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Structure and electrical properties of $In_2Se_3\langle Mn\rangle$ layered crystals

V.M. Kaminskii, Z.D. Kovalyuk, A.V. Zaslonkin, and V.I. Ivanov
I.M. Frantsevich Institute for Problems of Materials Science, NAS of Ukraine, Chernivtsi Department
5, Iryna Vilde str., 58001 Chernivtsi, Ukraine,
Phone: (0372)52-51-55, fax (03722) 3-60-18: e-mail: chimsp@ukrpost.ua

Abstract. Investigations of the crystalline structure and electrical properties of $In_2Se_3\langle 1$ wt. %Mn$\rangle$ and $In_2Se_3\langle 6$ wt. % Mn$\rangle$ crystals have been carried out. We have found formation of a substitutional solid solution for $In_2Se_3\langle 1$ % Mn$\rangle$ single crystals as well as existence of two phases (In_2Se_3 and $MnIn_2Se_4$) in polycrystalline ingots $In_2Se_3\langle 6$ % Mn$\rangle$. Temperature dependences of the conductivities across ($\sigma_{\perp C}$) and along ($\sigma_{\parallel C}$) the crystallographic *c* axis were measured in the range of 80 to 400 K. From the anisotropy $\sigma_{\perp C}/\sigma_{\parallel C}$ of conductivity temperature dependences of the energy barrier value ΔE_δ between the layers were calculated for the crystals under investigations.

Keywords: indium selenide, layered crystal, X-ray diffraction, substitutional solid solution, conductivity.

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1. Introduction

In_2Se_3 compound belongs to the group of semiconductor materials with a layered crystal structure. In_2Se_3 single crystals can be used for fabrication of ionizing radiation detectors, solid-state electrodes, photosensitive heterostructures. It is known that α-, β-, and γ- phases of In_2Se_3 exist [1], and the phase transition $\alpha \rightarrow \beta$ takes place at the temperature ≈ 200 °C, while $\beta \rightarrow \gamma$ occurs at ≈650 °C. According to [1], the α-In_2Se_3 phase has a hexagonal structure with the unit cell parameters $a = 4.0$ and $c = 19.24$ Å, whereas in [2] it was found that the structure of the phase is trigonal (the *R*3*mH* spatial group) with $a = 4.05$ and $c = 28.77$ Å.

Electrical properties of crystalline In_2Se_3 differ essentially, which is related to the technique of growing the crystals [1, 3, 4]. In particular, in [4] investigations of the electrical properties of In_2Se_3 single crystals doped with Cd, I, and Cu were carried out to have crystals with a wide spectrum of physical properties and suitable for application in optoelectronics. As to behaviour of Mn, as a magnetic dopant, in layered crystals, note that doping the InSe single crystals with manganese results in appearance of ferromagnetic interaction between Mn ions [5].

In this work, we present the investigations of the crystalline structure and electrical properties of In_2Se_3 crystals doped with Mn aimed to receive materials suitable for application in spintronics at room temperature.

2. Experimental

The doped $In_2Se_3\langle Mn\rangle$ single crystals were grown by the Bridgman method from stoichiometric melts in silica ampoules of 12 mm in diameter. Doping with manganese was carried out adding the dopant in the amounts 1 and 6 wt. % to the charge before synthesis of the compound. The rate of the growth of the ingots was 1 mm/h at the temperature gradient at the crystallization front of 15 °C/cm. Determination of the crystal structure of the grown single crystals was performed by using a DRON-3 installation in CuK_α-radiation. The obtained X-ray diffraction patterns have been analyzed by using a LATTIK-KARTA software. The Mn content and its distribution along the grown $In_2Se_3\langle 6$ % Mn$\rangle$ single crystal was determined by the X-ray fluorescence analysis by means of a TRACOR installation.

