# CHALCOGENIDE BROMIDES OF ANTIMONY AND BISMUTH

J.Horák, M.Kozáková and J.Klazar

*Department of General and Inorganic Chemistry,
Institute of Chemical Technology, Pardubice*

Crystals of SbSBr, SbSeBr and BiSBr have been investigated for the spectral distribution of the internal photoeffect, both at room temperature and at a temperature close to the boiling point of nitrogen. From the values of $\lambda_{\frac{1}{2}}$ for the polarizations $E \parallel c$ and $E \perp c$, the following approximate widths of the forbidden band, $E_g$, have been determined: $E_g(E \parallel c)$ (SbSBr) = 2·17 eV, $E_g(E \parallel c)$ (SbSeBr) = 1·84 eV, $E_g(E \parallel c)$ (BiSBr) = 1·88 eV at 293 K. These values are compared with those reported for the other chalcogenide-bromides of the type $A^V B^{VI} C^{VII}$. The relations of $E_g$ to the electronegativity of chalcogenes of orthorhombic and hexagonal crystals of chalcogenide-bromides and chalcogenide iodides have also been investigated. From changes in $\lambda_{1/2}$, $K$ for $E \parallel c$ and $E \perp c$ some general conclusions have been drawn on the probable changes of other quantities for $E \parallel c$ and $E \perp c$ of orthorhombic and stratified crystals of the compounds $A^V B^{VI} C^{VII}$.

In the last decade, the compounds $A^V B^{VI} C^{VII}$ have been paid much attention, the main reason being their particular physical properties. Some semiconductive crystals of the $A^V B^{VI} C^{VII}$ compounds exhibit striking ferroelectric and electromechanic properties, and an anomalous electro-optical effect. Most studies have dealt with crystals of SbSI. The other chalcogenide-iodides of the metals of Mendeleev's Vb group have also been studied in detail. Little attention has been paid to the chalcogenide bromides and chlorides of antimony and bismuth; apart from the structural parameters[1,2], knowledge of their physical properties is still rather poor. BiSBr has been investigated for the shift of the absorption edge with temperature[3,4]. The range of transition from the para to the ferroelectric state has been investigated with crystals of SbSBr and BiSBr[3,5], and some photoelectric properties with SbSeBr and SbSBr[6–8] crystals. Light absorption has been investigated[7,9,10] with crystals of BiSeBr and BiTeBr in the region of the absorption edges of the lattices. The cited papers do not reflect the properties of the group of chalcogenide bromides and their mutual relations. This fact is, to some extent, due to the difficulty in preparation of the crystals of $A^V B^{VI} C^{VII}$, where $A^V = $ Sb, Bi; $B^{VI} = $ S, Se, Te and $C^{VII} = $ Cl, Br.

The present paper describes the spectral distribution of the internal photoeffect of a group of chalcogenide bromides SbXBr and BiXBr, where X designates S, Se, or Te. From the curve relating the photoelectric current to the wave length of the incident light approximate widths of the forbidden bands, $E_g$, of these compounds were determined and compared with the $E_g$ values of the isostructural chalcogenide-iodides. In an attempt to elucidate the relations between the nature of the covalent bonds and the fundamental physical properties (parameters) of these semiconductors we have also correlated the electronegativity of the chalcogenides with the quantity $E_g$ of the compounds SbXBr, BiXBr, SbXI and BiXI.

