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CRYSTAL STRUCTURE AND OPTICAL PROPERTIES OF QUATERNARY SYSTEMS OF Bi-Sb-Te-Se

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The quaternary systems of Bi-Sb-Te-Se were synthesized by direct fusion technique. Thin films of these compounds were prepared by thermal evaporation under vacuum of 10^{-4} Pa. The structural properties of these compounds in powder and thin film forms were investigated by X-ray diffraction. The optical constants (absorption coefficient and band gap) of the thin films were determined by measurements of IR absorbance in the region $2.5-10$ μm. Analysis of the optical absorption spectra revealed the existence of two direct energy gaps.

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1. *Introduction*

Group V chalcogenides have been investigated primarily for thermoelectric cooling applications. The best materials for this application are found amongst the solid solutions of bismuth telluride with either antimony telluride or bismuth selenide. Excellent reviews of the thermoelectric properties of Bi_2Te_3 and related compounds have been published by Goldsmid [1] and Rosi [2].

Boikov et al. [3] made stoichiometric thin films of the ternary compound $Bi_{0.5}Sb_{1.5}Te_3$ using flash evaporation, with thermoelectric properties approaching those of bulk single crystals. Noro et al. [4] investigated the effect of substrate temperature on the composition and microstructure of Bi-Sb-Te-Se thin films.

Single crystals of $Bi_{1-x}Sb_xSe_3$ ($x = 0.0 - 0.20$) were prepared using a modified

Bridgman method [5]. X-ray structure analysis revealed that the volume of the unit of the $Bi_{1-x}Sb_xSe_3$ crystal lattice decreases with increasing value of x.

Solid solution on the basis of narrow band layered semiconductors $A_2^{V}B_3^{III}$ (where A = Bi, Sb and B = Te, Se) of tetradymite structure (space group D_{3d}^5) find a wide range of applications in the field of thermoelectric devices. Therefore, materials of this type are interesting for both theoretical and applied research [6 − 8].

In the present work, $BiSbTe_xSe_{3-x}$ with $x = 1$, 1.5, 2 and 3 was prepared and studied both in powder and thin film forms for different annealing temperatures. In addition, the optical properties were studied with the aim to correlate their dependence with the variation of composition.

2. *Experimental*

The compounds were made in stoichiometric ratio of high purity Bi, Sb, Te and Se (> 99.999), delivered from Johnson and Mathew Chemical Ltd. They were made using the preparation of bulk materials by direct fusion in sealed evacuated silica tubes.

The thin films were prepared by thermal evaporation onto glass substrates. The thin films were annealed at different temperatures (100, 150, 200 and 250°C) for 2 hours. The composition of both bulk and thin films of the ternary and quaternary systems was determined by energy dispersive X-ray analysis (EDX). The calculated contents of Bi, Sb, Te, Se wt % were found to be comparable with wt % of the calculated starting mixed materials, indicating that the prepared bulk and thin films are nearly stoichiometric.

The crystal structure of the material under investigation was analyzed by XRD using the Philips diffractometer (Diano Cooperation, U.S.A.)

Good quality polycrystalline thin films of $BiSbTe_xSe_{3-x}$ with $x = 1$, 1.5, 2 and 3, of thickness 150 − 220 nm, were deposited onto spec pure compressed KBr disks as substrate by vacuum deposition. The optical transmittance, T, of the films deposited on KBr substrates was measured at room temperature with unpolarized light at normal incidence in the wavelength range 2.5 − 10 μm, using a single-beam Fourier Transformation Infrared Spectrophotometer (FTIR-300E).

3. *Results and discussion*

3.1. *Structural*

X-ray diffraction patterns of the powder and thin films of $BiSbTe_3$, $BiSbTe_2Se$, $BiSbTe_{1.5}Se_{1.5}$, $BiSbTeSe_2$, as deposited and annealed at 100, 150, 200, 250 and 275 °C under vacuum for 2 hours, are shown in Figs. 1a, 1b, 1c and 1d, respectively. It is clear from the Figs. 1b, 1c and 1d that the peak intensity increases appreciably with increasing annealing temperature for the three prepared quaternary systems, $BiSbTe_2Se$, $BiSbTe_{1.5}Se_{1.5}$ and $BiSbTeSe_2$.