Electrical properties of $In_2Se_3\langle 1$ % Mn$\rangle$ and $In_2Se_3\langle 6$ % Mn$\rangle$ were measured in the temperature range 80 to 400 K. The samples for conductivity measurements along the layers $\sigma_{\perp C}$ had dimensions 11×2.5×0.75 mm with the conventional geometry of six contacts deposited by soldering with high purity indium. The measurements of the conductivity across the layers $\sigma_{\parallel C}$ were carried out by using a four-probe method with the contacts located at the opposite sides of the samples: two of them covered almost the whole cleavage surfaces and were used as current contacts, and two others close to them small-area contacts − as the probe ones.

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3. Results and discussions

Fig. 1a, b shows the X-ray diffraction patterns of $In_2Se_3\langle 1\ \%\ Mn\rangle$ and $In_2Se_3\langle 6\ \%\ Mn\rangle$ crystals registered from cleavage surfaces of the both ingots. For the $In_2Se_3\langle 1\ \%\ Mn\rangle$ single crystal the X-ray diffraction pattern (Fig. 1a) shows the reflections 00*l* (*l* = 6, 9, 12, 15, 18). The presence of an additional peak at 2θ = 26.5° is an evidence of the presence of selenium microinclusions. The measured parameters of the unit cell of the $In_2Se_3\langle 1\ \%\ Mn\rangle$ single crystal are $a = 4.000 \pm 0.003$ and $c = 28.330 \pm 0.009$ Å, which is some less than the lattice parameters for undoped In_2Se_3 [2]. So, one can assume the formation of $In_2Se_3\langle 1\ \%\ Mn\rangle$ substitutional solid solution because of the substitution of In atoms with those of Mn much less in size (the atomic radii of 1.63 and 1.37 Å, respectively [6]).

Fig. 1b shows the registered *hkl* reflections for $In_2Se_3\langle 6\ \%\ Mn\rangle$, which indicates polycrystalline structure of the grown crystal. From the carried out indexing of the X-ray diffraction pattern in Fig. 1b, we have found the existence of two phases in the grown ingot: α-In_2Se_3 and $MnIn_2Se_4$ of the trigonal structure (*R*3*mH* spatial group). The calculated interlayer distances d_{calc} determined on the basis of the α-In_2Se_3 and $MnIn_2Se_4$ lattice parameters [2, 7] as well as the experimental ones d_{exp} obtained from Fig. 1b are listed in Table. The measured values of the lattice parameters for α-In_2Se_3 ($a = 4.025$ and $c = 28.771$ Å) and $MnIn_2Se_4$ ($a = 4.052$ and $c = 39.420$ Å) are in good agreement to the data of [2, 7]. From our analysis of the intensities of all the registered reflections from α-In_2Se_3 and $MnIn_2Se_4$, it is determined that the content of these phases is 53.26 and 46.74 %, respectively. The carried out X-ray fluorescence analysis of the distribution of Mn impurity has shown that the content of Mn in the crystal $In_2Se_3\langle 6\ \%\ Mn\rangle$ increases monotonously from 0.83 at. % at the beginning of the ingot to 2 at. % near its end. The total amount of the dopant in the ingot was determined as 1.174 at. %. The presence of excess indium in the studied crystals was not found.

It is necessary to note that at the formation of $MnIn_2Se_4$ the next reaction $3Mn + 4In_2Se_3 = 3In_2MnSe_4 + 2In$ should take place between the initial components. We have carried out calculations and plotted dependences of weight content of the solid phases In_2Se_3, $MnIn_2Se_4$, and In on the amount of reacted Mn (in the range 0-8 %). It was ascertained that due to interaction between 4 % Mn and 96 % In_2Se_3, the mixture of In_2Se_3 (51 %), $MnIn_2Se_4$ (44 %), and In (5 %) was created. These data are in agreement to the results of X-ray structure and fluorescence analysis. One can assume that not reacted Mn and segregated In are rejected to the end of the ingot during growing the crystal. After interaction of 6 % Mn and 94 % In_2Se_3, the content of solid phases is as follows: 26.07 % In_2Se_3, 65.57 % $MnIn_2Se_4$, and 8.36 % In.

