction opposite to the shift of the zone. This conclusion flows from an analysis of the causes of the displacement of the substance and becomes clear from Fig. 4.

4. Methods of Purity Control

Multiple zonal passage provided a purification of the material and growth of crystals. In order to check whether the material was being purified we used the probe method of picking off the distribution of the potential along the specimen (Fig. 5). Curve 1 in Fig. 5 represents the distribution of the potential along ingot Sb_2S_3 after passage of seven zones without cutting off the end of the specimen. It is evident that admixtures are driven in the direction of the zone shift. The potential is almost unchanged at a distance of 1.6 cm from the end of the ingot. Thus, from the course of the potential along the ingot, we can more or less accurately determine the boundary of a sharp drop in the concentration of admixtures. This makes it possible to determine which part of the ingot should be cut off following zonal purification.

It is a known fact that determination of the specific resistance for ingots with a different number of zones (Fig. 6) constitutes a method of semiquality control. If the specimen is of uneven thickness and irregular shape, the four-probe method can be used to determine resistance

/8/. In the case, however, when the ingot has identical longitudinal dimensions, we use the two-probe method.

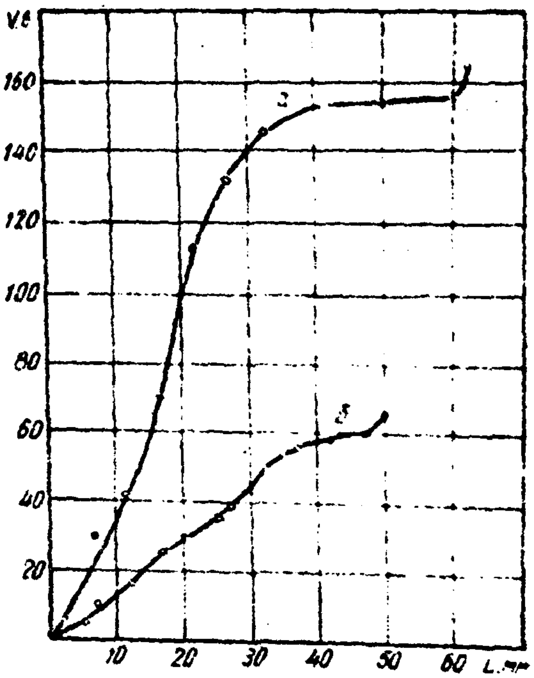

Fig. 5. Distribution of potential along ingots.

a -- distribution curve of potential along ingot following passage of seven zones. Ingot is without cutting off the last zone;

b -- distribution curve of potential along ingot Sb_2S_3 following passage of five zones. The last zone has been cut off (12 mm).

In the case of photosensitive substances, such as Sb_2Se_3 and Sb_2S_3, purification can be checked also by the change of photoelectric properties. The photosensitivity of Sb_2Se_3 and Sb_2S_3 increases with an increase of the number of zones (Figs. 7 and 8). This indicates that with an increase of purity of the substance there is a decrease of the number of centers of recombination and the lifetime of photoelectrons increases.

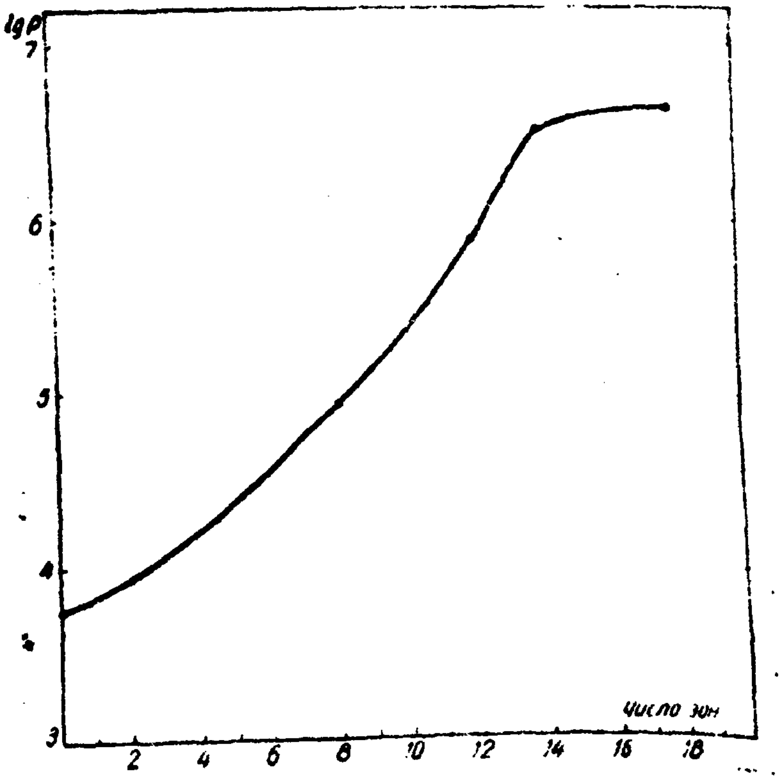

Fig. 6.

