# Purification of the Cd(Mn)Te For X-ray Detector Crystals by Special Annealing

Z. Zakharuk[1], S. Dremlyuzhenko[1], S. Solodin[1], E. Nykonyuk[2,*], B. Rudyk[2], O. Kopach[1],
A. Opanasyuk[3,†], P. Fochuk[1,‡]

[1] *Chernivtsi National University, 2, Kotziubynskogo Str., 58012 Chernivtsi, Ukraine,*
[2] *National University of Water and Environmental Engineering, 11, Soborna Str., 33000 Rivne, Ukraine,*
[3] *Sumy State University, 2, Rimsky Korsakov Str., 40007 Sumy, Ukraine*

To purify $Cd_{0.95}Mn_{0.05}Te$ ingots a modified travelling heater method (called «dry zone») was applied. Even one pass of the zone decreased essentially Te inclusions (size and density) in the ingot. The *p*-type conductivity and others electrical characteristics of the material almost didn't change, however the concentration of shallow ($\varepsilon_A \approx 0.05$ eV) acceptors reduced and the compensation degree of deeper acceptors ($\varepsilon_A \approx 0.17$ eV) increased. Such transformation of a defect-impurity system was manifested in decreasing of the ionized centers' concentration and in reducing of impurities absorption coefficients both at 0.1-0.5 eV and near the edge of fundamental band.

**Keywords:** Solid solutions $Cd_{1-x}Mn_xTe$, Purification, Electrical characteristics, Optical measurements, Inclusions, Thermal treatment.

## 1. INTRODUCTION

The potential ability of CdTe crystals and Cd(Zn)Te, Cd(Mn)Te (CMT) solid solutions for X-ray detectors application at room temperature is significantly limited by the presence of high content both own and foreign point defects as well as structural defects, including Te inclusions. A post-growth thermal treatment in temperature gradient for a reduction of the inclusions density is applied [1-6]. One of the thermal treatment modifications is traveling heater method. In our case the heater temperature was considerably less than the melting point of the crystal, but it slightly exceeded the Te melting point. This modification was called the method of «dry zone» (MDZ). The application of the MDZ to CdTe crystals [7] led to considerably reduction of Te inclusions and also to the transformation in point defects system. In particular, the common concentration of ionized centers decreased that led to conductivity type change. Therefore we supposed that application of the MDZ have to be reasonable to Cd(Mn)Te crystal purification.

## 2. EXPERIMENTAL PROCEDURE

The $Cd_{0.95}Mn_{0.05}Te$ ingot with a Te excess ($\sim 5 \cdot 10^{18}$ cm$^{-3}$) was grown by the vertical Bridgman method, using elementary components Cd, Te (6N) and Mn (5N) (crystal's code – CMT-348). The parts ($\sim 15$ mm) of the both ends of the ingot were used for the preparation of control samples (hereinafter – the samples before the MDZ). Further, the central part of the ingot was inserted in evacuated quartz container inside the set up, where a narrow heater was slowly moved along the ingot. The temperature of the hot zone was $\sim 785$ К, temperature gradient – 70 K/cm, growth rate – 0.2 mm/h.

The presence of Te inclusions before and after the MDZ was evaluated using IR microscopy. In general, $Cd_{1-x}Mn_xTe$ crystals were transparent in infrared range; instead, the inclusions were opaque. As a result, the infrared images showed the shape, size and location of inclusions and their distribution within the crystal. Infrared image of crystal's volume we obtained by a microscope Leitz, equipped with infrared camera Pixelink PL-A741.

Electro-physical measurements were carried out on rectangular samples ($12 \cdot 2 \cdot 1.5$ mm$^3$) with two pairs of potential contacts in DC mode. I-V curves were symmetrical and linear in the 85-350 K temperature range (applied voltage – 15 V/cm). Temperature dependencies (TD) of conductivity $\sigma$, Hall coefficient $R_H$ and the Hall carrier mobility $\mu = \sigma R_H$ were investigated. The sample position in the ingot characterized by a coordinate $g = s/l$, where $x$ – distance from a beginning of the crystal, and $l$ – a length of the crystal.

The transmission spectra of the samples before and after the MDZ were obtained using both infrared spectrophotometer IRS-29 (2.4-25 µm) and automated facility, based on the monochromator MDR-2 (0.80-0.95 µm).