Table. The experimental d_{exp} and calculated d_{calc} values of the interlayer distances diffraction peaks for In_2Se_3 and $MnIn_2Se_4$.

In_2Se_3			$MnIn_2Se_4$		
hkl	d_{calc}, Å	d_{exp}, Å	*hkl*	d_{calc}, Å	d_{exp}, Å
003	9.591	9.586	006	6.577	6.567
006	4.795	4.787	009	4.385	4.370
009	3.197	3.192	012	3.454	3.454
104	3.151	3.135	104	3.306	3.301
107	2.668	2.659	00.12	3.289	3.281
00.12	2.398	2.397	015	3.206	3.204
10.10	2.224	2.220	107	2.979	2.975
01.11	2.097	2.093	018	2.859	2.857
110	2.020	2.025	00.15	2.631	2.630
113	1.981	1.970	01.11	2.508	2.504
00.15	1.918	1.919	10.13	2.296	2.295
10.13	1.872	1.870	01.14	2.197	2.196
116	1.865	1.858	116	1.936	1.936
00.18	1.598	1.598	00.21	1.879	1.877
			00.24	1.6443	1.6438
			11.15	1.6050	1.6055

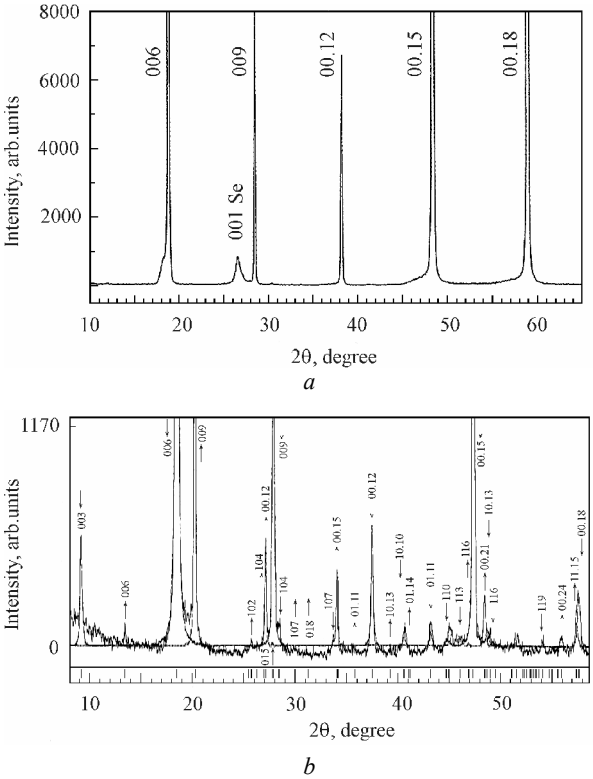

Fig. 1. X-ray diffraction patterns of $In_2Se_3\langle 1$ wt. % Mn$\rangle$ (a) and $In_2Se_3\langle 6$ wt. % Mn$\rangle$ (b) crystals in Cu-K_α- radiation. Diffraction lines of In_2Se_3 are marked as ↓ and those of $MnIn_2Se_4$ – as ↑.

The temperature dependences of the conductivity along ($\sigma_{\parallel C}$) and across ($\sigma_{\perp C}$) the crystallographic *c* axis of In_2Se_3, $In_2Se_3\langle 1\ \%\ Mn\rangle$, and $In_2Se_3\langle 6\ \%\ Mn\rangle$ samples are shown in Fig. 2a, b. It is necessary to note that the undoped In_2Se_3 sample has *n*-type conductivity with the free electron concentration $n = 4.9 \cdot 10^{17}$ cm^{-3} and the Hall electron mobility along the layers $\mu_{\perp C} = 405$ cm^2/V·s at