Relationship between purification of the materialand the resistance of Sb_2Se_3 .

In the investigation of photoelectric properties of Sb_2S_3 it was observed, depinding on the purity of the specimen, that the additional maximum of photosensitivity diminishes with an increase of the number of zones, and, at a certain number of zones (18) it practically disappears altogether (Fig. 7). This fact can serve as an additional confirmation of the increase of purity. Of course, we get an additional maximum of the admixture character.

It should be noted that in order to keep track of the purity of the material and to determine the least number of zones in which the effect of purification is still observed, it is necessary to make the trial purification not in the ampoule, but in a boat which is placed in the ampoule. The ampoule with the boat is pumped out to a high vacuum and unsoldered. The ingot from the boat will not have to be extracted in the experiment, and this will eliminate further contamination of the material.

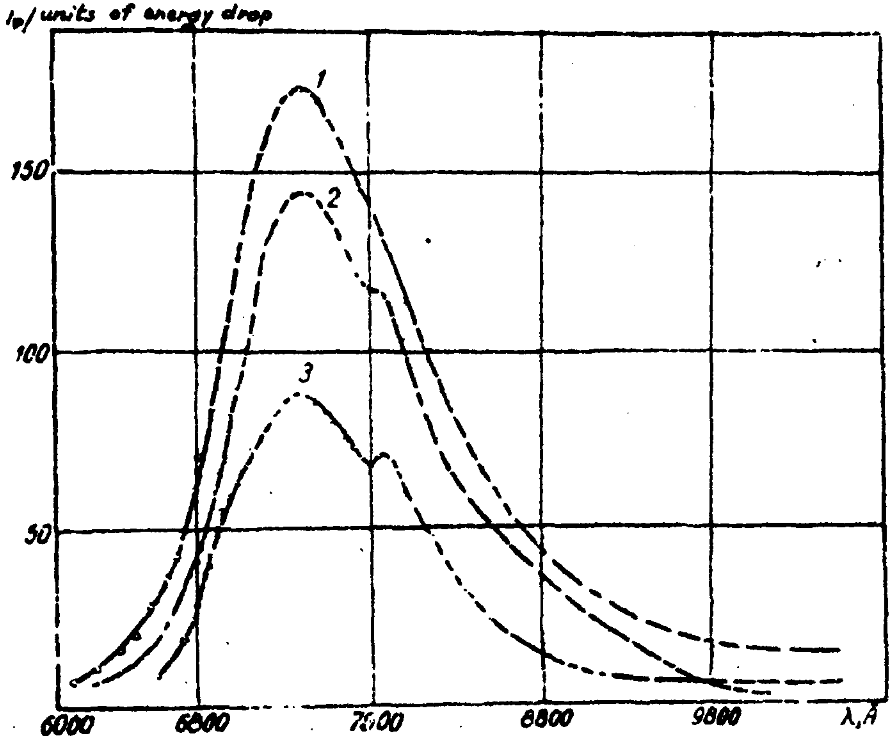

Fig. 7.

Relationship between purity of material and the spectral distribution of the photocurrent for single crystal Sb_2S_3.

1 -- Curve of spectral distribution of photocurrent for specimen No 15 of eighteen zones;
2 -- Curve of spectral distribution of photocurrent for specimen No 11 of eight zones;
3 -- Curve of spectral distribution of photocurrent for specimen No 5 of six zones. Temperature 20°C.

After multiple zone passage ingots were obtained which consisted of several single-crystal blocks. Both the single crystals Sb_2Se_3 and well as single crystals Sb_2S_3

easily split along the planes of cleavage. The cleavages are oriented along the direction of the motion of the zone. Both compounds crystallize in a rhomboid system /6/.

