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Materials with Layered Structures. VIII*. Subsolidus Phase Diagram of the System $MnIn_2S_4$–$MnIn_2Se_4$ and Characterization of the Layered Materials $MnIn_2S_xSe_{4-x}$ by Electrical Measurements and Diffuse Reflectance Spectroscopy

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In the quasibinary system $MnIn_2S_4$–$MnIn_2Se_4$ a series of solid solutions of general formula $MnIn_2S_xSe_{4-x}$ exists for $2.4 \geq x \geq 0.2$ with the layered $MgAl_2S_4$ structure. The samples have been characterized by X-ray powder diffraction and investigated by electrical measurements and diffuse reflectance spectroscopy. The compounds are semiconductors with optical band gaps varying between 1.6 and 1.2 eV depending on x. From Arrhenius plots of the conductivity data at least two different activation energies E_a can be obtained: in the temperature interval from 50 to 200°C we find $E_a = 0.5$ eV, independent of the composition of the samples, while in the high temperature region from 200 to 400°C, E_a varies with x from 1.35 to 0.56 eV.

1. Introduction

Some years ago we reported on the new compound $MnIn_2S_2Se_2$ which we found, from X-ray powder diffraction data, to crystallize in the layered centrosymmetric $MgAl_2S_4$-type rather than in the acentric $ZnIn_2S_4$(IIIa) structure (*1*). Recently Range *et al.* (2) found a polymorph of $MnIn_2Se_4$, one of the end-member compounds in the system studied in this paper, which crystallizes in the $MgAl_2S_4$-type as well, thus confirming our previous finding.

According to preliminary results given in our previous paper the material $MnIn_2S_2Se_2$ has a large phase width with respect to the S/Se ratio. In this paper we report on the subsolidus phase diagram of the system $MnIn_2S_4$–$MnIn_2Se_4$ and on the optical and electrical properties of the layered materials of $MnIn_2S_2Se_2$-type in the near-infrared and visible region.

2. Experimental Details

Samples of $MnIn_2S_xSe_{4-x}$ with $0 \leq x \leq 4$ were prepared by sintering stoichiometric mixtures of the binary sulfides in evacuated, sealed silica ampoules at 800°C. After a reaction time of 3 days the samples were homogenized and fired again for 3 days. After the second heat treatment the compounds were quenched to room temperature.

Structural studies of the powdered products were made by X-ray investigations with CuKα_1 radiation. The unit-cell dimensions were computed from Guinier radiographs obtained from an Enraf-Nonius Guinier IV camera using α-SiO_2 as internal standard ($a = 491.36$, $c = 540.54$ pm) and refined by the program LSUCR (*3*).

The electrical conductivity of the samples

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was measured by impedance spectroscopy in the frequency range 10 Hz–13 MHz using a computer-controlled impedance analyzer HP 4192ANF. The temperature of the sample was varied between room temperature and 440°C in steps of about 15°. Specimens for the impedance measurements were prepared by pressing fine powders of the samples (ca. 0.3 g) into cylindrical pellets of 13 mm diameter at 800 MPa. The density of these pellets was 90–95% of the theoretical density calculated from X-ray data. Contact with the pellets was made through platinum foils pressed against the pellet by pestles made from stenan. The whole sample holder was placed in a glass tube which was flushed with argon.

The diffuse reflectance spectra were recorded in the wavelength range 2500–400 nm using a Zeiss spectrophotometer DMR 21 for the room temperature measurements and a Zeiss PMQII for the low temperature investigation at 5 K. From 2500 to 1000 nm Sr_2ZnTeO_6 was used as standard material and from 1000 to 400 nm MgO. The reflectance spectra were evaluated according to Kubelka–Munk (*4*) to obtain the dispersion of the absorption coefficient.

3. Results

3.1. The System $MnIn_2S_4$–$MnIn_2Se_4$

The X-ray powder diffraction patterns of the quaternary compositions in the system $MnIn_2S_4$–$MnIn_2Se_4$ show the existence of three different phases. Additional to the two end-member compounds $MnIn_2S_4$ (*5*) and $MnIn_2Se_4$ (*2, 6*), there is a third phase with a powder pattern characteristic of compounds crystallizing in the $ZnIn_2S_4$(IIIa)-type (*7*) or in the $MgAl_2S_4$-type (*8*). By analogy with the results of Range *et al.* (*2*) we assume that this phase adopts the centrosymmetric $MgAl_2S_4$-structure.