## EXPERIMENTAL AND RESULTS

Synthesis of Chalcogenide Bromides of Sb and Bi

The elements employed, *viz.* Sb, Bi, S, Se and Te, were 99·999% pure. Antimony tribromide and bismuth tribromide were obtained by bromination of the metals; the bromine employed was freed from traces of chlorine by the addition of KBr, then it was dried and repeatedly distilled. The prepared antimony tribromide was three times distilled in the absence of aerial humidity, bismuth tribromide was twice sublimed. A polycrystalline chalcogenide bromide was obtained by direct synthesis from the metal, chalcogene and bromine in the stoichiometric ratio. Crystals of the chalcogenide bromides were then allowed to grow from the gaseous phase. The synthetized chalcogenide bromide of Sb or Bi was then brought into an ampoule, which was flushed with purified nitrogen and evacuated to a pressure of $\approx 0·1$ Torr. The ampoule was put into a horizontal silica oven with two separate windings, which made it possible to adjust different temperatures in the two parts of the oven. At the onset of the reaction the reactants were placed in the region of the higher temperature, $T_1$. After a time crystals of the chalcogenide-bromides were formed in the place of the lower temperature, $T_2$. Table I gives suitable temperatures for growth of the crystals. The temperatures $T_1$ and $T_2$ produce a temperature gradient along a distance of c. 10 cm. The crystals thus obtained were analysed by the Debye-Scherrer method. The lattice parameters of the compounds SbSBr, SbSeBr, BiSBr, BiSeBr and BiTeBr were verified with the aid of an X-ray goniometer URS-50 IM (Burevestnik, Leningrad, U.S.S.R.); the data proved identical with those reported by Dönges[1,2]. The physical properties were measured on crystals with perfectly developed planes. Especially perfect were the planes (110) and (010).The axes and planes of the crystals are denoted according to Dönges[1,2]; the modified symbols proposed by Bijvoet[11] are not employed.

Investigation of the Photoelectric Properties

The dependence of the photoelectric current $i_f$ on the wave length was investigated by the method described previously[12]. In determining the spectral distribution of the internal photoeffect the crystals were always so oriented that the light beam was perpendicular to the crystal plane (110); the light employed was linearly polarized, and $E \parallel c$ or $E \perp c$, where $E$ is the vector of intensity of the electric field of electromagnetic radiation. Since the ohmic resistance of the crystalline antimony chalcogenide bromides was very high (especially at low temperatures)

TABLE I

Synthesis Conditions of Some Chalcogenide Bromides of Sb and Bi
  Shape of crystals: needles, BiTeBr: leaflets.

| Compound | $T_1$, °C | $T_2$, °C | Time, days | Approx. dim., mm |
|----------|-----------|-----------|------------|------------------|
| SbSBr | 255 | 240 | 4 | $0·2 \times 0·2 \times 10$ |
| SbSeBr | 310 | 280 | 8 | $0·1 \times 0·1 \times 10$ |
| BiSBr | 518 | 466 | 7 | $0·6 \times 0·6 \times 10$ |
| BiSeBr | 420 | 371 | 28 | $0·4 \times 0·4 \times 5$ |
| BiTeBr | 443 | 402 | 10 | $8 \times 8 \times 0·1—0·3$ |

the relation of $i_f$ to $\lambda$ was investigated with the use of a polarization tension as high as 450 V. The contacts were made with a gallium solder. The results of the measurements at 293 K and 88 K are given in Table II. The plots of $i_f$ $vs$ $\lambda$ for the crystals of SbSBr, SbSeBr and BiSBr are shown in Figs 1 to 3.

Measurement of the Hall Voltage

The Hall voltage was measured on crystals of BiTeBr. The contacts were made with an alloy of In (90%) and Ag (10%). The crystals were so oriented that $H \parallel c$ ($H$ denotes intensity of the magnetic field) and $E_1 \perp c$. We also report values of the Hall effect for a crystal of BiTeBr, prepared by the method described earlier:

| $T$, K | $R_H$, cm$^3$ A$^{-1}$ s$^{-1}$ | $\varrho_{\perp c}$, cm | $\mu_{\perp c}$, cm$^2$ V$^{-1}$ s$^{-1}$ | $N$, cm$^{-3}$ |
|---|---|---|---|---|
| 293 | $1\cdot44 \cdot 10^{-1}$ | $8\cdot4 \cdot 10^{-4}$ | 171 | $4\cdot4 \cdot 10^{19}$ |
| 78 | $1\cdot44 \cdot 10^{-1}$ | $4\cdot5 \cdot 10^{-4}$ | 320 | $4\cdot4 \cdot 10^{19}$ |

