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Electrical and optical properties of $Ge_{20}Sb_{15-x}Bi_xBi_{65}$ glasses

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Preliminary results of a study on the preparation, optical and electrical properties of $Ge_{20}Sb_{15-x}Bi_xS_{65}$ glasses are presented. It is shown that the substitution of antimony by bismuth atoms results in the red shift of the short wave length absorption edge in decreasing resistivity and in the appearance of n-type conductivity. The p to n transition is in the vicinity of $3.5 < x < 5$.

1. Introduction

In recent years attention has been paid to the study of both preparation and properties of n-type bulk glasses. A method of preparation and some electrical properties of n-type bulk glasses ($Ge_{20}Bi_xSe_{80-x}$) was first described in [1–4]. Some of the most important results of these papers are: (a) doping of bismuth atoms of concentration higher than 7.5 at % leads to n-type conductivity, and (b) rapid cooling is necessary to obtain glasses with a higher content of bismuth atoms (cooling in liquid nitrogen was used).

Subsequently, [15] the influence of bismuth, arsenic, copper and indium atoms in Ge–Se and Ge–Te glasses was examined. It was shown that only the addition of bismuth atoms leads to n-type conductivity. From the results of [3–5] it also follows that the substitution of selenium by tellurium atoms is not very important for the appearance of n-type conductivity in the studied glasses. It was recenty shown in [6] that: (a) n-type conductivity exists also in the Ge–Bi–S non-crystalline system ($Ge_{20}Bi_xS_{80-x}$) analogously as in $Ge_{20}Bi_xSe_{80-x}$ glasses, and (b) the influence of bismuth atoms on the appearance of n-type conductivity was manifested by substitution of antimony atoms by bismuth atoms in $(GeSe_{3.5})_{88}Sb_{12-x}Bi_x$ glasses.

In this paper the influence of substitution of antimony atoms by bismuth atoms on the optical properties in the region of short wavelength absorption edge (SWE) and on the electrical conductivity and thermoelectric power on $Ge_{20}Sb_{15-x}Bi_xS_{65}$ glasses is examined.

2. Experimental procedure

2.1. Preparation of $Ge_{20}Sb_{15-x}Bi_xS_{65}$ glasses

As mentioned [1, 2] a relatively high cooling rate is necessary to obtain non-crystalline materials in the case of bismuth doped glasses (cooling in liquid nitrogen was used in [1–4]). It is, however, well known that the cooling rate in liquids depends also on the vapour solubility in the liquid used. It seems that cooling down ampoules from temperatures at ~ 1000 K (or higher) in liquid nitrogen cannot be so effective. For a qualitative estimation of the cooling rate we examined the cooling of the NiCr–Ni thermocouple inserted in a silica ampoule (inner diameter 4.5 mm, thickness 0.8 mm and ampoule length 8 cm). The results are summarized in Fig. 1 for different cooling media: air (1); liquid nitrogen (2); ice water (3) and cold 10% KOH solution (4). It is clear (Fig. 1) that the cooling rate in 10% KOH solution is higher than that in liquid nitrogen. Therefore cooling in 10% KOH solution has been used.

The $Ge_{20}Sb_{15-x}Bi_xS_{65}$ glasses studied were prepared in the conventional way by the melting of a mixture of pure elements in evacuated ($P \sim 10^{-2}$ Pa) quartz ampoules in a rotary furnace. 5N purity germanium, antimony and bismuth were used, sulphur mark DAB-6 was purified by the Wartenberg method. After annealing (~ 710 K for 4 h) and homogenization (~ 1173 K for 24 h) the ampoules were cooled in 10% KOH solution. The total weight of elements was 8 g, inner volume of ampoule 5.5 cm^3, the thickness of the wall of ampoule used was 1 mm. Prepared materials were dark (except for $Ge_{20}Sb_{15}S_{65}$ – orange coloured) with a metallic appearance and typical conchoidal fracture. No inclusion of the crystalline phase was found by X-ray diffraction analysis. The densities of prepared glasses were determined using a hydrostatic method. The glass transition temperatures (T_g) were determined using differentia thermal analysis (DTA) technique on bulk samples (heating rate 10 K min^{-1}). The softening temperatures (T_s) were estimated using a penetration method [7] in low sensitivity mode (load 40 g).

