

# Plasmon – ionized impurity – phonon interaction in PbTe doped with Ni

J. TRAJIĆ\*, N. ROMČEVIĆ, M. ROMČEVIĆ, Z. LAZAREVIĆ, T. A. KUZNETSOVA<sup>a</sup>, D. R. KHOKHLOV<sup>a</sup>

*Institute of Physics, P.O. Box 68, University of Belgrade, 11080 Belgrade, Serbia*

<sup>a</sup>*Department of Physics, Moscow State University, 119899 Moscow, Russia*

Vibrational properties of PbTe single crystals doped with Ni are determined using far – infrared spectroscopy in wide temperature range. Far – infrared reflection spectra were analyzed using a fitting procedure based on the modified plasmon – ionised impurity – phonon interaction model. Together with the strong coupling we obtained three local modes of Ni at about 130, 165 and 190  $\text{cm}^{-1}$ , which correspond to the impurity atoms in different valence states. The positions of these modes depend on the impurity center charge, while their intensities depend on the temperature and Ni concentration.

(Received March 22, 2013; accepted July 11, 2013)

*Keywords:* Semiconductors, Crystal growth, Phonons, Plasmon – phonon interaction

## 1. Introduction

The coupling of elementary excitations in solids [1 – 3] and free – carrier absorption by phonon – ionised impurity – plasmon processes [4, 5] has been investigated by many authors. These processes are important for polar semiconductors with high static (lattice) dielectric constant and high carrier concentration. Free – carrier absorption consists then in individual – carrier excitations (individual – carrier scattering), as well as in collective carrier excitations (plasmon generation).

Photon – plasmon processes were studied, as a rule, in more general framework of photon – plasma – imperfection (deformation) interactions, where also individual – carrier excitations were taken into account [6 – 9]. Both nondegenerate and degenerate plasmas were considered. Usually, a theory is formulated starting from the knowledge of dielectric function for free carriers in perfect crystals. Phenomenological approach to this problem is formulated by several authors [9 – 11]. Our approach [10, 11] is based on creating specific dielectric function, which has to explain registered process, while comparisons with parameters obtained by classical approach [1, 2] yield the physical explanation of the processes that are taking place in the doped semiconductors.

The doping of  $A^{IV}B^{VI}$  semiconductor compounds with transition metal impurities has significant scientific and practical interest due to the new materials preparing possibilities. Lead telluride (PbTe) belongs to the  $A^{IV}B^{VI}$  IR – sensitive narrow – gap semiconductor group, which acquire new properties as a consequence of doping [12 – 14]. Electrical properties in such manner obtained materials strongly depend on the type and concentration of the added impurity. For instance, when PbTe is doped with chromium, free carrier concentration  $n$  increases to  $1.3 \cdot 10^{19} \text{ cm}^{-3}$ , and after that slowly decreases to  $1.2 \cdot 10^{19} \text{ cm}^{-3}$  with the further increase of the Cr concentration, up

to the chromium solubility limit [14]. This means that Cr in small concentration enter the PbTe lattice as donor impurity in the 3+ state. Further, when concentration increases, we have both 3+ and 2+ (as neutral) states, and finally in highly doped semiconductor we have impurities in all three – valence states: 3+, 2+ and 1+ (as acceptor). The mentioned behaviour of transition elements causes strong correlation between an impurity center and the lattice. A change of the electronic state of the impurity center provokes a change of the frequency of the local mode [4].

In this paper, we present further studies of far – infrared reflection spectra of Ni doped PbTe single crystal samples. Ni doped PbTe crystals were already subject of our research. Considering our new experimental and theoretical work, we analyzed these spectra using a fitting procedure based on the modified plasmon – phonon interaction model. Also, we obtained three local modes of Ni, which correspond to the impurity atoms in different valence states.

## 2. Samples and experiment

Single crystals of PbTe(Ni) were grown by the Bridgman method in evacuated sealed 12 – 15 mm quartz tubes with a cone shaped lower end by moving in the temperature gradient of 15 – 20 K/cm. The impurity concentrations in the starting mixture were  $3.3 \cdot 10^{20}$  and  $4.6 \cdot 10^{20} \text{ at./cm}^3$ . The Ni concentration in the crystals used here were  $1 \cdot 10^{19}$  and  $2 \cdot 10^{19} \text{ at./cm}^3$  respectively, determined by chemical analysis. Solubility limit and segregation effect for Ni doped PbTe were discussed in more details in Ref. [15]. The structural characteristics were obtained by the XRD powder technique. All the samples were examined under the same conditions; using a Philips PW 1729 X – ray generator, a Philips 1710 diffractometer and the original APD software. The

radiation source was an X–ray LFL tube with copper radiation and graphite monochromator. The radiations were  $\lambda_{\text{CuK}\alpha 1} = 0.154178$  and  $0.154438$  nm. The anode tube load was 40 kV and 30 mA. Slits of 1.0 and 0.1 mm were fixed. For product identification, the MPDS program and JCPDS (ASTM) (Joint Committed on Powder Diffraction Standards) cards files were used. The unit cell was calculated by the least square methods. All the registered reflections corresponded to PbTe crystals and gave the parameter of the cubic unit cell of  $a = 0.6455(3)$ , which are in good agreement with values cited in literature [16]. The dislocation densities were  $(5 - 7) \cdot 10^{-4} \text{ cm}^{-2}$ , registered by selective etching [17].