The lattice constants obtained for the different phases in the samples of different composition are tabulated in Table I. The powder diffraction data of $MnIn_2Se_4$ could be indexed on the basis of the orthorhombic lattice given by Neumann *et al.* (*11*) with $a = 1326.7(7)$, $b = 1244.7(5)$ and $c = 1664(2)$ pm. From these data one can see that (i) single phase samples with spinel structure can be obtained for $3 \leq x \leq 4$, (ii) the second end-member compound $MnIn_2Se_4$ has no detectable phase width, (iii) single phase compounds with the layered $MgAl_2S_4$ structure are formed between $x = 2.4$ and $x = 0.2$ and (iv) no two phase region could be obtained between $MnIn_2Se_4$ and the sample with $x = 0.2$. As would be expected from Vegard's law, the lattice parameters of the layered mixed crystals as well as of those with a spinel structure show a linear dependence on the composition.

TABLE I

LATTICE PARAMETERS OF $MgAl_2S_4$-TYPE AND SPINEL-TYPE PHASES IN THE SYSTEM $xMnIn_2S_4$–$(4 - x)$ $MnIn_2Se_4$

		$MgAl_2S_4$-type	
x	Spinel-type a(pm)	a(pm)	c(pm)
0.2	—	404.8(1)	3946.0(20)
0.4	—	404.1(1)	3932.0(20)
0.6	—	403.1(1)	3931.0(20)
0.8	—	402.6(1)	3921.0(20)
1.0	—	401.6(1)	3909.1 (8)
1.2	—	401.2(1)	3903.8 (7)
1.4	—	400.2(1)	3892.0(10)
1.6	—	399.4(1)	3882.1 (5)
1.8	—	398.5(1)	3875.0(10)
2.0	—	397.7(1)	3860.0(10)
2.2	—	396.9(1)	3856.0(20)
2.4	—	396.4(1)	3846.2 (5)
3.0	1084.6(1)	—	—
3.2	1083.0(1)	—	—
3.4	1079.9(1)	—	—
3.6	1078.0(1)	—	—
3.8	1075.7(1)	—	—

3.2. Electrical Conductivity of Mixed Crystals with the $MgAl_2S_4$ Structure

A typical impedance diagram of a specimen prepared by the above mentioned method is shown in Fig. 1a. It is made up of two overlapping semi-circles resulting from

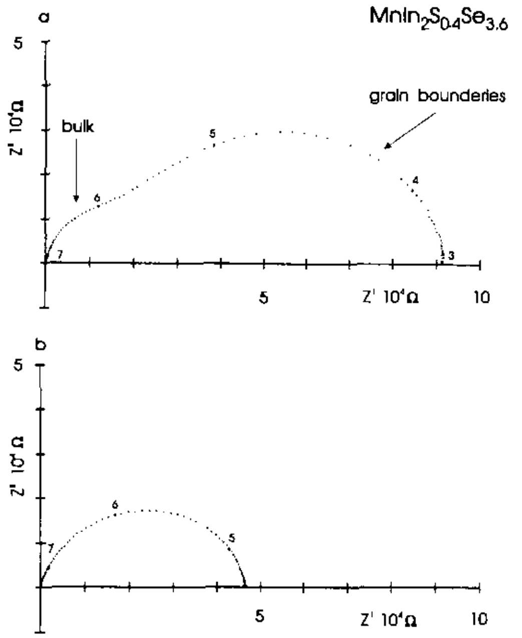

FIG. 1. Impedance diagram of $MnIn_2S_{0.4}Se_{3.6}$ of (a) a cold pressed sample and (b) after annealing the pellet at 920°C.