2.2. d.c. conductivity and thermopower measurements

The d.c. conductivity was measured in a sandwich arrangement. Aquadac contacts were used. Measurements were made at $P \sim 10^{-1}$ Pa and, before resistance measurements, each sample was annealed for 30 min at 350 K in order to remove traces of moisture.

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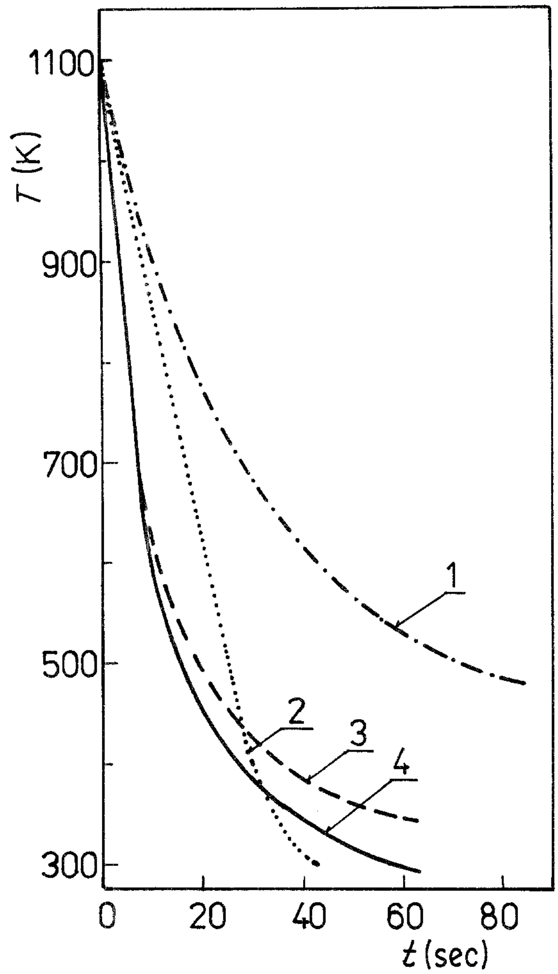

Figure 1 Results of measurements of cooling rate of NiCr–Ni thermocouple in silica ampoule. Cooling media: (1) air; (2) liquid nitrogen; (3) ice water; and (4) 10% KOH solution.

The resistance was measured using a Keithley 610C electrometer in "fast mode" for sample resistance $R_s > 10^{10}\,\Omega$ and in "normal mode" $R_s < 10^{10}\,\Omega$. In the fast mode the measurements were carried out in stationary conditions with special low capacity cable (R_s was read 20 min after stabilization of temperature). In the normal mode the measurements were made in a dynamical regime (the heating was approximately $1\,\mathrm{K\,min^{-1}}$).

The measurements of thermopower were made in a sandwich arrangement using a device described in [8]. The sample was first contacted using Aquadac, and after that stuck using Ag-paste between the sample's copper holders. Thermopower was measured using the Keithley 610C electrometer. Traces of water (from the Aquadac contacts) and solvent (from the Ag-paste) were removed by annealing (for ~ 30 min at ~450 K and $P \sim 10^{-1}$ Pa).

2.3. Optical properties measurements

Optical properties in the region of SWE were measured in the way mentioned in [9]. Samples for the measurement of optical properties were prepared by cutting from the bulk and polishing to optical quality (thickness of the sample was $0.01 < d < 0.3$ cm). Thin layers of glasses were prepared by hot pressing between two quartz plates (thickness of the samples was $0.001 < d < 0.003$ cm). For composition $x = 0$ (where x is at% of bismuth) the measurements were carried out also on annealed thin films prepared by flash evaporation. We remark that compositions for $x > 0$ have been decomposed by flash evaporation and hot pressed thin layers of compositions $x = 12$ and 15 were crystallized.