$R_H$ designates the Hall constant, $\varrho$ the specific resistance, $\mu$ the mobility of free carriers of the electric current and $N$ denotes the concentration of these free carriers. The data were calculated from the equation

$$R_H = -r\gamma/Ne .$$

Since in this case the semiconductor is a degenerated one the Hall factor $r$ can[13] be set equal to 1. The coefficient $\gamma$ is related to the anisotropy of the effective mass of the free carriers and to the

TABLE II

Maxima of the Photoelectric Current and the Corresponding Widths of the Forbidden Bands for Compounds SbXBr and BiXBr

Type of conductance N.

| Compound | Space group | $T$ K | $\lambda_{1/2}$[$E\parallel c$] nm | $\lambda_{1/2}$[$E\perp c$] nm | $E_g$[$E\parallel c$] eV | $E_g$[$E\perp c$] eV | $\varrho$ $\Omega$ cm | $\beta$-in the paraelectric phase eV K$^{-1}$ |
|---|---|---|---|---|---|---|---|---|
| SbSBr | $D_{2h}^{16}$ | 293 | 572 | 560 | 2·17 | 2·21 | $10^5(\parallel c)$ | $-8 \cdot 10^{-4}$ |
| | | 88 | 540 | 534 | 2·30 | 2·32 | — | — |
| SbSeBr | $D_{2h}^{16}$ | 293 | 675 | 664 | 1·84 | 1·87 | $10^3{-}10^4(\parallel c)$ | $\approx -7 \cdot 10^{-4}$ |
| | | 88 | 625 | 616 | 1·98 | 2·01 | — | — |
| BiSBr | $D_{2h}^{16}$ | 293 | 660 | 645 | 1·88 | 1·92 | $10^2{-}10^3(\parallel c)$ | $-(6{-}7) \cdot 10^{-4}$ |
| | | 88 | 610 | 600 | 2·03 | 2·07 | — | — |
| BiSeBr | $D_{2h}^{16}$ | 293 | — | — | 1·50 | 1·54 | $\approx 10^{-2}(\parallel c)$ | — |
| | | 88 | — | — | — | — | — | — |
| BiTeBr | $D_{3d}^3$ | 293 | — | — | — | 0·59 | $\approx 10^{-3}(\perp c)$ | $-1·6 \cdot 10^{-4}$ |
| | | 88 | — | — | — | 0·62 | — | — |

relaxation time. In the case of the studied crystal its value could not be determined for lack of necessary data was not considered.

## DISCUSSION

Determination of the width of the forbidden band of SbSBr or SbSeBr crystals was difficult since the structure of the absorption edge of the crystal lattice remains obscure. For the existing preparation methods make it possible to prepare orthorhombic needle-like crystals of these compounds (excepting BiSBr) in dimensions smaller than $0.2 . 0.2 . 10$ mm. Since the condition of an accurate measurement is $Kd = 1$ ($K$ designates the absorption and $d$ the crystal thickness) it was possible to investigate only a certain region of the absorption edge, so that a quantitative interpretation could not be attempted. As all orthorhombic $A^V B^{VI} C^{VII}$ compounds proved to exhibit a marked internal photoeffect in the region of the absorption edge of the crystal lattice we have evaluated the photoelectric measurements with the aid of the assumption introduced by Moss[14]. According to this assumption the value of $E_g$ can be determined from the wave length, $\lambda_{1/2}$, corresponding to the half intensity of the photo current in the long-wave part of the curve $i_f(\lambda)$. The values of $\lambda_{\frac{1}{2}}$ for the polariza-
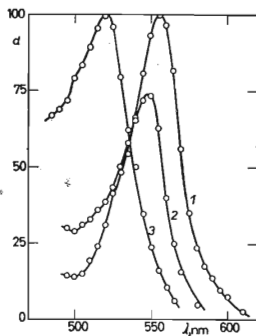