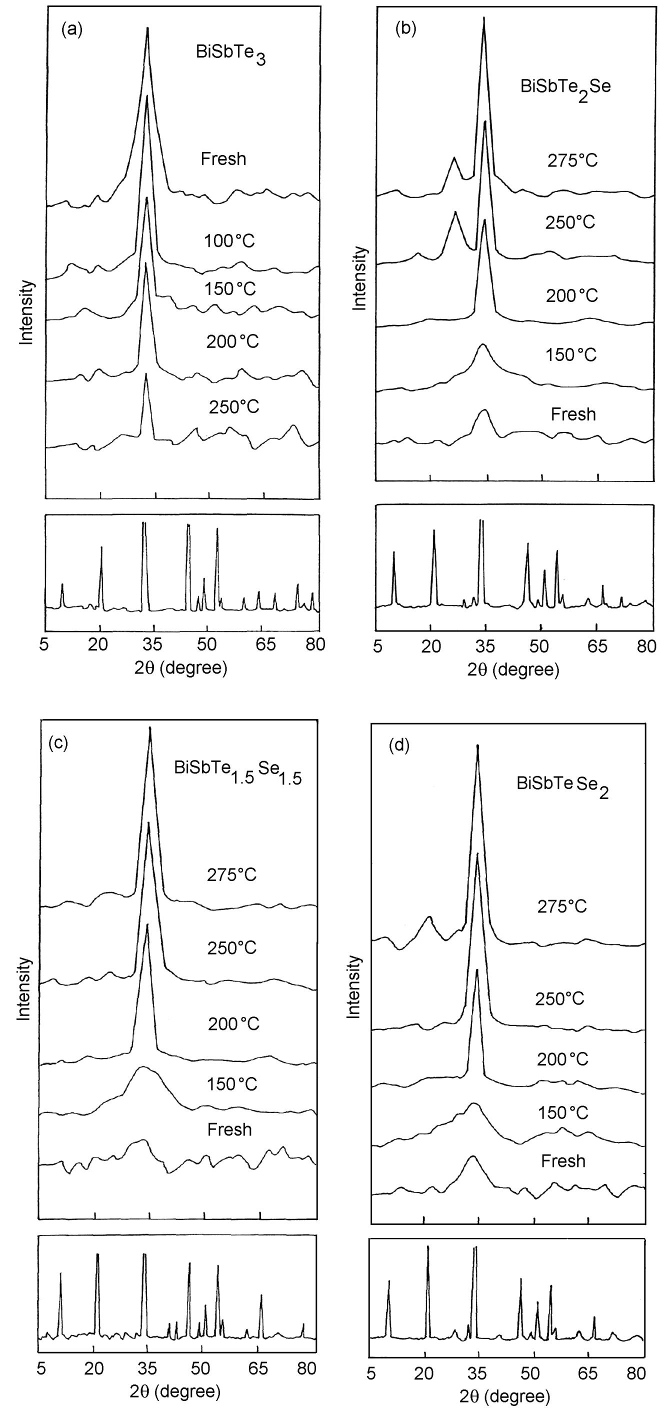


Fig. 1. XRD patterns of powder and thin film for different annealing temperatures of:
a) $BiSbTe_3$,
b) $BiSbTe_2Se$,
c) $BiSbTe_{1.5}Se_{1.5}$,
d) $BiSbTeSe_2$.

For the ternary system having the composition $BiSbTe_3$, the intensity of the selected X-ray diffraction line shows abnormal behaviour, i.e., it decreases with the increase of the annealing temperature, while the line broadening increases also, indicating the rise to small crystallite size. This can be explained by the fact that each sample of the investigated series has its optimum annealing temperature. Beyond this temperature, one expects that there is no correlation between the crystallite size and the annealing temperature. This sample shows minimum annealing temperature corresponding to maximum X-ray diffraction intensity of the selected reflection and minimum broadening. This explains the abnormal behaviour of this composition at elevated temperature.

From the X-ray powder diffraction patterns of these compounds, the lattice parameters of each of the systems can be calculated. From these results it can be shown that the prepared compounds in the bulk form have the rhombohedral crystal structure with the hexagonal space group.

The lattice parameters (a and c) together with the c/a ratio as a function of composition are shown in Fig. 2. From this figure, it is quite clear that the characteristics of both lattice parameters (a and c) for all prepared systems $BiSbTe_xSe_{3-x}$

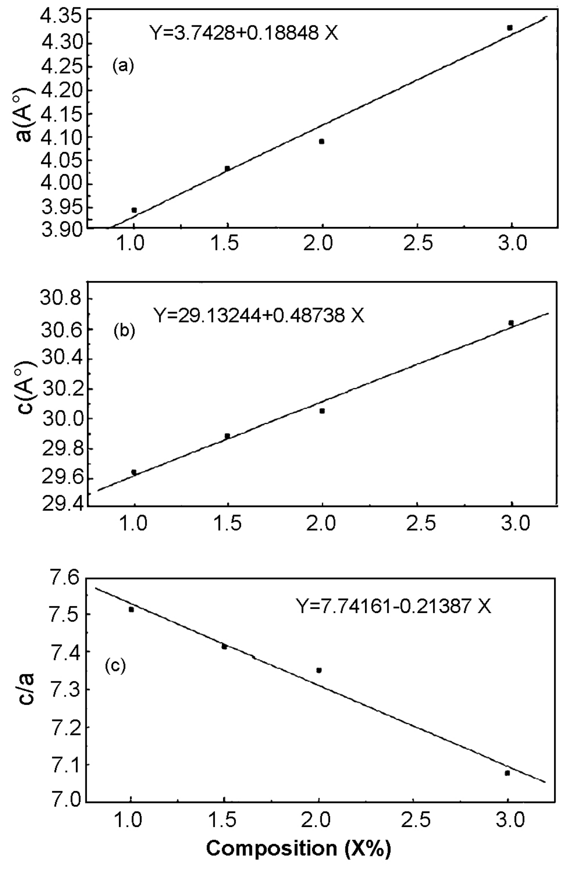


Fig. 2. Variation of lattice parameters with the composition x for $BiSbTe_xSe_{3-x}$ compounds: a) lattice parameter a, b) lattice parameter c and c) the ratio of lattice parameters c/a.