The Hall effect and conductivity measurements showed that the both crystals exhibit n – type conductivity with room – temperature electron concentration of  $6 \cdot 10^{16} \text{ cm}^{-3}$  (in sample with Ni concentration of  $1 \cdot 10^{19} \text{ at./cm}^3$ ) and  $4 \cdot 10^{16} \text{ cm}^{-3}$  (sample with  $2 \cdot 10^{19} \text{ at./cm}^3$ ). The far – infrared measurements were carried out with a BOMEM DA - 8 FIR spectrometer. A DTGS pyroelectric detector was used to cover the wave number rang from 40 to  $400 \text{ cm}^{-1}$ .

### 3. Reflectivity analysis and fitting procedure

The theoretical model of the bulk dielectric function has been discussed by several authors [11, 18]. For a description of the PbTe optical properties simple model for dielectric function were used [19]:

$$\varepsilon = 1 + \chi_{\text{valenceelectrons}} + \chi_{\text{polarphons}} + \chi_{\text{freecarriers}} \quad (1)$$

Interaction of electromagnetic radiation with plasmons in nonperfect lattices may become comparable or even higher than single – particle scattering [4]. This is especially the case for semiconductors with high – static dielectric constant. Because of that, the FIR spectra might be interpreted with the help of a frequency dependent dielectric function with no less than two classical oscillators ( $l \geq 2$ ) corresponding to the TO modes superimposed by a Drude part taking into account the free carrier contribution [2, 3]:

$$\varepsilon(\omega) = \varepsilon_{\infty} + \sum_{k=1}^l \frac{\varepsilon_{\infty}(\omega_{LOk}^2 - \omega_{TOk}^2)}{\omega_{TOk}^2 - \omega^2 - i\gamma_{TOk}\omega} - \frac{\varepsilon_{\infty}\omega_p^2}{\omega(\omega + i\gamma_p)} \quad (2)$$

where  $\varepsilon_{\infty}$  is the bound charge contribution and it is considered as a constant,  $\omega_{LOk}$  and  $\omega_{TOk}$  are the longitudinal and transverse optical – phonon frequencies,  $\omega_p$  is the plasma frequency, and  $\gamma_{TOk}$  and  $\gamma_p$  are the phonon and plasma damping.

In the doped PbTe – based systems the pure LO – modes ( $\omega_{LO, \text{PbTe}}$ ) of the lattice are strongly influenced by the plasmon mode ( $\omega_p$ ) of free carriers. As a result a combined plasmon – LO phonon modes ( $\omega_j, j = 1, 2$ ) were observed [1], whereupon in the experimental spectra only coupled mode positions were observable. Therefore, the determination of LO mode is connected with the

elimination of free carrier influence [9, 10, 20]. Impurity local modes have the same behaviour. This means that impurity local mode, characterized by its characteristic frequency  $\omega_0$ , can interact with free carriers [21]. In this case there is no separation on TO and LO mode, and as a result, coupled frequency could appear [4, 21]. Considering this fact, in the analysis of reflectivity spectra of Ni doped PbTe we have decided to use dielectric function that takes into account the existence of free carriers – phonon interaction in advance [9]:

$$\varepsilon(\omega) = \varepsilon_{\infty} \frac{\prod_{j=1}^2 (\omega^2 + i\gamma_j\omega - \omega_j^2) \cdot \prod_{k=1}^n (\omega^2 + i\gamma_{Lk}\omega - \omega_{Lk}^2)}{\omega^{n+1} (\omega + i\gamma_p) (\omega^2 + i\gamma_l\omega - \omega_l^2) \prod_{k=1}^n (\omega^2 + i\gamma_{ok}\omega - \omega_{ok}^2)} \prod_{m=1}^s \frac{\omega^2 + i\gamma_{LOm} - \omega_{LOm}^2}{\omega^2 + i\gamma_{TOM} - \omega_{TOM}^2} \quad (3)$$

In our case  $n$  is number of local phonons. The first term in Eq. 3 represents the coupling of one plasmon and  $n + 1$  phonons, and second term represents the uncoupled modes of the crystal ( $s$ ), while  $l = n + s + 1$ . The first term in Eq. 3 consist of two parts. The  $\omega_j$  ( $j = 1, 2$ ),  $\omega_l$  and  $\gamma_p$  represents plasma and PbTe LO phonon mode interaction ( $\omega_j$  and  $\omega_l$  are frequencies and  $\gamma_p$  is damping). The second part of this term represents interaction between plasma and nickel local phonons, where the  $\omega_{ok}$  ( $k = 1, n$ ) is local phonon characteristic frequencies and  $\omega_{Lk}$  is coupled frequency;  $\gamma_{ok}$  and  $\gamma_{Lk}$  are the damping. The second term represents uncoupled crystal modes, where the  $\omega_{LOm}$  and  $\omega_{TOM}$  are the longitudinal and transverse uncoupled modes frequencies, while  $\gamma_{LOm}$  and  $\gamma_{TOM}$  are damping.