TABLE I Glass transition temperatures, softening temperatures and densities of $Ge_{20}Sb_{15-x}Bi_xS_{65}$ glasses

Parameter	x									
	0	0.5	1	2	3.5	5	7	9	12	15
ϱ (g cm^{-3})	3.30	3.32	3.34	3.43	3.52	3.59	3.75	3.86	4.01	4.34
T_g (K)	567	571	576	571	567	562	563	567	567	566
T_s (K)	593	602	610	610	606	605	610	613	613	595

3. Results and discussion

Values of density (ϱ), glass transition temperature (T_g) and softening temperature (T_s) are summarized in Table I. As shown, ϱ increases with increasing bismuth atom content and analogously as in other binary and multicomponent glassy alloys there exists a simple linear dependence between ϱ and relative molecular weight ($\bar{M}$) in the form $\varrho = 0.07\bar{M} - 0.431$.

The values of T_g and T_s seem to be practically independent of composition. Assuming in the first approximation that T_g is connected with the mean coordination number [10] (i.e. T_g reflects the structure and structural changes) we can suppose that substitution of antimony by bismuth atoms is most probably by isostructural substitution*.

Optical properties of studied glasses in the region of SWE are characterized by spectral dependences of absorption coefficient (K). Values of K were calculated from the relation

$$K = d^{-1}\ln \times (\{(1 - R)^2 + [(1 - R)^4 + (4R^2I^2)]^{1/2}\}/2I) \quad (1)$$

where I, R, d are transmittance, reflectivity and sample thickness, respectively. Spectral dependences of K are presented in Fig. 2 (for all points the condition $0.5 \leqslant Kd \leqslant 1.5$ is fulfilled). In the studied spectral region (with the exception of the thin film of $x = 0$ composition) spectral dependences of K can be described by a well known relation which is valid for many chalcogenide glasses

$$K \sim \exp(\hbar\omega - E_g^{\mathrm{opt}})/\Delta \quad (2)$$

where Δ is the reciprocal slope of absorption edge and $\hbar\omega$ is photon energy. In the insert of Fig. 2 is shown the spectral dependence of K of well annealed thin film $x = 0$ glass for $(K\hbar\omega)^{1/2}$ against $\hbar\omega$. Assuming the validity of the relation

$$(K\hbar\omega)^{1/2} \sim (\hbar\omega - E_g^{\mathrm{opt}}) \quad (3)$$

the value of the optical gap for this composition is $E_g^{\mathrm{opt}}(0) = 2.54$ eV. As evident from Fig. 2 the substitution of antimony atoms by bismuth atoms leads to the red shift of SWE practically without the change in the slope of the absorption edge (see also Table II). Thus

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*This seems to be reasonable since crystalline Sb_2S_3 and Bi_2S_3 are isostructural semiconducting compounds.