are identical, whereas both a and c are found to decrease linearly with increasing selenium content, i.e., by increasing the tellurium content, ($x = 1$ to $x = 3$). The calculated ratio c/a of these systems, as shown in Fig. 2c, was found to decrease by increasing the tellurium content over the whole composition range.

Taking into consideration the atomic weight of Se and Te (78.96 and 127.6, respectively), their atomic radii (1.91 and 2.11, respectively) and their electronegativity (2.55 and 2.1, respectively) as well as their crystalline lattice parameter values a and c ($a = 3.910$, $c = 5.080$ for Se) and ($a = 4.456$, $c = 5.921$ for Te), the results are acceptable. They confirm that both a and c appear to follow the usual known linear "Vegard behaviour" over the whole composition range of both selenium and tellurium in the prepared systems.

The decrease of c/a values by increasing the tellurium content can be explained by considering that the rate of change of the lattice parameter a was higher than that obtained for the change in the lattice parameter c, resulting in lower values of c/a when increasing the tellurium content. The values obtained for the lattice parameters a and c are in fair agreement with the JCPDS data for $BiSbTe_3$ [9] and of Masui et al. [10].

From the X-ray analysis measurements with the compound containing the higher content of tellurium, $BiSbTe_3$, it is clear from Fig. 3a that the particle size of the prepared thin film gradually decreased when increasing the annealing temperature over the range from 100 °C up to 250 °C. This characteristic indicates the decrease in crystallinity of the prepared thin film with the increase of the annealing temperature as reflected from the X-ray diffraction pattern shown in Fig. 1a.

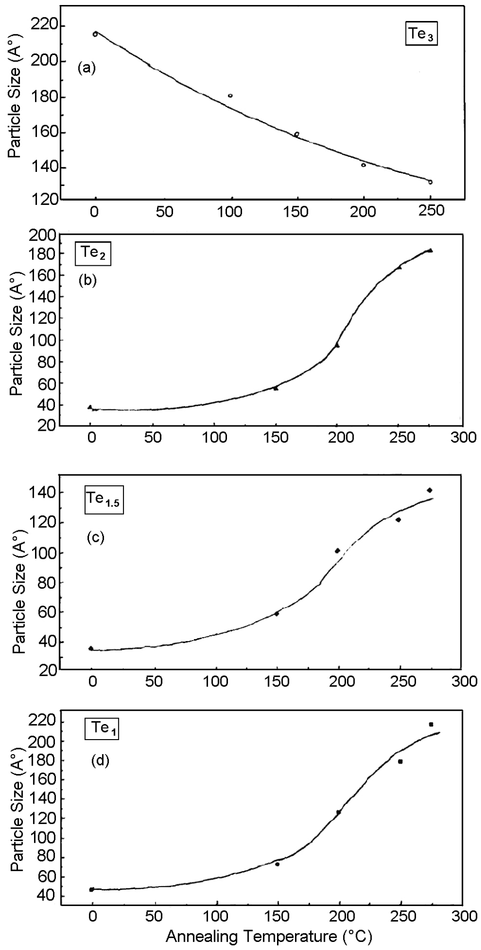
Taking into consideration the calculated strain values in relation to the annealing temperature, as shown in Fig. 4a, it can be stated that the strain also decreased by increasing the annealing temperature from 100 °C to 250 °C. This behaviour is acceptable regarding the fact that the strain generally decreased when raising the annealing temperature.

Replacing the tellurium gradually by selenium to prepare the composition of $BiSbTe_2Se$, it was found that the characteristic behaviour of the particle-size variation when increasing the annealing temperature was reversed, i.e. the particle size increased when increasing the annealing temperature.

Regarding the results for the strain of thin film of this compound, the same behaviour was obtained, i.e., the strain decreases when increasing the annealing temperature.

For the compound $BiSbTe_2Se$, the strain was found to be higher than that of the compound having no selenium ($BiSbTe_3$) for the same annealing temperature. This behaviour can be referred to the differences in both ionic radii and atomic weights of selenium and tellurium, as well as of their electronegativity.