FIG. 1

Spectral Distribution of the Internal Photo-effect of SbSBr Crystals

*1* **E** $\parallel$ *c*, $T = 293$ K; *2* **E** $\perp$ *c*, $T = 293$ K; *3* **E** $\parallel$ *c*, $T = 88$ K. The energy of the incident radiation $\approx 4 . 10^{-4}$ Ws cm$^{-2}$, frequency of interruption of light 445 Hz. The value of $i^f$ in arbitrary units of d.
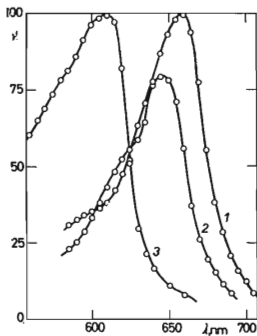
FIG. 2

Spectral Distribution of the Internal Photo-effect of SbSeBr Crystals

See the legend to Fig. 1.

tions $E \parallel c$ and $E \perp c$ at 293 K and 88 K are given in Table II for the crystals of SbXBr and BiXBr (space group $D_{2h}^{16}$). The values of $E_g$ for the crystals of BiSeBr and BiTeBr, given in Table II for the sake of comparison of the properties of chalcogenide bromides, are taken from the literature[7,10]. As Table II shows, no internal photoeffect has been observed with the heavier chalcogenide-bromides BiSeBr and BiTeBr. Crystals of either compound are highly conductive in the dark. Measurements of the electric properties have shown that probably they are degenerated electronic semiconductors. With the crystals of BiTeBr this view is substantiated by measurements of the Hall effect.

The high concentration of the free carriers at room temperature $(10^{19}\ \mathrm{cm}^{-3})$ and a lower value of Seebeck's coefficient (100 to 130 $\mu$V K$^{-1}$ at 300 K) allow an estimate of the Fermi limit, which at room temperature should occur in the region of the conductance band. Consequently, it cannot be ruled out that the width of the forbidden band of BiTeBr crystals will be smaller than the value obtained from the transmission measurement. Thus it can be expected that the crystals of BiTeBr will exhibit the Moss–Burstein effect, which we demonstrated[15] on crystals of BiTeI. The values of width of the forbidden band of chalcogenide bromides of Sb and Bi show that in a series of isostructural compounds a lower value of $E_g$ invariably corresponds to a heavier substituent. The dependence of $E_g$ on the "molecular weight" is in good agreement with this regularity. This dependence is given in Fig. 4, along with the values for chalcogenide iodides[16] of Sb, Bi and for AsSeI.
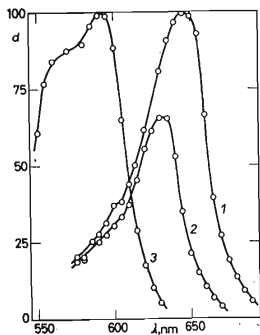


FIG. 3

Spectral Distribution of the Internal Photoeffect of BiSBr Crystals
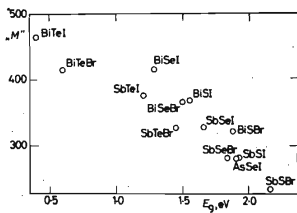
See the legend to Fig. 1.

FIG. 4

The Width of the Forbidden Band, $E_g$, of Compounds $A^V B^{VI} C^{VII}$ in Relation to their "Molecular Weight" ($M$)

Since with the increasing atomic weight in the columns of the periodic table the electronegativity of the elements decreases we have refined the relations between the nature of the chemical bond and the $E_g$ value of the corresponding compounds $A^V B^{VI} C^{VII}$. This was done by comparing the value of $E_g$ with the electronegativity of chalcogenes in a series of chalcogenide bromides and iodides.