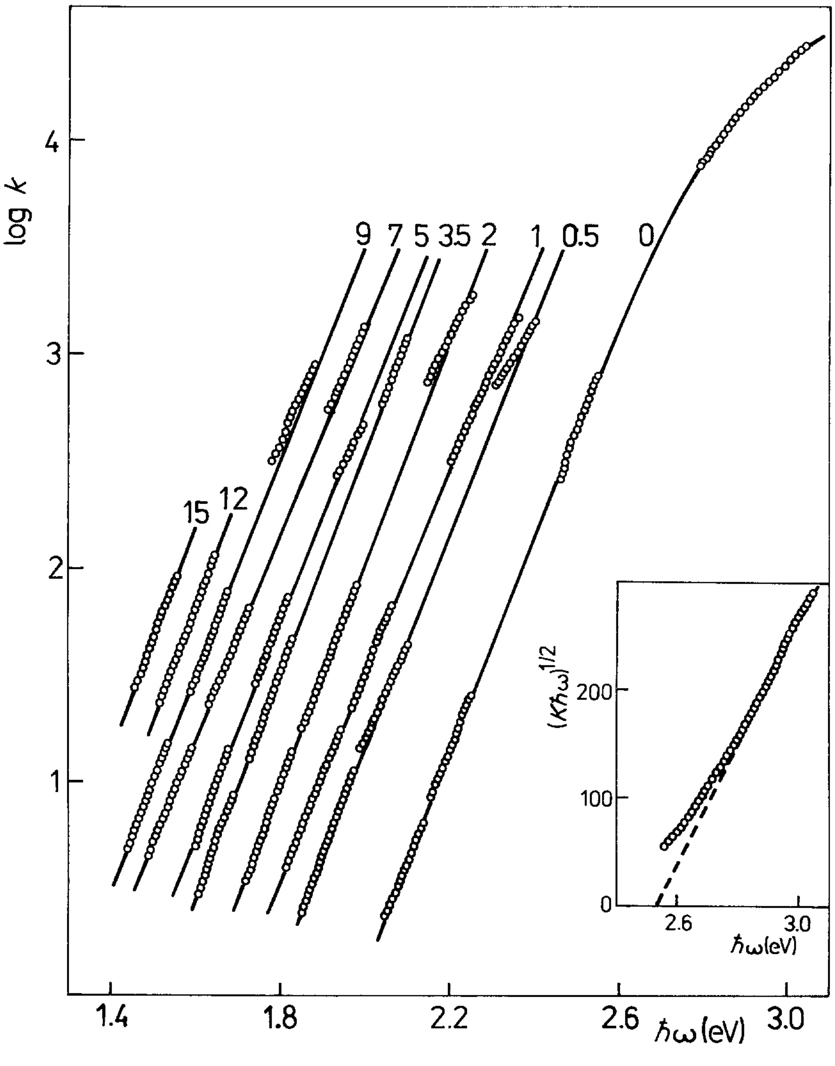

Figure 2 Spectral dependences of absorption coefficient for $Ge_{20}Sb_{15-x}Bi_xS_{65}$ glasses in the region of SWE. Chemical compositions (x) are marked by numbers. Insert: determination of E_g^{opt} for annealed thin film $x = 0$ glass. Units of k are cm^{-1}.

we suppose that the shift of the SWE is mainly due to the decreasing of E_g^{opt}. The values of E_g^{opt} of individual compositions can be estimated assuming

$$E_g^{opt}(x) = E_g^{opt}(0) - \delta(x) \qquad (4)$$

Value $\delta(x)$ is the shift of the SWE for composition x of the studied glass. Values of $E_g^{opt}(x)$ estimated in this way are compared in Table II with the values of energy corresponding to the value of the absorption coefficient $K = 10^3\,cm^{-1}$ (E_{03}) often used for estimation of E_g^{opt}.

Temperature dependences of the d.c. conductivity (σ) are summarized in Fig. 3. For all studied compositions the $\sigma(T)$ dependences can be described by the relation

$$\sigma = \sigma_0 \exp(-E^{\sigma}/kT) \qquad (5)$$

where the values of the pre-exponential factor (σ_0) vary in the region $0.1 < \sigma_0 < 500\,\Omega^{-1}cm^{-1}$, the values of activation energy for d.c. conductivity (E^{σ}) are shown in the lower part of Fig. 6. From Fig. 3 it

TABLE II Optical parameters of $Ge_{20}Sb_{15-x}Bi_xS_{65}$ glasses

Parameter	x									
	0	0.5	1	2	3.5	5	7	9	12	15
$1/\Delta(eV^{-1})$	11.9	12.0	11.3	11.9	11.9	11.7	11.3	11.9	12.0	11.8
E_g^{opt}(eV)	2.54	2.34	2.29	2.17	2.07	2.03	1.96	1.88	1.81	1.73
E_{03}(eV)	2.57	2.37	2.32	2.19	2.09	2.05	1.98	1.90	1.83	1.75