By introducing selenium in place of tellurium to prepare the compounds having the composition $BiSbTe_{1.5}Se_{1.5}$ and $BiSbTeSe_2$, the same behaviour of the particle size variation with annealing temperature of both compounds was obtained as shown in Figs. 3.



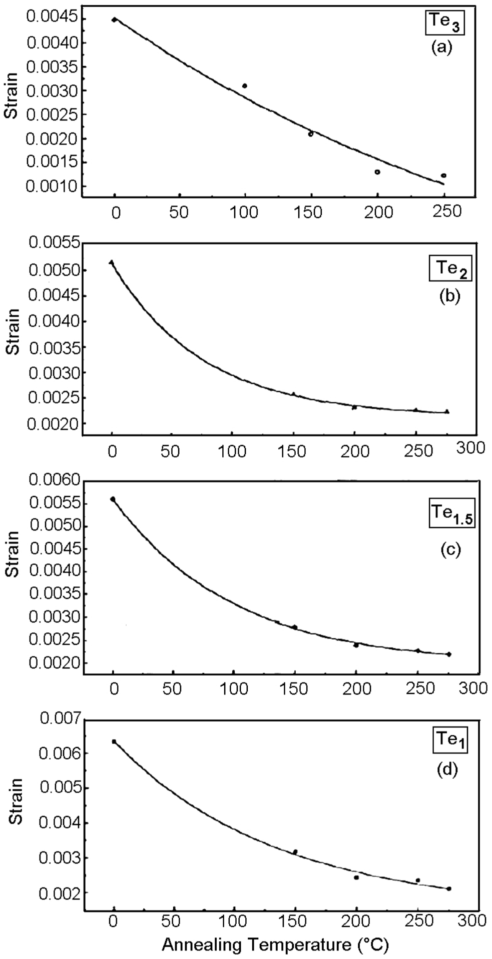


Fig. 3 (left). Variation of the particle size with annealing temperature for $BiSbTe_xSe_{3-x}$ *thin films.*

Fig. 4. Variation of the strain with annealing temperature for $BiSbTe_xSe_{3-x}$ *thin films.*

For $BiSbTe_{1.5}Se_{1.5}$, the particle size obtained at 100 °C was smaller than the particle size of $BiSbTeSe_2$ at the same annealing temperature. By increasing the annealing temperature, the particle size gradually increased, indicating the increase of the particle size when increasing the selenium content.

Concerning the strain variations when changing the annealing temperature for the compounds $BiSbTe_{1.5}Se_{1.5}$ and $BiSbTeSe_2$, it is quite clear that both compounds show the same behaviour, i.e. the strain decreased when increasing the annealing temperature over the full range of temperature.

It is also observed that the values of the strain obtained, for example, at 100 °C showed the same behaviour, that is to say, the strain increased by increasing the selenium content.

Generally, it can be stated that for this series of compounds, given by the formula $BiSbTe_xSe_{3-x}$, one can conclude the following characteristic behaviour: 1) Except the for the normality of Bi $SbTe_3$, the particle size increased by increasing the annealing temperature for the same selenium content, and by the increasing the selenium content at the same annealing temperature. 2) The strain was found to decrease by increasing the annealing temperature, whereas at the same annealing temperature the strain increased by increasing the selenium content.

4. Optical properties

The I.R. optical transmittance of the films deposited on KBr substrates were measured at room temperature.

Figure 5 illustrates the spectral behaviour of the observed transmittance of the $BiSbTe_xSe_{3-x}$ thin films with $x = 1, 1.5, 2$ and 3, in the wavelength range 2.5 − 10 μm. These curves show that the transmittance has low values (about 0.15 − 0.18) at $\lambda = 2.5$ μm, starts to increase with increasing λ, and reaches higher saturated values (from about 0.94 to about 0.98) at $\lambda = 9.1$ μm, indicating that absorption is negligible beyond the saturated transmittance values.

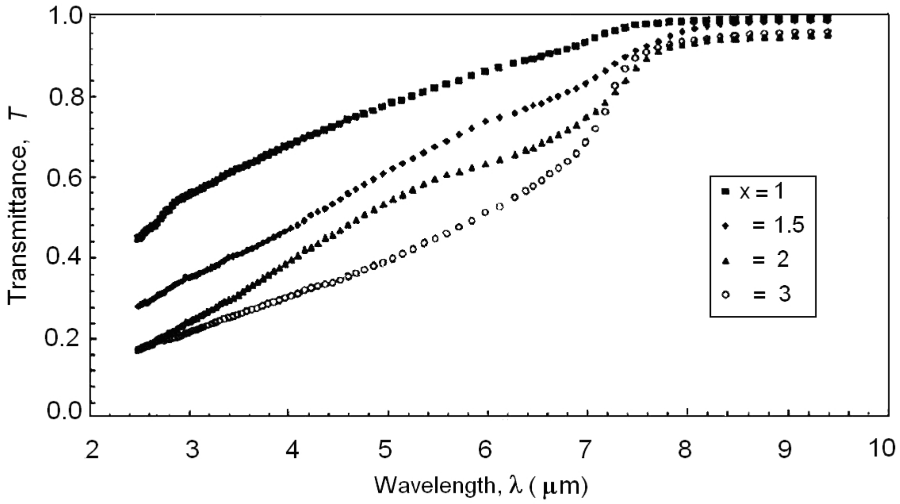


Fig. 5. Variation of the transmittance, T, with the wavelength λ for $BiSbTe_xSe_{3-x}$ *compounds.*

The absorbance of the film, $A_f = \log(I_0/I_f)$, can be determined either from the film transmittance, T_f, or from the difference between the measured values of the film plus the substrate absorbance and that of substrate absorbance ($A_{fs} - A_s$).