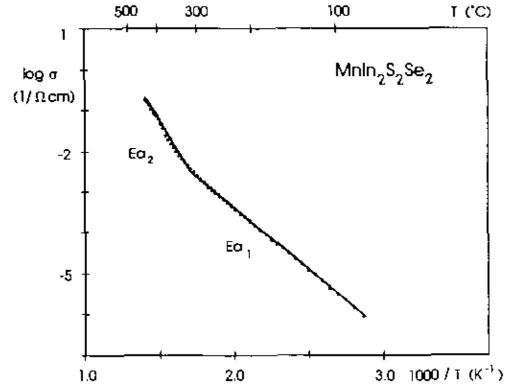

FIG. 2. Temperature dependence of the electrical conductivity of $MnIn_2S_2Se_2$.

the conductivity of the bulk and the grain boundaries. To reduce the effect of the grain boundaries the pellets were sintered at 920°C for two days in evacuated silica ampoules prior to the measurement. By this treatment the density of the pellets increased to 96–98% of the theoretical density. The impedance diagrams of these sintered samples consist of only one semicircle (see Fig. 1b).

The DC resistances R of the pellets were obtained by extrapolation of the semicircles to the real axis. The specific resistances of the samples R_S were computed from these values by multiplication with the cell constants obtained from the ratios of surface area and thickness of the pellets and corrected for the deviation of the density of the specimen from the theoretical density. The specific resistances of the different samples are about 106 Ω · cm at 50°C and decrease with increasing temperature to about 10 Ω · cm at 400°C.

The specific conductivities $\sigma = 1/R_s$ were plotted as an Arrhenius plot, i.e. log σ vs $1/T$. An example of these plots is shown in Fig. 2. The Arrhenius plots consisted of at least two regions with linear dependence of the conductivity on the reciprocal temperature. Activation energies computed from the different slopes of the linear parts of the plot are summarized in Table II.

The activation energies at low temperatures are independent of the composition and only those energies obtained at temperatures above 300°C exhibit a marked depen-

TABLE II

ACTIVATION ENERGIES E_a [eV] OF THE ELECTRICAL CONDUCTIVITY AND ENERGY GAPS OBTAINED FROM EXTRAPOLATION (E_g(ex)) OR MCLEAN ANALYSIS (E_g(McL)) OF THE DIFFUSE REFLECTANCE SPECTRA OF SAMPLES IN THE SYSTEM $MnIn_2S_xSe_{4-x}$

Sample x	E_a	Temperature interval (°C)	E_g(ex)	E_g(McL)
2.4	0.4	69–231		
	0.7	239–341		
	1.3	348–443	1.5	1.6
2.0	0.6	84–290		
	1.2	324–442	1.5	1.6
1.6	0.6	76–195		
	0.5	202–283		
	1.0	290–443	1.4	1.5
1.2	0.6	69–290		
	0.9	312–443	1.3	1.4
0.8	0.4	39–136		
	0.6	180–443	1.2	1.3
0.4	0.5	29–128		
	0.6	136–443	1.1	1.3

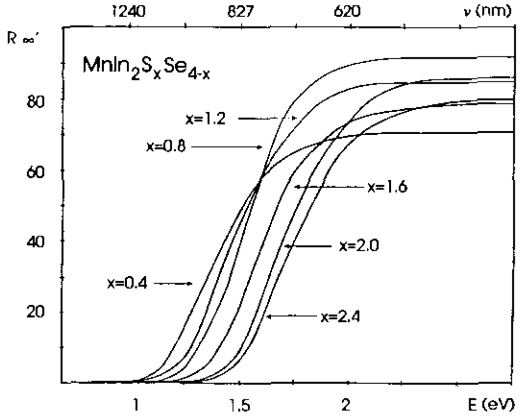

FIG. 3. Diffuse reflectance spectra of the solid solutions $MnIn_2S_xSe_{4-x}$.

dence on the S/Se ratio in the compounds. To obtain the band gap energies, the activation energies have to be multiplied by a factor 2.

3.3 NIR/VIS-Spectra of Mixed Crystals with the $MgAl_2S_4$ Structure

The diffuse reflectance spectra of single phase samples of $MnIn_2S_xSe_{4-x}$ with x = 0.4, 0.8, 1.2, 1.6, 2.0, and 2.4 are shown in Fig. 3. The spectra show only one absorption due to the excitation of electrons from the valence band to the conduction band. From these spectra the band gap energies can be obtained by extrapolation of the steep edges to the baselines (*9*). The values for the optical band gaps obtained by this method are tabulated in Table II.