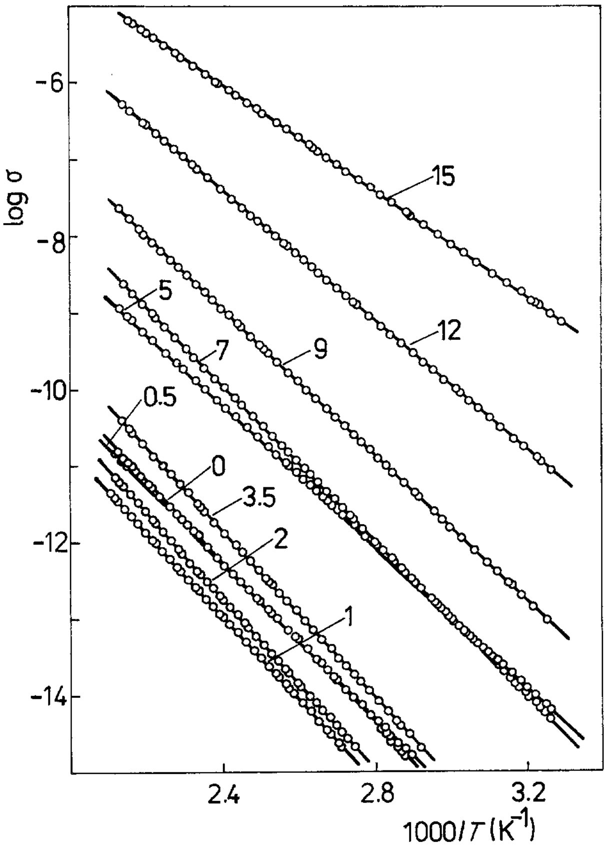

Figure 3 Temperature dependences of d.c. conductivity of $Ge_{20}Sb_{15-x}Bi_xS_{65}$ glasses. Chemical compositions (x) are marked by numbers. Units of σ are $\Omega^{-1}cm^{-1}$.

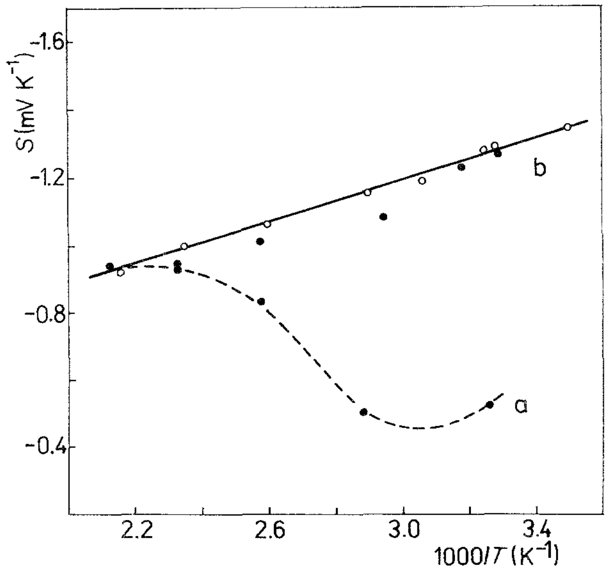

Figure 4 The influence of contacts and annealing of contacts on temperature dependence of the Seebeck coefficient of $x = 15$ glass. – – –: Curve A; —: Curve B.