Since the absorbance is equal to the optical density [11], i.e.

$$A_{\rm fs} = \log(I_0/I_{\rm fs}) \quad \text{and} \quad A_{\rm s} = \log(I_0/I_{\rm s}) \,,$$

$$A_{\rm fs} - A_{\rm s} = \log(I_0/I_{\rm fs}) - \log(I_0/I_{\rm s}) = \log[(I_0/I_{\rm fs})/I_0/I_{\rm s})] = \log(I_{\rm s}/I_{\rm fs}) = A_{\rm f}$$

The absorption coefficient of the film $\alpha_{\rm f}$ can be derived from the absorbance, $A_{\rm f}$, where

$$\alpha_{\rm f} = A_{\rm f}/t_{\rm f} = (1/t_{\rm f}) \log(I_0/I_{\rm f})$$

where $t_{\rm f}$ is the thickness of the thin film. The variation of the computed absorption coefficient $\alpha_{\rm f}$ as a function of the photon energy ($h\nu$) for the different compositions ($BiSbTe_xSe_{3-x}$, $x = 1$, 1.5, 2 and 3) are shown in Figs. 6. The general features of the results for all compositions are that:

- The values obtained for α are fairly high (about 10^3 to 10^5 cm^{-1}) as in most semiconductors with a high carrier concentration.
- The values of α were found to increase with the increase of Te content at a certain $h\nu$ value.
- The absorption coefficient decreases sharply below a certain photon energy (about 0.2 eV), for all compositions of the system. This is quite reasonable, since near the fundamental absorption edge, the absorption coefficient varies rapidly with wavelength (frequency).

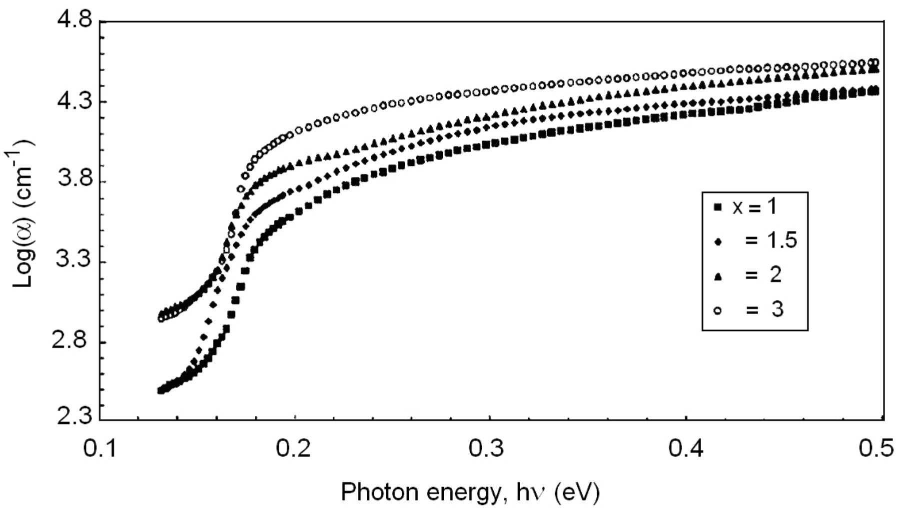


Fig. 6. Variation of the absorption coefficient (α) with the photon energy ($h\nu$) for different compositions $BiSbTe_xSe_{3-x}$.

4.1. Determination of the optical energy band gaps

The electronic transition between the valence and the conduction bands starts at the absorption edge, corresponding to the minimum energy difference between the lowest energy of the conduction band and the highest energy of the valence band in the crystalline materials. In the case of Bi-Sb salts, the extreme lies at the same point of k space and hence the transitions are of the direct type.