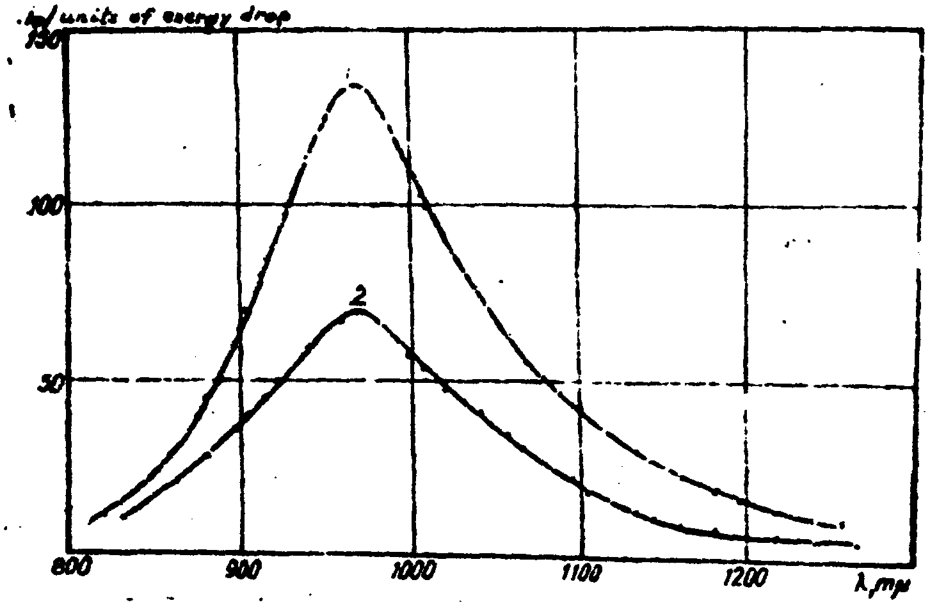

Fig. 8.

Relationship between purity of material and the spectral distribution of the photocurrent for single crystal Sb$_2$Se$_3$.

1 -- Curve of spectral distribution of photocurrent for specimen No 7 of twelve zones;

2 -- Curve of spectral distribution of photocurrent for specimen No 40 of fourteen zones. Temperature 20°C.

The plucking out of single crystal specimens from individual ingots was made on a special stand made of organic glass. Different dimensions of specimens can be obtained (for example, 2 X 10 X 4 mm^3). The X-Ray pictures of some specimens showed that they were single crystal.

These single crystals were obtained at a zone width of 6 - 8 - 10 mm, which constituted 1/8 or 1/10 of the length of the entire ingot. The rate of zone displacement was 4.4 to 5 mm/hr.

Conclusions

1. Equipment was designed and tested for zonal melting, growing of crystals and homogenization of compounds (Sb_2Se_3, Sb_2S_3, Sb_2Te_3 and others) and three-component systems of elements of the V and VI group of Mendeleyev's table.

2. An engineering method was designed and tested of preparing compounds and mixtures of these elements in quartz ampoules.

3. Conditions of synthesis of compounds were investigated. It was determined that in the case of Sb_2S_3 synthesis is successfully achieved (almost without blisters) by heating to 850 - 900°C over a period of 10 to 12 hours with subsequent slow cooling. The synthesis of Sb_2Se_3 proceeds more actively and requires heating to 900 - 950 °C over a period of 6 to 8 hours.

4. Conditions of purification of material were investigated. Attention was drawn to mechanical changes in the purification of compounds. There is a displacement of substance in Sb_2Se_3 and Sb_2S_3 in mutually opposite directions. It is therefore necessary to give a proper tilt to the equipment. Sb_2Se_3 increases its volume during melting, and Sb_2S_3 decreases it. Possible causes of explosion of ampoules were pointed out.

5. For qualitative control of purification a method was proposed of picking off the distribution of the potential along the ingot (of uniform cross-section). This method makes it possible to determine fairly simply the position of the boundary of an acute change of concentration of admixtures and the dimensions of cut-off ends of ingots.

6. In the case of photosensitive substances, such as Sb_2Se_3 and Sb_2S_3 , purification can also be checked by the change of photoelectric properties, and in the case of Sb_2S_3 we also observe the disappearance of the additional (admixture) maximum of photosensitivity.

7. Ingots were obtained by the zonal melting method

which consisted of large single crystal blocks. The rate o the zone is 4.5 to 5 mm/hr, and the width 8 to 10 mm. The vacuum during unsoldering is (1.5 0 3) $\cdot 10^{-5}$ mm. It was comparatively easy to pluck out specimens of single crystals of the required dimensions. Monocrystallicity was checked by X-Ray analysis.

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