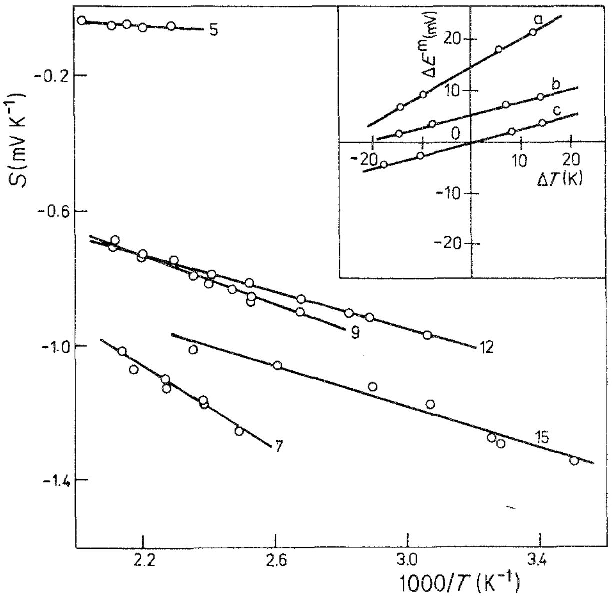

Figure 5 Temperature dependences of the Seebeck coefficient for $Ge_{20}Sb_{15-x}Bi_xS_{65}$ glasses. Chemical compositions are marked by numbers. Insert: the influence of the number of thermal cycles on ΔE^m against ΔT for $x = 2$, (a) first measurement, (b) second measurement, and (c) third and fourth measurements.

is clear that substitution of antimony by a small amount of bismuth ($0.5 < x < 2$) leads to little decrease in conductivity, while for $x > 3.5$ the d.c. conductivity is increasing.

The measurements of thermopower of chalcogenide glasses are accompanied by some difficulties due to the existence of a "residual" voltage superimposed on the thermoelectric voltage (ΔE) measured for the temperature gradient (ΔT).[†] Analogously as in [6, 8] it was necessary to measure potential difference ΔE^m at different values of ΔT in both directions. The slope of ΔE^m against ΔT dependence was taken as a Seebeck coefficient (S). The influence of contacts and annealing of the contacts on the values of S are shown in Fig. 4. Curve A shows the $S(T)$ dependence of the sample $x = 15$ with the Ag-paste contact only. The measurements were made without preliminary annealing of the sample to remove traces of solvent from the Ag-paste. Curve B shows $S(T)$ values from the second measurements of the same sample (i.e. second thermal cycle). Open circles are values of $S(T)$ of another sample of the same composition with contacts prepared and annealed using procedure described in Section 2.2.

Due to the described contact behaviour we used the last type of contacts and annealing procedure for all measurements of thermopower. The results of thermopower measurements are summarized in Figs. 5 and 6. For compositions with $x < 5$ only values of S at ~478 K were determined due to a very high resistance of these samples. The compositional dependence of S for 478 K is shown in the upper part of Fig. 6. It is evident that there exists a transition from p to n type conductivity at $3.5 < x < 5$. The important influence of bismuth atoms on the appearance of n-type conductivity seems to be confirmed. We assume in the first approximation that $S(T)$ dependence (see Fig. 5) can be described using the relation [11]