Therefore, the rise of α's in the photon energy range $h\nu < 0.22$ eV follows the relation

$$\alpha h\nu = A_1(h\nu E_{g1})^{1/2}$$

The variation of $(\alpha h\nu)^2$ with photon energy $h\nu$ for $BiSbTe_xSe_{3-x}$ films is shown in Figs. 7a, b, c and d for $x = 1$, 1.5, 2 and 3, respectively. One can see that the plots

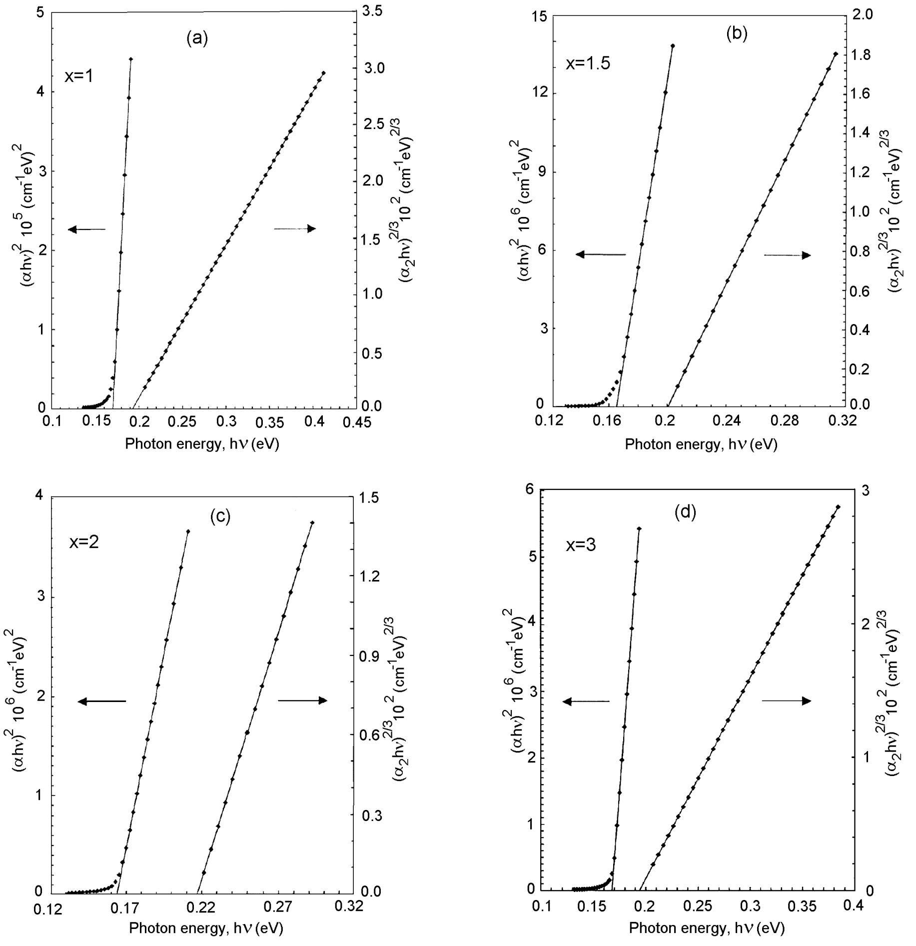


Fig. 7. Plot of $(\alpha h\nu)^2$ *and* $(\alpha h\nu)^{2/3}$ *vs.* $h\nu$ *for the compounds: a)* $BiSbTeSe_2$, *b)* $BiSbTe_{1.5}Se_{1.5}$, *c)* $BiSbTe_2Se$ *and d)* $BiSbTe_3$.

of $(\alpha h\nu)^2$ versus $h\nu$ are linear over a wide range of photon energies indicating the direct type transitions from the valence band maximum to the conduction band minimum. The intercepts of extrapolations of these plots (straight lines) on the energy axis give the energy band gaps. The dependence of the band gap, $E_{g1}(x)$, on composition is shown in Fig. 9 and is given in Table 1.