In the diffuse reflectance spectra measured at 5 K for $x = 2.0$, 1.2, and 0.4, the absorption edges are shifted to higher energies by about 0.1 eV. The values obtained by the extrapolation method are 1.6, 1.4 and 1.3 eV, respectively.

4. Discussion

As already claimed in our previous paper on $MnIn_2S_2Se_2$ (*1*) this layered material exhibits a relatively large region of homogeneity with respect to the S/Se ratio. As the site preferences of Mn^{2+} and In^{3+} will not be altered dramatically by exchange of only a small part of selenium by sulfur, we assume according to the result of the determination of the structure of $MnIn_2Se_4$ (*2*) that the quaternary compounds also have the centrosymmetric $MgAl_2S_4$ structure, i.e., the same cation distribution as the pure selenium compound. But contrary to the finding of Range *et al.* (*2*) we were not able to prepare the end member compound $MnIn_2Se_4$ in the modification described by those authors. An extrapolation of the lattice constants given in Table I to $MnIn_2Se_4$ results in a = 405.5 and c = 3960 pm, where especially the c-axis is larger by 14 pm than the one given in (*2*). This may be caused by a certain amount of nonstoichiometry due to the chemical transport reaction by which the sample used for the structure determination was prepared. Perhaps some In^{3+} has been replaced by Al^{3+} from the transporting agent $AlCl_3$.

From the temperature dependence of the electrical conductivity of the mixed crystals and the nature of the optical absorption it is revealed that the materials studied are semiconductors. The activation energies obtained from the electrical measurements at temperatures between room temperature and about 250°C are independent of the composition and probably are due to defects within the forbidden gap.

Analysis of the diffuse reflectance spectra according to McLean (*10*), assuming the scattering coefficient to be constant over the interesting wavelength range, by plotting the absorption coefficient α^n for $n = 2, \frac{2}{3}, \frac{1}{2}$ and $\frac{1}{3}$ vs energy of the radiation did not result in really good straight lines over a wider wavelength range for all values of n. As the best agreement between the band gap energies obtained by this analysis and those determined by the extrapolation method (*9*) is found for $n = 2$ these values are includes in Fig. 4.

For the orthorhombic form of $MnIn_2Se_4$ Neumann *et al.* (*11*) found an indirect transition at 1.378 eV followed by a second one

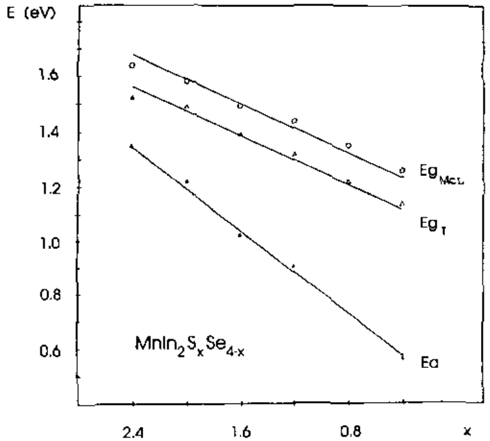

FIG. 4. Plot of the optical band gaps obtained from the diffuse reflectance spectra by extrapolation, E_g(T), and by the McLean analysis, E_g(McL), and activation energies for the electrical conductivity (E_a) vs composition of the solid solutions $MnIn_2S_xSe_{4-x}$.

at 1.56 eV which is supposed to be direct. The difference between these values and that expected for a $MnIn_2Se_4$ with $MgAl_2S_4$ structure by an extrapolation of our data (1.1–1.2 eV), suggest the conlusion that the band structures near the fundamental absorption edge of both modifications are totally different.

The absorption edges obtained by the extrapolation method and by the McLean analysis and the activation energies for the electrical conductivity are plotted vs the composition of the mixed crystals in Fig. 4. There is a linear dependence of the gap energies on the S/Se ratio with a shift to lower energies with increasing selenium content of the mixed crystals. The activation energies obtained by conductivity measurements in the high temperature range show the same dependence on the composition (see Fig. 4), but with a steeper slope: while for the selenium-rich samples the activation energies are half that of the optical gap, as that should be according to the theory for intrinsic semiconductors, the sulfur-rich compounds show a much wider thermal band gap. This finding is not understood until now but we will investigate this effect further by either Hall effect measurements or by an investigation of the spectral dependence of the photoconductivity.

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