Optical properties of $(3HgSe)_{0.5}(In_2Se_3)_{0.5}$ crystals doped with Mn or Fe

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Abstract. The mean refractive index and the reflection coefficient of $(3HgSe)_{0.5}(In_2Se_3)_{0.5}$ crystals doped with Mn and Fe have been investigated basing on the studies of their optical reflectance and transmittance at the room temperature and the wavelengths of 0.9–26.6 μm. The influence of temperature on the optical transmittance has been studied in the interval of 125–300 K.

Keywords: semiconductors, chalcogenides, optical coefficients.

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1. Introduction

Solid solutions based on chalcogenides of indium and mercury embrace a large number of materials some of which are zero-gap semiconductors (HgSe), while the others represent wide-gap ones (In_2Se_3). Changes in their chemical composition lead to gradual rearrangement of the energy-band structure of these solid solutions [1]. The presence of a magnetic component (Mn or Fe) in semimagnetic semiconductors leads to different types of exchange interactions, which affect the band parameters of crystals. Moreover, the exchange interaction can be altered by the content of magnetic component and the influences of magnetic field, temperature and thermal processing, being also dependent on the pairs of components (Hg, Se) [2]. It is also known that the solid solutions $(3HgSe)_{1-x}(In_2Se_3)_x$ contain defect fragments and furthermore, similar to $Hg_3In_2Te_6$, they should reveal high enough resistance to neutron irradiation [3].

We have been the first to obtain the crystals of a novel semimagnetic solid solution $(3HgSe)_{0.5}(In_2Se_3)_{0.5}$, both undoped and doped with the atoms of manganese (N_{Mn}~10^{20} cm^{-3}) and iron (N_{Fe} ~ 10^{20} cm^{-3}). In order to obtain the crystal, ultra-pure mercury, indium, sulphur and manganese or iron (in the case of doping) have been sealed in vacuum quartz ampoules with a tapered conic bottom. After that we synthesised $(3HgSe)_{0.5}(In_2Se_3)_{0.5}$ in horizontal furnaces. The crystal growth by the Bridgman method has been performed in the same ampoules. The process of growing has resulted in poly-block crystals of cylindrical form, with the length of ~ 6 cm and the diameter of ~ 1 cm.

The aim of the present work is to investigate the basic optical properties of the semimagnetic, semiconducting solid solutions $(3HgSe)_{0.5}(In_2Se_3)_{0.5}$, both undoped and doped with Mn or Fe, with the purpose of further determining their energy band parameters.

2. Sample preparation and experimental procedures

When preparing the optical experiments, we paid great attention to obtaining plane-parallel samples, with their surfaces having small depths of a destroyed layer. With this aim, the samples were grinded and then polished. The grinding process was performed on a flat glass using an emulsion of grinding powders, with decreasing gradually the size of the powder grain from 28 μm to 5 μm. Then the samples were polished with a diamond paste and afterwards washed by alcohol.

For measuring the optical reflection, our samples were processed using only mechanic polishing. To eliminate possible multiple light reflections inside the sample, the output surface of the latter was grinded only, with no further polishing. The sample thickness and plane-parallelism were controlled by means of micrometer, with the accuracy not less than ±5 μm. The parallelism of the surfaces was checked while measuring sample thickness for a number of points. Finally, the samples thicknesses, d, satisfied the condition $\alpha d \sim 1$ (see [4], where α is the absorption coefficient and $d = 100$– 200 μm the samples thickness).

The errors occurring during determination of the absorption coefficient have been discussed in the monograph [4]. This analysis shows that the main contributions here originate from the measurements of transmittance (T), reflectance (R) and sample thickness. The account for all of the errors under consideration yields the total error for the absorption coefficient of about 5%.

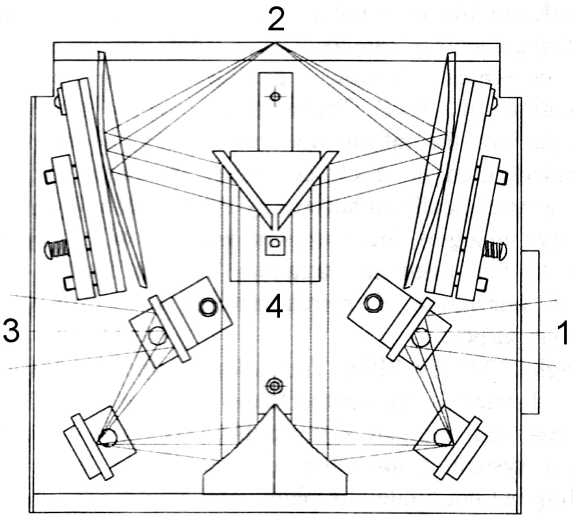

Fig. 1. Optical scheme of the *Pike* Technologies Accessory for investigating reflection spectra:
1 – inlet, 2 – sample, 3 – outlet, and 4 – system of mirrors enabling to change the incidence and reflection angles.