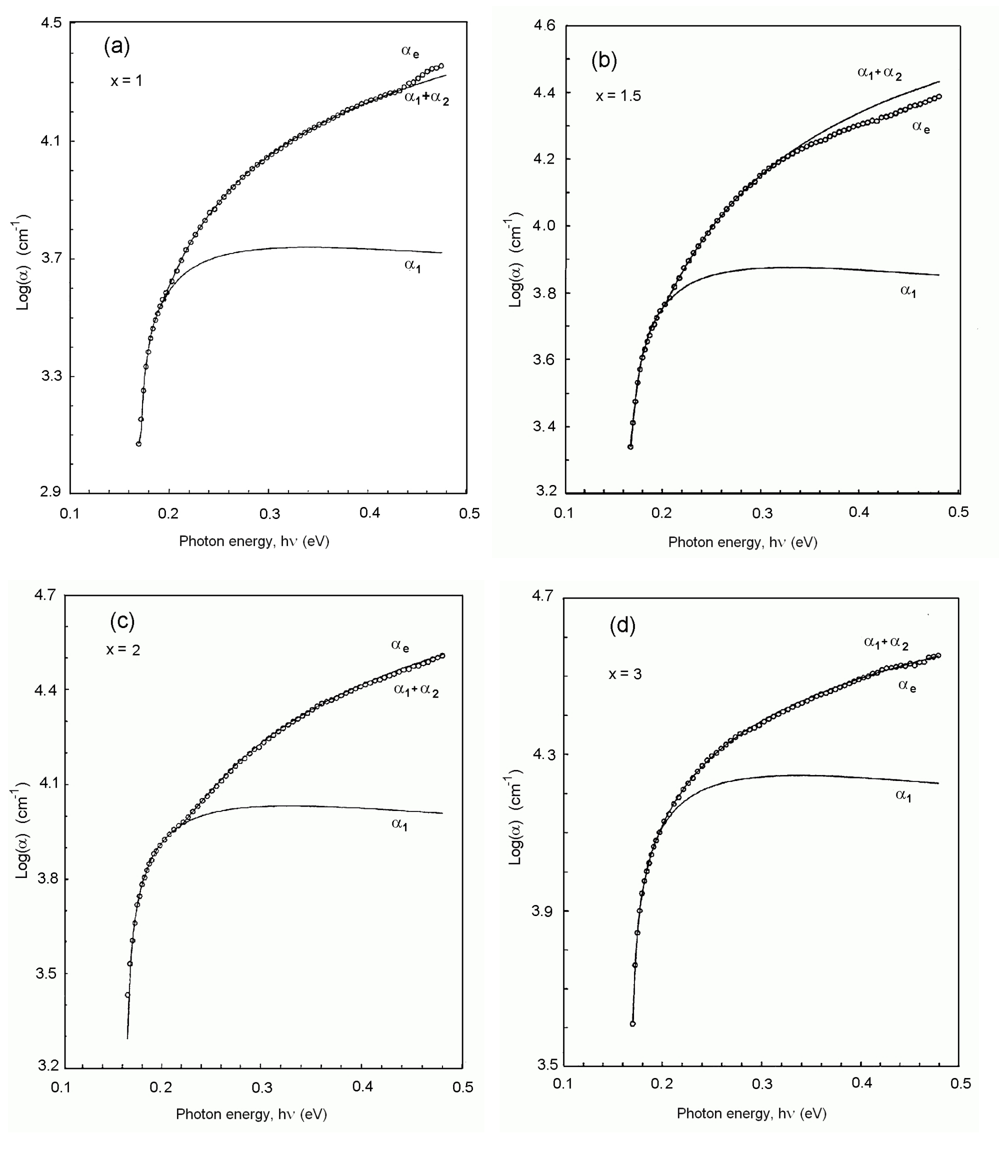


Fig. 8. Plot of $\log(\alpha)$ *vs.* $h\nu$ *for the compounds: a)* $BiSbTeSe_2$, *b)* $BiSbTe_{1.5}Se_{1.5}$, *c)* $BiSbTe_2Se$ *and d)* $BiSbTe_3$.

However, if we calculate α_1 for each x using A_1 and E_{g1} determined from Figs. 7a, b, c and d for energies above 0.22 eV, we find that α_1 is considerably smaller than the absorption coefficient, α, measured experimentally, as is shown in Figs. 8a, b, c and d for x = 1, 1.5, 2 and 3, respectively. This difference in α between the calculated and measured values indicates the existence of an additional absorption process. This additional absorption is characterized by an absorption coefficient $\alpha_2 = \alpha - \alpha_1$, i.e to the difference between the experimental absorption coefficient and the calculated one α_1. The analysis of the additional optical ab-

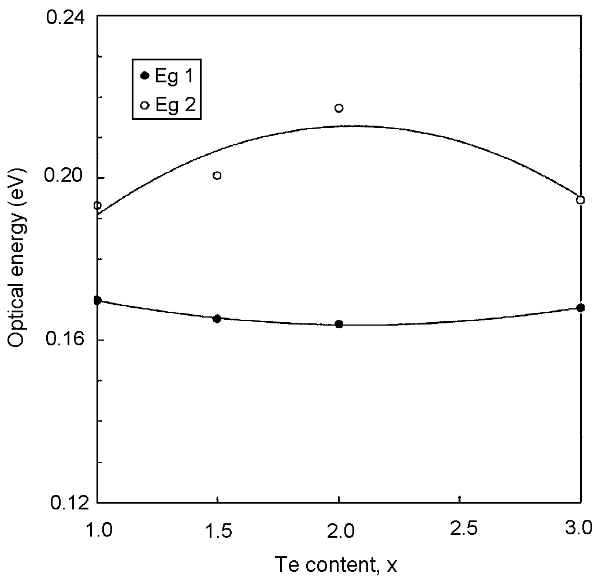


Fig. 9. The variation of the optical energy gaps as a function of composition of $BiSbTe_xSe_{3-x}$.