$$S = \pm \frac{k}{e}\left[\frac{E^s}{kT} + A\right] \tag{6}$$

where k is Boltzmann's constant, e the elementary

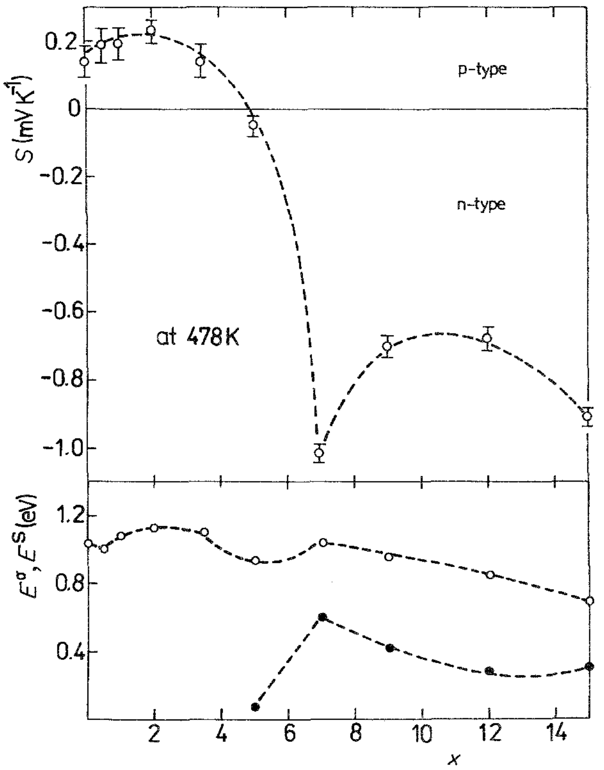

Figure 6 Compositional dependences of the Seebeck coefficient measured at 478 K (upper part) and activation energies of temperature dependence for d.c. conductivity (open circles) and the Seebeck coefficient (full circles) for $Ge_{20}Sb_{15-x}Bi_xS_{65}$ glasses (lower part). The dashed curves have no physical meaning.

[†] The residual voltage for some glasses seems to be depending on the number of thermal cycles (see insert of Fig. 5). All values of S in this paper are taken from measurements in such a thermal cycle (e.g. dependence (*c*) in the insert of Fig. 5) where residual voltage shows stable behaviour.

charge and A a constant. The values of activation energy from thermopower (E^s) and from d.c. conductivity are compared in the lower part of Fig. 6. The difference between these parameters is commonly observed in many chalcogenide glasses [11]. In a simple one-band model, where the Fermi level is pinned in the vicinity of the middle of the gap, the difference (ΔE) between E^σ and E^s can be taken as a mobility activation energy. In our case ΔE seems to be too high ($0.4 < \Delta E < 0.8$) for mobility activation energy. On the other hand if conduction occurs at more than one level within a material the ΔE is rather a consequence of the ratio of the conductivities on the individual levels and a sum of thermopower of individual levels

$$S = (\sigma_1 S_1 + \sigma_2 S_2)/(\sigma_1 + \sigma_2) \qquad (7)$$

This is also the case of ambipolar conductivity. As it follows from Fig. 5 in the vicinity of p to n transition the $S(T)$ dependence seems to be almost temperature independent ($x = 5$) which can be connected with ambipolar conductivity assuming that $N_e \approx N_h$ while $\mu_e > \mu_h$ (N and μ are concentration of current carriers and mobility, respectively. The subscripts e and h correspond to electron and holes). With increasing bismuth content ($x > 5$) the effect of electrons on conductivity will probably increase ($N_e > N_h$). The lower value of E^s (in comparison with E^σ) for $x > 5$ can be connected with the fact that the p-type conduction mechanism still makes a non-negligible contribution to the whole conductivity. Accepting this qualitative description of behaviour of $S(T)$ dependence we can explain the results of the conductivity measurements as follows. In pure $x = 0$ glass the Fermi level is below the middle of the gap (p-type conduction. Substitution of antimony by bismuth atoms ($0 < x < 2$) leads to the shift of the Fermi level close to the middle of the gap and the conductivity decreases (Fig. 3). Further increases of bismuth content ($x \geqslant 3.5$) leads to the shift of the Fermi level to slightly above the middle of the gap and the conductivity increases.

We suppose that the substitution of antimony by bismuth atoms leads to a redistribution and appearance of new defect states in the gap. The influence of donor-like states slightly increases and also the mobility of electrons in comparison with the mobility of holes increases.

4. Conclusion

The substitution of antimony atoms by bismuth atoms in glasses $Ge_{20}Sb_{15-x}Bi_xS_{65}$ leads to the transition from p to n type conductivity in the vicinity $3.5 < x < 5$. Analogously as in [1–4] the important influence of bismuth atoms on appearance of n-type conductivity was confirmed also in sulphide glasses. With increasing content of bismuth atoms the optical gap decreases and the electrical conductivity increases.

The results of measurements of thermopower and d.c. conductivity can be qualitatively explained assuming ambipolar conductivity. It seems that the Fermi level is pinned by defect states a little below half the gap for compositions with $x < 3.5$ and little above half the gap for $x > 5$.

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