For determining the optical coefficients, a technique based on independent measurements of the reflectance (R) and transmittance (T) was applied. The measurements of the optical coefficients T and R were performed in the interval of wavelengths $\lambda = 0.9 \div 26.6$ μm using a spectrometer Nicolet 6700. While measuring the R coefficient, the Pike Technologies Accessory was used (see Fig. 1). With this accessory, the incidence angle for measuring the reflectance could be changed in the region of 30–80°.

3. Experimental results

The analysis of dependences of the R coefficient on the incidence angle of non-polarised radiation (see Fig. 2) shows that, within the incidence angles ranging from 30° to 45°, the R value changes only slightly and so we can assume that $R(0°) \div R(45°) \approx$ const.

Under condition of normal incidence of the beam, the dependence of the R coefficient upon the refractive and absorption indices n and k is described by the following relation [4]:

$$R = \frac{(n-1)^2 + k^2}{(n+1)^2 - k^2} . \quad (1)$$

In semiconductor crystals, the region of energies of the incident electromagnetic radiation, in which the absorption can be neglected, is small in most cases. However, the condition $n^2 >> k^2$ ($k \sim 10^{-3}$) is satisfied in a much wider region. As a result, the refractive index was determined from the reflection coefficient values for the non-polarised radiation (at the incidence angles tending to zero), using the following relation:

$$R = \frac{(n-1)^2}{(n+1)^2} . \quad (2)$$

This has given rather reliable values of the refractive index n for a wide interval of photon energies (at least for $\hbar\omega << E_g$). We have found that the n value for the $(3HgSe)_{0.5}(In_2Se_3)_{0.5}$ crystals doped with Mn or Fe does not change with changing wavelength (see also Table 1).

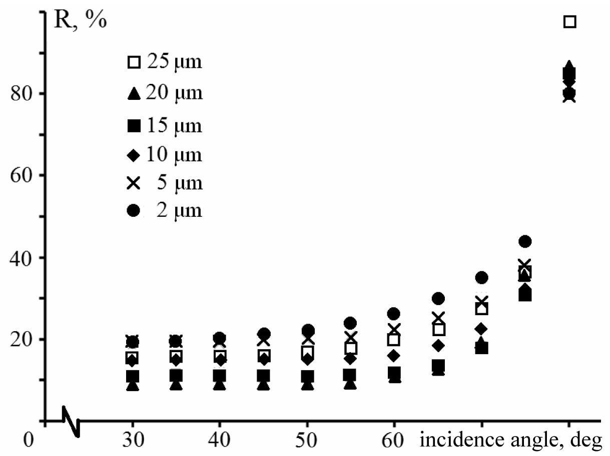

Fig. 2. Dependences of reflection coefficient R on the incidence angle for the undoped $(3HgSe)_{0.5}(In_2Se_3)_{0.5}$ crystals (the wavelengths of the incident electromagnetic radiation are shown in the legend).

Table 1. Refractive indices of pure $(3HgSe)_{0.5}(In_2Se_3)_{0.5}$ crystals and the same crystals doped with Mn or Fe.

Crystal	Mean refractive index, n
$(3HgSe)_{0.5}(In_2Se_3)_{0.5}$	2.55
$(3HgSe)_{0.5}(In_2Se_3)_{0.5}$:Fe	2.72
$(3HgSe)_{0.5}(In_2Se_3)_{0.5}$:Mn	2.37

One of the properties of quasi-plasma formed by electrons and holes in a semiconductor crystal is its effort to keep electrical neutrality in each point of the crystal. If this neutrality is broken by electromagnetic radiation, the charged particles start oscillating with a certain plasma frequency, ω. These oscillations lead to subsequent absorption of the radiation, independent on the mechanism of scattering of free charge carriers [5]. This property is clearly seen (see Fig. 3 and Fig. 4) in decrease of the reflection coefficient occurring in the vicinity of the plasma frequency (a so-called 'plasma minimum').

As an example, Fig. 3 presents dependence of the reflection coefficient for $(3HgSe)_{0.5}(In_2Se_3)_{0.5}$:Mn on the wavelength of electromagnetic radiation. For all the samples under study, the reflection coefficient decreases monotonously with increasing wavelength from 17–22% to 7–12%, passes through a minimum and then increases dramatically, reaching the values as high as 50%.