TABLE 1. The dependence of the optical band gaps of $BiSbTe_xSe_{3-x}$ *films on composition value, x.*

Mole fraction	Observed optical transitions	
x	E_{g1} (meV)	E_{g1} (meV)
1	169.9	192.5
1.5	165.2	200.4
2	163.7	217.0
3	167.7	194.1

sorption coefficient, $\alpha_2 = \alpha - \alpha_1$, showed that the dependence of α_2 on $h\nu$ can be described by the relation

$$\alpha_2 h\nu = A_2((h\nu E_{g1})^{3/2}$$

The variation of $(\alpha_2 h\nu)^{2/3}$ with photon energy for $BiSbTe_xSe_{3-x}$ films are also shown in Figs. 7a, b, c and d for $x = 1$, 1.5, 2 and 3 respectively. One can see that the plots $(\alpha_2 h\nu)^{2/3}$ versus $h\nu$ are linear over a wide range of photon energy up to about 0.5 eV, indicating a forbidden direct transition with a band gap E_{g2}, due to the transitions from the crystal-field-splitted valence band to the conduction band minimum. The extrapolations intercept of the straight line on the energy axis gives E_{g2}. Also, the compositional dependence of the direct forbidden transition due to the crystal field splitting of the conduction band $E_{g2}(x)$ are shown in Fig. 9 and is given in Table 1.

We calculated α_2 for each x using A_2 and E_{g2} determined from Figs. 7a, b, c and d and compared the sum $(\alpha_1 + \alpha_2)$ for each composition, x, to the corresponding observed one as shown in Figs. 8a, b, c and d. These curves show a good fit between the calculated values $(\alpha_1 + \alpha_2)$ and the observed values of α, indicating that other transitions are not present.

So, the analysis of the optical absorption spectra revealed two optical transitions, A and B, that correspond to the energy gaps E_{g1} and E_{g2} which are attributed to the fundamental absorption edge and the valence band splitting by crystal-field effects, respectively (as shown in Fig. 10).

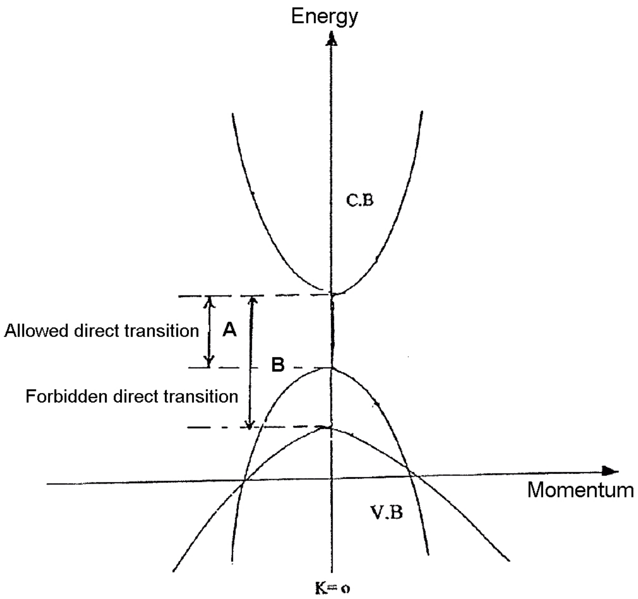


Fig. 10. Expected band structure of $BiSbTe_xSe_{3-x}$.

The dependence of the measured transition energies E_{g1} and E_{g2} on composition (shown in Fig. 9) shows a quadratic polynomial dependence characterized by the following relations:

$$E_A = (0.0051x^2 - 0.0213x + 0.186)\ \mathrm{eV}$$

and

$$E_B = (-0.02x^2 + 0.0821x + 0.128)\ \mathrm{eV}$$

Unfortunately, no previous data are known to have been reported for such compositions for a comparison to our reported results.

5. *Conclusions*

The narrow-gap semiconductors $BiSbTe_xSe_{3-x}$ ($x = 1$, 1.5, 2 and 3) have been prepared both in bulk and thin film forms. The prepared compound in the bulk form has the rhombohedral crystal structure with the hexagonal space group. By decreasing the selenium content, the lattice parameters c and a increase, while c/a decreases.

Analysis of the optical absorption spectra revealed the existence of two direct optical transitions with energy gaps E_{g1} and E_{g2} which were attributed to the fundamental absorption and the valence band splitting by crystal field effect. It was found that $BiSbTe_2Se$ has the lowest E_{g1} and the highest E_{g2}.

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KRISTALNA STRUKTURA I OPRIČKA SVOJSTVA SUSTAVA Bi-Sb-Te-Se

Sintetizirali smo sustave Bi-Sb-Te-Se sa četiri sastavnice izravnom metodom staljivanja. Tanke slojeve tih spojeva pripremali smo isparavanjem u vakuumu (na 10^{-4} Pa). Primjenom rendgenske difrakcije odredili smo strukturna svojstva praha i tankih slojeva tih spojeva. Optičke konstante tankih slojeva (koeficijent apsorpcije i procijep među vrpcama) odredili smo mjerenjem apsorpcije u području $2.5-10$ μm. Analiza optičkih apsorpcijskih spektara pokazuje dva izravna procijepa.