The cause of the deviation from linearity (Fig. 5) in the series of antimony chalcogenide iodides is difficult to explain. It may be due to the fact that bismuth telluride halides are not isostructural with the crystals of the other compounds $A^V B^{VI} C^{VII}$. Yamada and Chihara[17] have advanced the view that, in an approximation, the compounds $A^V V^{VI} C^{VII}$ can be regarded as composed of ions $(A^V B^{VI})^+$ and $(C^{VII})^-$. The linkage S—Sb is probably covalent (the assumption of covalency is supported by the interatomic distances[1]). On the basis of this simplified view it seems justified to assume that the valence band is due to the overlapping $3p$ orbitals of bromide ions, whereas the conductance band is associated with the overlapping bonding orbitals of the $(SbS)^+$ ions. The distance of the upper edge of the valence band from the zero energy level is common to all bromides and according to Rose[18] it corresponds to 6·2 eV. In the case of iodides the value of this difference is 5·85 eV.

The measured $E_g$ values of chalcogenide bromides and iodides correspond to a smaller difference, 0·2 to 0·25 eV, as can be seen from the data in Fig. 5 (the difference in $E_g$ between $(SbS)^+ Br^-$ and $(SbS^+)I^-$ is 0·23 eV). The greatest difference from the ionic model can be expected with crystals whose ionic character is not
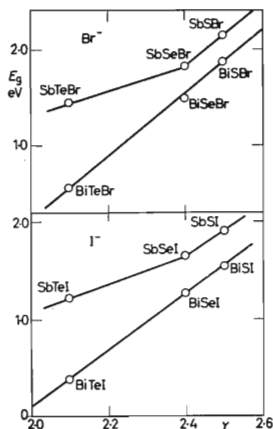


Fig. 5

The Width of the Forbidden Band of SbXBr, BiXBr, SBXJ and BiXJ in Relation to the Electronegativity $Y$

The electronegativities were calculated according to Pauling. The value of $E_g$ of SbTeBr, which compound has not yet been synthetized, was calculated from $E_g$ (SbTeJ), employing the ionic model described

pronounced. This idea accords with the determined values of $E_g(\text{BiTeBr}) = 0.59$ eV and $E_g(\text{BiTeI}) = 0.39$ eV. The difference is merely $0.20$ eV and in view of the stated electric properties of BiTe Br, this difference might be smaller still. The small width of the forbidden band suggests a very weak ionic character between the halogen and bismuth.

A review of the physical properties of chalcogenide bromides also reveals that the parameter $\beta = (\partial E_g/\partial T)_P$, characterizing the paraelectric phase, decreases with the decreasing width of the forbidden band. (The width of the forbidden band, $E_g$, changes with temperature according to the equation $E_g(T) = E_g(0) + \beta T$). The temperature dependence of the maximum photoelectric current and the value of $\lambda_{1/2}$ SbSBr (Fig. 1) are in good agreement with the results reported by Fridkin and co-workers[3]; they also accord with the temperature shift of the maximum photoelectric current observed with BiSBr[4]. What is further characteristic of chalcogenide bromides of Sb and Bi is the change of position and height of the maximum of photoelectric current with a position change of the vector $\mathbf{E}$ in respect to the axis $c$. With crystals of chalcogenide bromides it applies[19] that $K(\mathbf{E} \perp c) < K(\mathbf{E} \parallel c)$. In connexion with this inequality it holds that the reflectance $R(\mathbf{E} \perp c) < R(\mathbf{E} \parallel c)$, the refractive index $n_s(\mathbf{E} \parallel c) > n_s(\mathbf{E} \perp c)$ and $E_g(\mathbf{E} \parallel c) < E_g(\mathbf{E} \perp c)$. The anisotropy of the absorption edge, expressed by different values of $K(\mathbf{E} \parallel c)$ and $K(\mathbf{E} \perp c)$, also determines the change of the photoelectric current if the vector $\mathbf{E}$ is turned in respect to the $c$ acis.