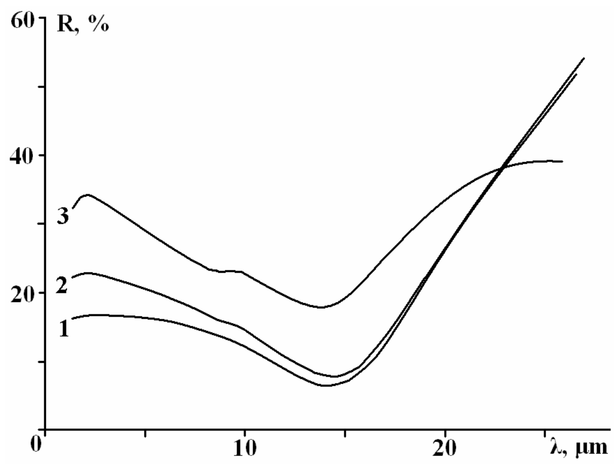

Fig. 3. Dependences of reflection coefficient on the wavelength of electromagnetic radiation for the $(3HgSe)_{0.5}(In_2Se_3)_{0.5}$:Mn crystals measured at different incidence angles: 1 – 30, 2 – 50, and 3 – 70°.

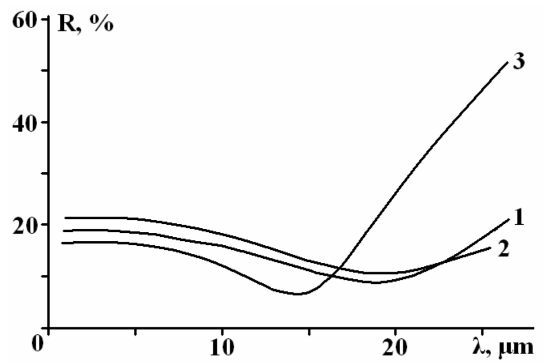

Fig. 4. Dependences of reflection coefficient on the wavelength of electromagnetic radiation (for the incidence angle 30°):
1 – $(3HgSe)_{0.5}(In_2Se_3)_{0.5}$,
2 – $(3HgSe)_{0.5}(In_2Se_3)_{0.5}$:Fe, and
3 – $(3HgSe)_{0.5}(In_2Se_3)_{0.5}$:Mn.

The results for the transmission coefficient as a function of wavelength for the undoped crystals $(3HgSe)_{0.5}(In_2Se_3)_{0.5}$ and those doped with Mn and Fe are shown in Fig. 5. Here the multiple light reflections can be ignored under the conditions of our experiments (see also the discussion given above). Notice also that the spectral transmission curves are displayed only in the region limited by the wavelengths of 5–8 μm from above, because no optical transmission in these materials occurs for the larger wavelengths.

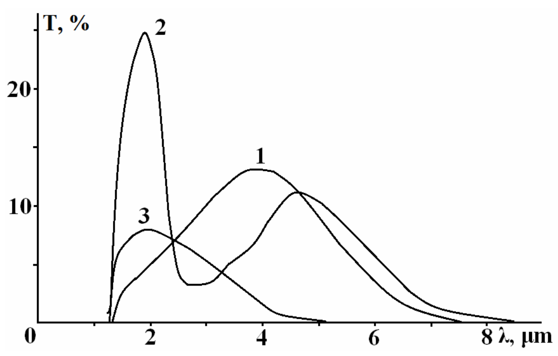

Fig. 5. Dependences of transmission coefficient on the wavelength of electromagnetic radiation at 300 K:
1 – $(3HgSe)_{0.5}(In_2Se_3)_{0.5}$,
2 – $(3HgSe)_{0.5}(In_2Se_3)_{0.5}$:Fe, and
3 – $(3HgSe)_{0.5}(In_2Se_3)_{0.5}$:Mn.

In order to check a possible influence of temperature on the optical transmittance of our crystals, we have also measured the transmission coefficient in the region of 125–300 K, using a special cryostat. The corresponding experimental results obtained for both the undoped crystal and that doped with Fe are presented in Fig. 6 and Fig. 7.