## 3. RESULTS AND DISCUSSION

In the Fig. 1 are represented the IR images of two samples, cut from the beginning (Fig. 1) and the end of the ingot (Fig. 2) before and after applying the MDZ. It can be seen the effectiveness of this method, since there is a significant reduction in the size of large (> 20 microns) inclusions and removal of small ones. Based on a series of infrared images we built a 3*D* model (Fig. 3) of inclusion distribution in the crystal volume ($\sim 5$ mm$^3$). As the situation observed in Fig. 1b

* semirivne@gmail.com
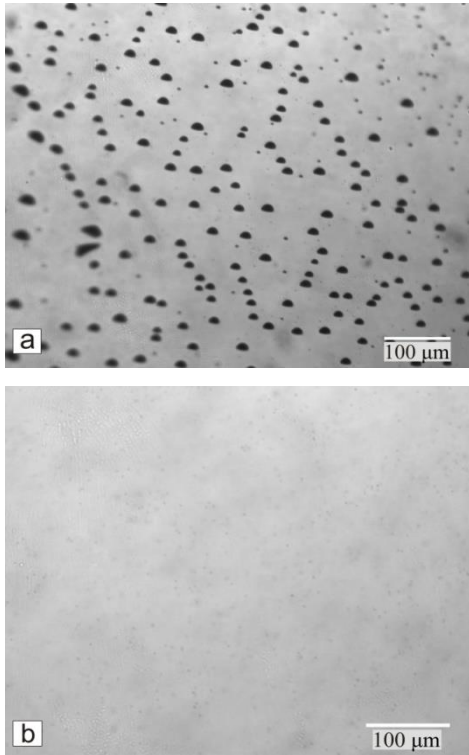† opanasyuk_sumdu@ukr.net
‡ p.fochuk@chnu.edu.ua

**Fig. 1** – IR images of samples, cut from the CMT-348 ingot beginning, before (a) and after (b) purification by the MDZ
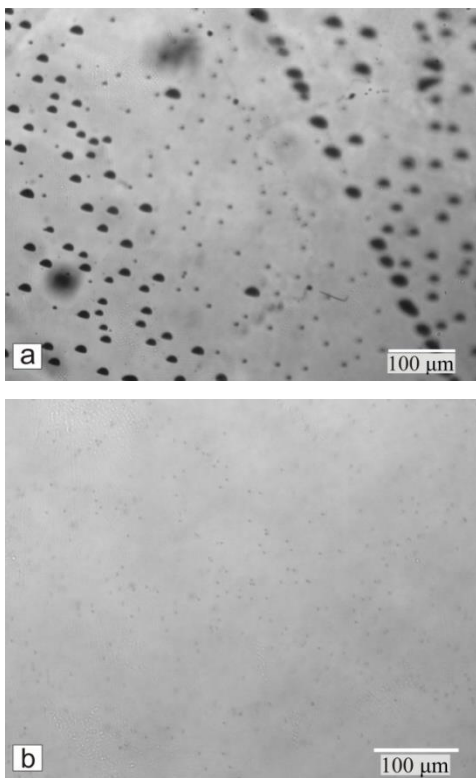


**Fig. 2** – IR images of samples, cut from the CMT-348 ingot end, before (a) and after (b) purification by the MDZ

and 2b was a typical for crystal after the MDZ, thus 3D model after the MDZ was not necessary

Samples, fabricated from the initial crystal (before the MDZ) and from the crystal after the MDZ, possessed
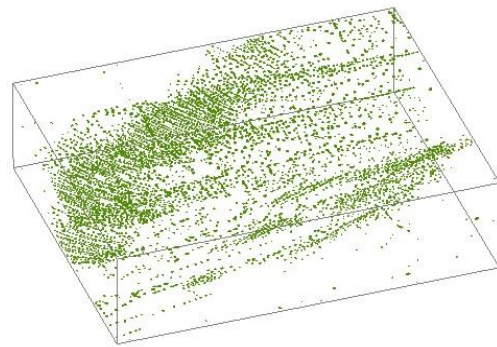