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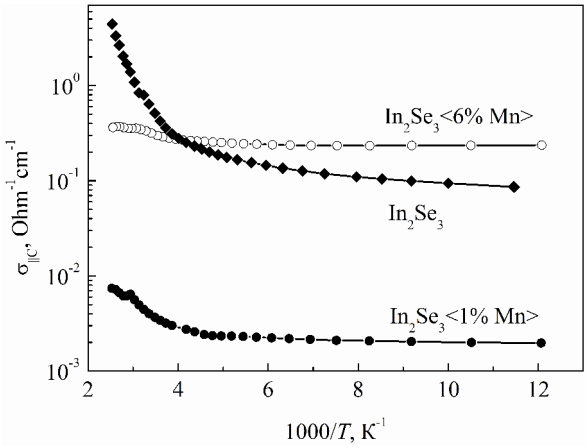
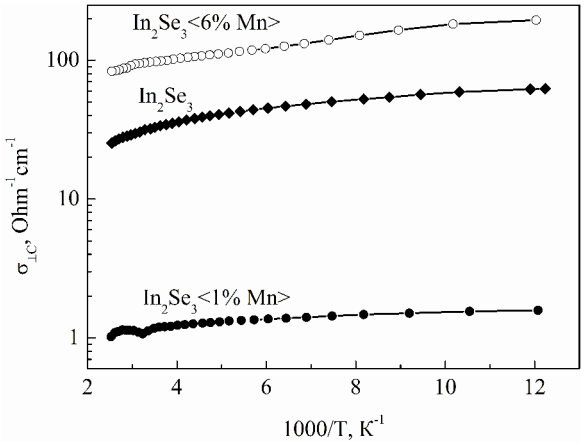


a



b

Fig. 2. The temperature dependences of conductivities $\sigma_{\|C}$ (a) and $\sigma_{\perp C}$ (b) for In_2Se_3, $In_2Se_3\langle 1$ wt. % Mn$\rangle$, and $In_2Se_3\langle 6$ wt. % Mn$\rangle$ crystals.

room temperature. The values of the conductivity components are $\sigma_{\|C} = 0.7$ and $\sigma_{\perp C} = 32$ Ohm^{-1}cm^{-1} at $T =$ 300 K. As follows from Fig. 2a, b, the temperature dependences of the $\sigma_{\|C}$ and $\sigma_{\perp C}$ components differ essentially and demonstrate semiconductor and "metallic" character, which is caused by a distinction in the charge transport mechanisms in the different crystallographic directions. It is possible to suppose that the semiconductor character of $\sigma_{\|C}(T)$ is related to a preferable increase of the electron concentration n, whereas the metallic character of $\sigma_{\perp C}(T)$ is caused by a prevailing decrease of the mobility $\mu_{\perp C}(T)$ over the increase of n. The observed decrease of $\sigma_{\|C}$ and $\sigma_{\perp C}$ values for the $In_2Se_3\langle 1$ % Mn$\rangle$ sample in the whole temperature range can be explained by a decrease of the mobility due to scattering of carriers on spatial inhomogeneities caused by formation of substitutional solid solution and the presence of selenium microinclusions.

For the two-phase polycrystalline sample of $In_2Se_3\langle 6$ % Mn$\rangle$, we have found that the conductivities $\sigma_{\|C}$ and $\sigma_{\perp C}$ are increased nearly by two orders of magnitude over the whole temperature range in comparison to that with 1 wt. % of manganese. One can suppose that in this case the conductivity mechanism has a complex character and is caused by the presence of In_2Se_3 and $MnIn_2Se_4$ grains as well as by possible influence of the intercrystallite boundaries on the charge transport processes. As the resistivity of the $MnIn_2Se_4$ phase is higher than that for In_2Se_3 [8], the increase of the conductivity components $\sigma_{\|C}$ and $\sigma_{\perp C}$ for $In_2Se_3\langle 6$ % Mn$\rangle$ in comparison to In_2Se_3 can be considered as caused by an increase of different type defects, the aggregation of which creates drain channels for trapped charge. A generalized barrier model predicts both an increase and decrease of the resistivity of polycrystalline samples in comparison to single crystals [9].