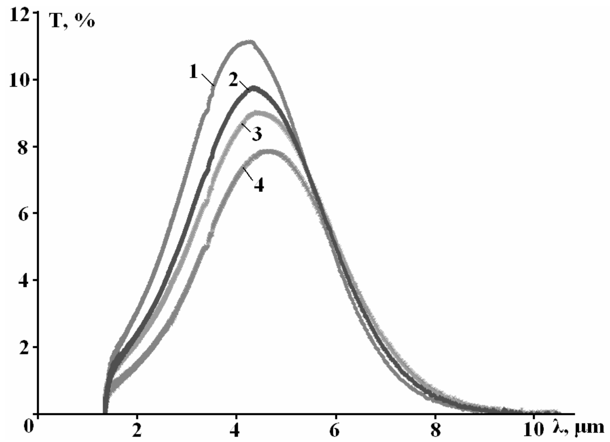

Fig. 6. Dependences of transmission coefficient on the wavelength of electromagnetic radiation for $(3HgSe)_{0.5}(In_2Se_3)_{0.5}$ crystals at different temperatures: 1 – 291 K, 2 – 261 K, 3 – 232 K, and 4 – 153 K

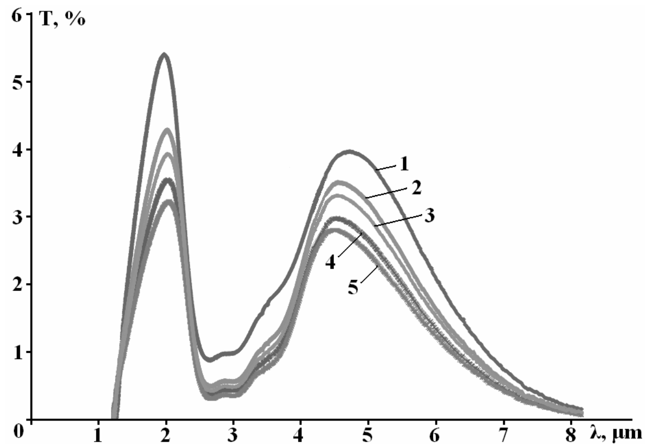

Fig. 7. Dependences of transmission coefficient on the wavelength of electromagnetic radiation for $(3HgSe)_{0.5}(In_2Se_3)_{0.5}$:Fe crystals at different temperatures:
1 – 292 K,
2 – 175 K,
3 – 154 K,
4 – 146 K, and
5 – 125 K

4. Conclusions

The studies of the optical properties of $(3HgSe)_{0.5}(In_2Se_3)_{0.5}$ semiconductors doped with Mn and Fe have resulted in the following main conclusions:

- the analysis of dependences of the *R* coefficient on the incidence angle for the case of non-polarised radiation has shown that the *R* value changes only slightly within the incidence angles ranging from 30° to 45°;
- the mean refractive index for the crystals under study is equal to 2.35÷2.70 and the corresponding dispersion is very weak;
- the optical transmission detected by us is nonzero only in the spectral region from 1.3 to 5–8 μm and no transmission is observed for the wavelengths larger than 5–8 μm.

References

1. Maryanchuk P D and Gavaleshko N P, 1982. Transition between a gapless semiconductor and common semiconductor in $Mn_xHg_{1-x}Se$. Ukr. Phys. J. **27**: 1259–1261.
2. Maryanchuk P D and Maistruk E V, 2008. Effect of heat treatment in sulphur and mercury vapours on the magnetic susceptibility of $Hg_{1-x}Mn_xTe_{1-y}S_y$ crystals. Inorganic Materials. **44**: 475–480.
3. Koshkin V M, Dmitriyev Yu N, Zabrods'kiy Yu R, Tarnopolskaya R A and Ulmanis U A, 1984. Anomalous radiation hardness of loose structures. Phys. Techn. Semicond. **18**: 1373–1378.
4. Uhanov Yu I. Optical properties of semiconductors. Moscow: Nauka (1977).

5. Spitzer W C and Fan H J, 1957. Determination of optical constants and carrier effective mass of semiconductors. Phys. Rev. 106: 882–890.

Koziarskyi I.P., Marianchuk P.D. and Maistruk E.V., 2011. Optical properties of $(3HgSe)_{0.5}(In_2Se_3)_{0.5}$ crystals doped with Mn or Fe. Ukr.J.Phys.Opt. 12: 137-142.

Анотація. *На основі вимірювань коефіцієнтів відбивання та пропускання кристалів* $(3HgSe)_{0.5}(In_2Se_3)_{0.5}$*, легованих Mn і Fe, проведених за кімнатної температури в інтервалі довжин хвиль 0,9–26,6 мкм, визначено показник заломлення, а також коефіцієнти відбивання та поглинання досліджених кристалів. Вплив температури на оптичне пропускання досліджено в інтервалі T = 125–300 K.*