**Fig. 3** – 3D model of inclusions in a sample, cut from CMT-348 ingot end, before purification (2,7x2,3x1,0 mm$^3$)

a hole conductivity. Electrical parameters of samples (resistivity $\rho$ and hole mobility – $\mu$) at 300 K (Table 1) didn't indicate on the effect of the MDZ. Ionization energy of acceptors $A_2$ ($\varepsilon_A = 0.16$-$0.17$ eV), determined by TD of $R_H$ (Fig. 4), also remained unchanged. The concentration of these acceptors, determined from the analysis of the $R_H$ TD, using a model of partly compensated centers, was practically unchanged through the MDZ application (Table 1). However, it was observed a decreasing of fully compensated shallow acceptors $A_1$ concentration. This conclusion was based on the analysis of the Hall data TD for hole mobility (Fig. 5).
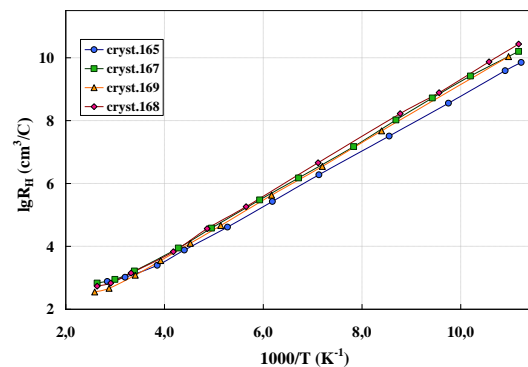


**Fig. 4** – Temperature dependencies of Hall coeficient $R_H$ for the samples before (165, 167) and after MDZ (168, 169)

At first sight the values of mobility were similar in all four samples, especially at low temperatures, which would indicate the proximity of the concentration of ionized scattering centers $N_I$. However, a monotonous $\mu_p$ increase (without maximum) simultaneously with temperature decreasing indicated that a concentration of $N_I$ didn't exceed $3 \times 10^{17}$ cm$^{-3}$. Then at 300 K can be expected $\mu_p$ values not lower than 72 cm$^2$/(V×s), taking into account the two main mechanisms of carrier scattering: on optical vibrations of crystal lattice and on ionized centers. As shown in Table 1, the experimental values of mobility are significantly lower than expected ones. So we need to involve the third scattering mechanism, namely, scattering on the space charge region (SCR), which do not overlap with mobility $\mu_s$ [9]. For the further analysis we selected two samples (167 and 168), which were situated side by side in the ingot. The ionization energy of acceptors was almost the same for the two samples and hence the composition, but the first (167) did not subject to the MDZ, while the second

(168) was after the MDZ applying. At first, optimal values $\mu_s$ at 300 K were set: 260 cm²/(V×s) for the sample 167 and 170 cm²/(V×s) for the sample 168. Then the TD of $\mu_s$ was calculated [9]. Afterwards, using the Mattisen rule and based on the experimental data

(Fig. 5), we have established the mobility, conditioned by a total scattering only on optical vibrations of the crystal lattice and on ionized centers ($\mu_{oI}$). TD of $\mu_{oI}$ is represented in Fig. 6.

**Table 1** – Electro-physical characteristics of the samples from the CMT-348 ingot before and after the MDZ

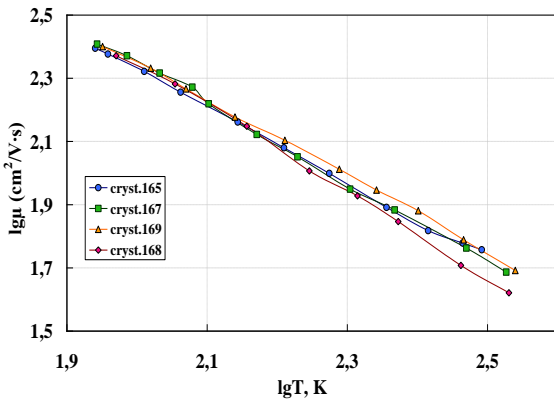| №  crystal | State of crystal (before or after MDZ) | Sample' position the in the ingot (g) | T = 300 К | | $\varepsilon_A$, eV | $[A_2]\times10^{-16}$, cm$^{-3}$ | $N_I\times10^{-16}$, cm$^{-3}$ | $[A_1]\times10^{-16}$, cm$^{-3}$ |
|---|---|---|---|---|---|---|---|---|
| | | | $\rho$, (Ohm×cm) | $\mu$, cm²/(V×s) | | | | |
| 165 | before | ~ 0.2 | 19 | 57 | 0,16 | 3.7 | – | – |
| 169 | after | ~ 0.25 | 19 | 60 | 0,17 | 2.8 | – | – |
| 167 | before | ~ 0.9 | 23 | 55 | 0,17 | 3.3 | 20 | 7,7 |
| 168 | after | ~ 0.8 | 24 | 50 | 0,17 | 2.7 | 9 | 2,3 |