The temperature dependences of the conductivity anisotropy for $In_2Se_3\langle 1$ % Mn$\rangle$ and $In_2Se_3\langle 6$ % Mn$\rangle$ samples (Fig. 3) show the increase of $\sigma_{\perp C}/\sigma_{\|C}$ with decreasing temperature over the whole temperature range. In comparison to the data from [4] for undoped In_2Se_3 (the anisotropy ratio is 660 and 450 at 80 and 300 K, respectively), there is an increase of the conductivity anisotropy due to doping with Mn.

High values of the conductivity anisotropy in layered crystals are caused by peculiarities of the energy bands forming the edge of fundamental absorption [10] as well as by the influence of structural defects on charge transport processes. The presence of weak Van der Waals coupling between the layers promotes localization of impurities in octahedral and tetrahedral sites in the interlayer spaces and also the formation of stacking faults. The planar structure defects form additional energy barriers ΔE_δ for the transport of charge carriers along the crystallographic c axis. In this case, according to [11] the anisotropy ratio can be written as

$$\frac{\sigma_{\perp C}}{\sigma_{\|C}} \approx \exp\frac{\Delta E_\delta}{kT}. \qquad (1)$$

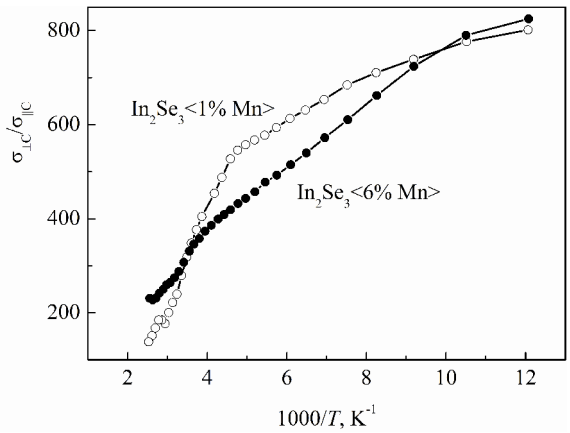


Fig. 3. Temperature dependences of the conductivity anisotropy $\sigma_{\perp C}/\sigma_{\|C}$ for $In_2Se_3\langle 1$ wt. % Mn$\rangle$ and $In_2Se_3\langle 6$ wt. % Mn$\rangle$ crystals.

Here, k is the Boltzmann constant. To determine the magnitude of this barrier, the conductivity anisotropy temperature dependences were plotted in the coordinates of Arrhenius ($\ln(\sigma_{\perp C}/\sigma_{\|C})$ *vs* $10^3/T$). From the slopes in the low temperature range, we have found that ΔE_δ is

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equal to 5.5 and 18 meV for the $In_2Se_3\langle 1\ \%\ Mn\rangle$ and $In_2Se_3\langle 6\ \%\ Mn\rangle$ samples, respectively.

4. Conclusions

From the X-ray investigations, we have established the formation of a substitutional solid solution in $In_2Se_3\langle 1\ \%\ Mn\rangle$ single crystals as well as the existence of two phases In_2Se_3 (53.26 %) and $MnIn_2Se_4$ (46.74 %) in polycrystalline $In_2Se_3\langle 6\ \%\ Mn\rangle$ ingots.

The obtained temperature dependences of the conductivity components $\sigma_{\|C}$ and $\sigma_{\perp C}$ have semiconductor and "metallic" behaviour, respectively, and their values increase with increasing the dopant content.

The high values of the conductivity anisotropy $\sigma_{\perp C}/\sigma_{\|C}$ are caused by the presence of structural defects localized in the interlayer space of the crystals. The energy barrier value ΔE_δ between the layers estimated from the $\sigma_{\perp C}/\sigma_{\|C}$ temperature dependences in the low temperature range is equal to 5.5 and 18 meV for $In_2Se_3\langle 1\ \%\ Mn\rangle$ and $In_2Se_3\langle 6\ \%\ Mn\rangle$ crystals, respectively.

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