As the photoelectric current is proportional to the absorption coefficient it applies that $i_f(\mathbf{E} \parallel c) > i_f(\mathbf{E} \perp c)$; this relation was discovered in examining the spectral distribution of the internal photoeffect (Figs 1−3). As can be seen from Table II the differences between $\lambda_{\frac{1}{2}}(\mathbf{E} \parallel c)$ and $\lambda_{\frac{1}{2}}(\mathbf{E} \perp c)$ vary around $0.03$ eV; this indicates a considerable value of the expression $2\left[K(\mathbf{E} \parallel c) - K(\mathbf{E} \perp c)\right] \left[K(\mathbf{E} \parallel c) + K(\mathbf{E} \perp c)\right]^{-1}$, which is a measure of dichroism in the considered crystallographic direction. A marked anisotropy is also observed with the layer-type crystals of bismuth telluride halides (space group $D_{3d}^3$). In contrast to the orthorhombic crystals it holds for the absorption of these crystals: $K(\mathbf{E} \perp c) > K(\mathbf{E} \parallel c)$; this is not in disagreement with theory.

Consequently, it is probable that $E_g(\mathbf{E} \perp c) > E_g(\mathbf{E} \parallel c)$, $R(\mathbf{E} \perp c) > R(\mathbf{E} \parallel c)$, $n_s(\mathbf{E} \perp c) > n_s(\mathbf{E} \parallel c)$. These inequalities probably hold even in the region of the resonance frequency of the plasm, so that the real part of the relative permittivity $\varepsilon_1(\mathbf{E} \perp c) > \varepsilon_1(\mathbf{E} \parallel c)$. At $\mathbf{E} \parallel c$ the minimum reflexion occurs in the region of longer wave lengths than at $\mathbf{E} \perp c$. Hence it follows that the effective mass $m_{ef \perp c} < m_{ef \parallel c}$ and, consequently, the electric conductivity $\sigma_{\parallel c} < \sigma_{\perp c}$. This conclusion accords with the experimental data, showing that the electric conductivity in the perpendicular direction to the layers is invariably lower on all layer-type crystals.

**REFERENCES**

1. Dönges E.: Z. Anorg. Allgem. Chem. *263*, 112 (1950).
2. Dönges E.: Z. Anorg. Allgem. Chem. *263*, 280 (1950).
3. Fridkin F. M., Gerzanič E. I., Grosik I. I., Ljachovickaja V. A.: Ž. Experim. i Teor. Fiz. *4*, 201 (1966).
4. Horák J., Turjanica I. D., Kozáková M., Lajbnerová L.: Československ. čas. fyz. *A 19*, 35 (1969).
5. Fatuzzo E., Harbecke G., Merz J. W., Nitsche R., Roetschi H., Ruppel W.: Phys. Rev. *127*, 2036 (1962).
6. Nitsche R., Merz J. W.: J. Phys. Chem. Solids *13*, 154 (1960).
7. Horák J., Turjanica I. D., Klazar J., Kozáková M.: Kristall u. Technik *3*, 241 (1968).
8. Klazar J., Horák J.: This Journal *33*, 973 (1968).
9. Turjanica I. D., Horák J., Kozáková M.: This Journal *33*, 300 (1968).
10. Horák J., Rodot H.: Compt. Rend. *267*, 1427 (1968).
11. Bijvoet J. M.: Structure Reports *13*, 208 (1954).
12. Horák J., Fiala J.: Československ. čas. fyz. *A 17*, 29 (1967).
13. Eggert H. in the book: *Festkörperprobleme*, I (F. Santer, Ed.), p. 291. Akademie Verlag, Berlin 1962.
14. Moss T. S.: *Optical Properties of Semiconductors*, p. 40. Butterworths, London 1959.
15. Horák J.: J. Phys. *31*, 121 (1970).
16. Rodot H., Hrubý A., Horák J.: Czechoslov. J. Phys., in press.
17. Yamada Y., Chihara H.: J. Phys. Soc. Japan *21*, 2085 (1966).
18. Rose A.: *Osnovy Teorii Fotoprovodimosti*, p. 185. Izd. Mir, Moscow 1966.
19. Harbecke G.: J. Phys. Chem. Solids *24*, 957 (1963).

Translated by J. Salák.