**Fig. 5** – Temperature dependencies of hole mobility for the samples, cut from CMT-348 crystal (numbering of the samples corresponds Fig. 4)
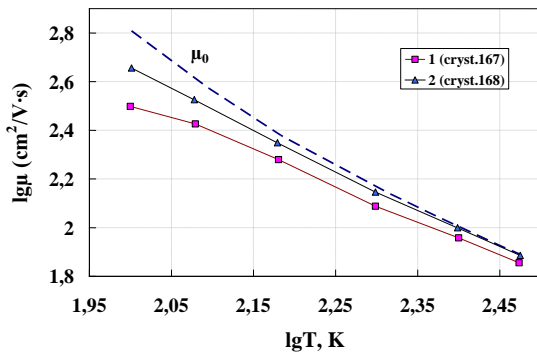


**Fig. 6** – Temperature dependency of the calculated carrier mobility ($\mu_{oI}$) in the samples: 1 – before the MDZ, 2 – after the MDZ ($\mu_0$ – holes mobility, limited by optical vibrations of the crystal lattice)

Using the Mattisen rule and Brooks-Herring formula for carrier mobility, limited by scattering on ionized centers, we calculated the concentrations of ionized scattering centers $N_I$ (Table 1). It is evident that the MDZ procedure reduced $N_I$ value (> 2 times). Since the concentration of acceptors $A_2$ didn't change practically, so we conclude that the concentration of the fully compensated more shallow acceptors $A_1$ decreased: $[A_1^-] = [A_1] = 0,5N_I - [A_2^-]$ as well as compensating donors. Note that a similar situation occurred in *p*-CdTe crystal [10] at a self-purification during a vacuum heat treatment.

In the absorption spectra for (0.05-0.5) eV photons

region it is clearly visible two areas: A – an impurity absorption and B – the absorption on free carriers (Fig. 7).
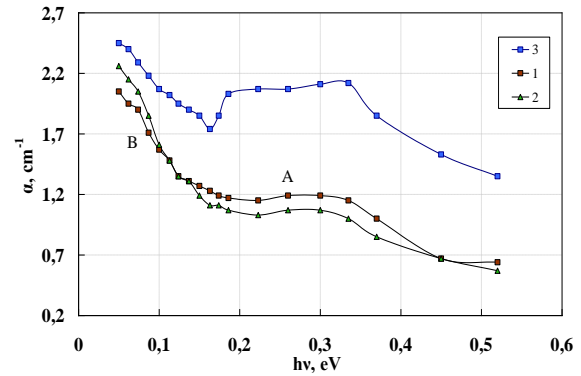


**Fig. 7** – Infrared absorption spectra ($\alpha_1$ in Table 2) of the samples of CMT-348 ingot: 1, 2 – after the MDZ (the end and beginning of the ingot, respectively), 3 – before the MDZ

Although it was difficult to separate reliable these bands, it could be argued that the position of long-wave edge of the impurity band correlated well with the ionization energy of acceptors $A_2$. Then, the absorption process could be described by the reaction:

$$A_2^0 + (h\nu)_1 \rightarrow A_2^- + h^+. \qquad (1)$$
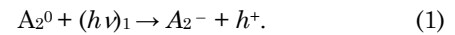
So, it was advisable to compare the value of impurity absorption coefficients $\alpha_1$ with calculated acceptor concentrations $A_2^0$ in the samples before and after the MDZ (Table 2).

**Table 2** – Impurity absorption coefficients and the concentration of correspondingly acceptors in the samples of the CMT-348 crystal

| Sample | $[A_2^0]$, cm$^{-3}$ | $\alpha_1$, cm$^{-1}$ | $[A_1^-]$, cm$^{-3}$ | $\alpha_2$, cm$^{-1}$ (1.53 eV) |
|---|---|---|---|---|
| 167 | $1.1\cdot10^{16}$ | 2.15 | $7.7\cdot10^{16}$ | 44 |
| 168 | $0.5\cdot10^{16}$ | 1.15 | $2.3\cdot10^{16}$ | 15 |

Acceptors $A_1$ were also involved in the processes of light absorption in correspondence with the reaction:

$$A_1^- + (h\nu)_2 \rightarrow A_1^0 + e^-. \qquad (2)$$
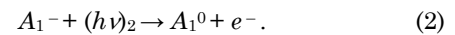
As acceptors $A_1$ were shallow ($\varepsilon_{A1} \approx 0.05$ eV), then the absorption band was adjacent to the fundamental

band (Fig. 8). To evaluate the absorption coefficient it was selected $h\nu = 1.53$ eV, which was slightly higher than the energy threshold of the reaction (2): $E_g - \varepsilon_{A1} \approx 1.51$ eV.
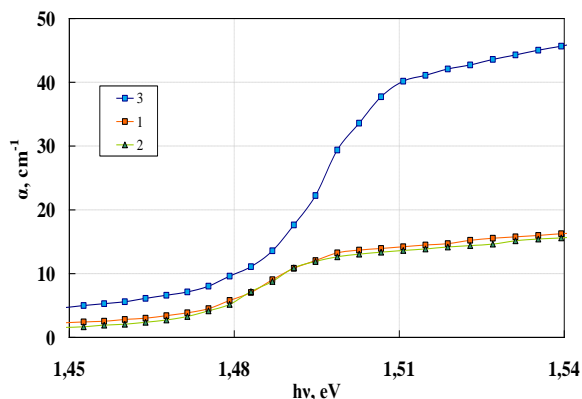


**Fig. 8.** – The spectral dependence ($\alpha_2$ in Table 2) of absorption coefficient in the samples of CMT-348 ingot: 1, 2 – after the MDZ (beginning and end of the ingot, respectively), 3 – before the MDZ

Indeed, as can be seen from the Table 2, for the both of impurity bands is a decent correlation between the absorption coefficient and corresponding acceptor concentrations in the respective charge states.

As was shown in Fig. 7 (particularly, curve 3) the A band is a superposition of two bands that overlap. Thus, in the formation of the A band are involved two acceptors, which are located energetically similarly. So the ionization energy value determined from the electrical measurements (Table 1) is slightly overestimated. Indeed, for $Cd_{1-x}Mn_xTe$ with $x = 0.05$ the formula $\varepsilon_A = 0.12(1 + 5,5x)$ eV [8] gives a value of 0.15 eV, that is less (0.02 eV) than the experimental one.

## 4. CONCLUSIONS

The modified method of heater moving («dry zone» method) applied to the Cd(Mn)Te crystal provided the following effects:
– significant reduction of tellurium inclusion density in the bulk;
– reduction of shallow acceptors $A_1$ ($\varepsilon_A \approx 0.05$ eV) concentration, which lead to reduction of light absorption coefficient near the edge of fundamental band;
– increase in the compensation degree of acceptors $A_2$ ($\varepsilon_A = 0.17$ eV), which reduces the coefficient of light absorption in the infrared region (0.15-0.5) eV.

---

**Очистка кристаллов Cd(Mn)Te для детекторов рентгеновского излучения специальным отжигом**

З.И. Захарук[1], С.Г. Дремлюженко[1], С.В. Солодин[1], Е.С. Никонюк[2], Б.П. Рудык[2], О.В. Копач[1], А.С. Опанасюк[3], П.М. Фочук[1]

[1] *Черновицкий национальный университет имени Юрия Федьковича, ул. Коцюбинского, 2, 58012 Черновцы, Украина*
[2] *Национальный университет водного хозяйства и природопользования, ул. Соборная, 11, 33028 Ровно, Украина*
[3] *Сумский государственный университет, ул. Римского-Корсакова, 2, 40007 Сумы, Украина*

С целью очистки слитков $Cd_{0,95}Mn_{0,05}Te$ был применен модифицированный метод подвижного нагревателя (названный «сухая зона»). Даже один проход зоны существенно уменьшал включения Те (размер и концентрацию) в слитке. Проводимость $p$-типа и другие электрические характеристики материала почти не изменились, однако концентрация мелких $\varepsilon_A \approx 0,05$ эВ) акцепторов уменьшилась, а степень компенсации более глубоких акцепторов ($\varepsilon_A \approx 0,17$ эВ) увеличилась. Такое преобразование дефектно-примесной системы проявилось в уменьшении концентрации ионизованных центров и в снижении коэффициентов поглощения примесей как при 0,1-0,5 эВ, так и вблизи края фундаментальной зоны.

**Ключевые слова**: Твердые растворы $Cd_{1-x}Mn_xTe$, Очистка, Электрические характеристики, Оптические измерения, Включения, Термическая обработка.

---

**Очистка кристалів Cd(Mn)Te для детекторів рентгенівського випромінювання спеціальним відпалом**

З.І. Захарук[1], С.Г. Дремлюженко[1], С.В. Солодін[1], Є.С. Никонюк[2], Б.П. Рудик[2], О.В. Копач[1], А.С. Опанасюк[3], П.М. Фочук[1]

[1] *Чернівецький національний університет імені Юрія Федьковича, вул. М. Коцюбинського, 2, 58012 Чернівці, Україна*
[2] *Національний університет водного господарства та природокористування, вул. Соборна, 11, 33000 Рівне, Україна*
[3] *Сумский державний університет, вул. Римского-Корсакова, 2, 40007 Суми, Україна*

З метою очищення злитків $Cd_{0,95}Mn_{0,05}Te$ застосований модифікований метод рухомого нагрівника (названий «суха зона»). Навіть один прохід зони суттєво зменшував вкраплення Te (розмір і концентрацію) в злитку. Провідність $p$-типу та інші електричні характеристики матеріалу майже не змінилися, однак концентрація мілких ($\varepsilon_A \approx 0,05$ eB) акцепторів зменшилася, а ступінь компенсації більш глибоких акцепторів ($\varepsilon_A \approx 0,17$ eB) збільшився. Таке перетворення дефектно-домішкової системи проявилось у зменшенні концентрації іонізованих центрів і у зниженні коефіцієнтів поглинання домішок як при 0,1-0,5 eB, так і поблизу краю фундаментальної зони.

**Ключові слова**: Тверді розчини, $Cd_{1-x}Mn_xTe$, Очистка, Електричні характеристики, Оптичні вимірювання, Вкраплення, Термічна обробка.

## REFERENCES

1. A.E. Bolotnikov, G.S. Camarda, Y. Cui, K.T. Kohman, L. Li, M.B. Salomon, R.B. James, *IEEE T. Nucl. Sci.* **57**, 821 (2007).
2. Z.I. Zakharuk, I.M. Rarenko, Y.P. Stetsko, *Neorgan. Mater.* **32**, 148 (1998) [in Russian].
3. P. Fochuk, R. Grill, O. Kopach, A.E. Bolotnikov, E. Belas, M. Bugar, G.S. Camarda, W. Chan, Y. Cui, A. Hossain, K.H. Kim, I. Nakonechnyi, O. Panchuk, G. Yang, R.B. James, *IEEE T. Nucl. Sci.* **59**, 256 (2012).
4. K.H. Kim, J. Suh, A.E. Bolotnikov, P.M. Fochuk, O.V. Kopach, G.S. Camarda, Y. Cui, A. Hossain, G. Yang, J. Hong, R.B. James, *J. Cryst. Growth* **354**, 62 (2012).
5. G. Yang, A.E. Bolotnikov, P.M. Fochuk, G.S. Camarda, A. Hossain, U.N. Roy, Y. Cui, R. Pinder, J. Gray, R.B. James, *phys. status. solidi c* **11**, 1328 (2014).
6. E. Belas, R. Grill, J. Franc, P. Moravec, P. Hlidec, P. Höschl, *J. Electron. Mater.* **37**, 1212 (2008).
7. P. Fochuk, Z. Zakharuk, Ye. Nykonyuk, I. Rarenko, M. Kolesnik, A.E. Bolotnikov, G. Yang, R.B. James, *IEEE T. Nucl. Sci.* **63**, 1839 (2016).
8. P.M. Fochuk, Ye.S. Nykonyuk, Z.I. Zakharuk, S.G. Dremlyuzhenko, O.V. Kopach, S.V. Solodin, A.S. Opanasyuk, *J. Nano- Electron. Phys.* **8**, 04011 (2016).
9. L.R. Weisberg, *J. Appl. Phys.* **33**, 1817 (1962).
10. Ye.S. Nykonyuk, V.L. Shlyahovyj, Z.I. Zakharuk, M.A. Kovalets, *Inorgan. Mater.* **31**, 185 (1995) [in Russian].