The parameters adjustment was carried out automatically, by means of the least – square fitting of theoretical ( $R$ ) and experimental ( $R_e$ ) reflection coefficients at  $q$  arbitrarily taken points:

$$\sigma = \sqrt{\frac{1}{q} \sum_{j=1}^q (R_{ej} - R_j)^2}, \quad (4)$$

where:

$$R = \left| \frac{\sqrt{\varepsilon} - 1}{\sqrt{\varepsilon} + 1} \right|^2 \quad (5)$$

and  $\varepsilon$  is given by Eq. 3. The value of  $\sigma$  was minimized until it became comparable with the usual experimental error (less than 2%). The cross – sections of multi – dimensional  $\sigma(\omega, \gamma)$  surface were calculated, multiplying each parameter alternately by a varying factor ( $1 \pm \delta$ ) while all the others were fixed on a determined level. Such sections gave evidence of the precision of the analyses. Practically, for all samples the determination errors of the eigenfrequencies and damping coefficients were in the range of 3 – 6 % and 10 – 15 %, respectively.

### 4. Results and discussion

The far – infrared reflection spectra of PbTe(Ni) with Ni concentration of  $1 \times 10^{19}$  (a) and  $2 \times 10^{19} \text{ at./cm}^3$  (b) single crystals in the temperature range from 80 to 300 K, and spectral range from 40 –  $400 \text{ cm}^{-1}$  are shown in Fig. 1.

The experimental data are marked by circles. The solid line was obtained using the dielectric function from Eq. 3, where  $n = 1$  (Fig. 1.a) and  $n = 3$  (Fig. 1.b). This means that in the sample with  $1 \times 10^{19}$  at./cm<sup>3</sup>, besides PbTe TO/LO pair exists one Ni local phonon which also interacts with free carriers, while in sample with  $2 \cdot 10^{19}$  at./cm<sup>3</sup> where Ni existed in the three valence states, there are three Ni local phonons participating in the interaction. Mode at about 73 cm<sup>-1</sup> ( $s = 1$  in Eq. 3), denoted with x in Fig. 1.a, is well known PbTe Brillouin zone edge mode [20].

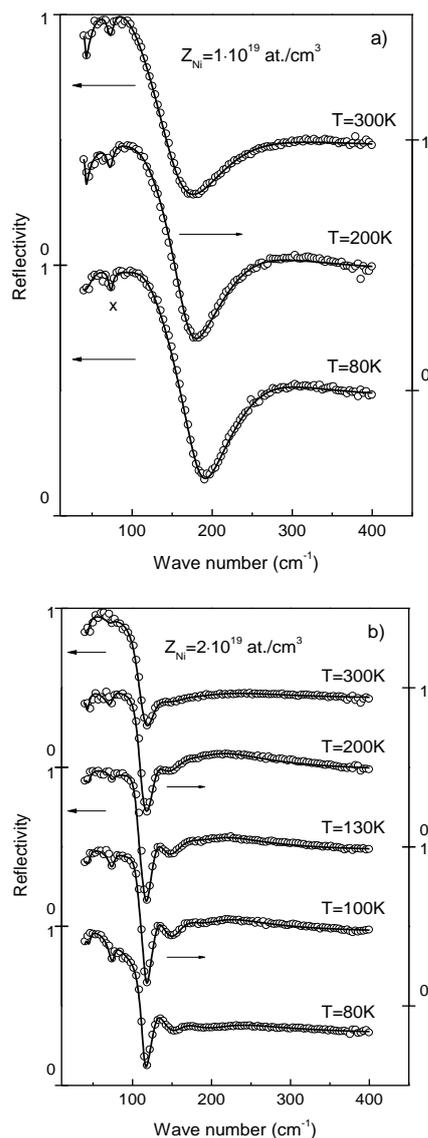


Fig. 1. Far – infrared reflection spectra of PbTe(Ni) single crystals:  $Z_{Ni} = 1 \cdot 10^{19}$  at./cm<sup>3</sup> (a) and  $2 \cdot 10^{19}$  at./cm<sup>3</sup> (b) in the temperature range from 80 to 300 K. Experimental spectra are presented by circles. Solid line is calculated spectra obtained by the fitting procedure based on the model for plasmon – phonon coupling (Eq.

3): (a)  $n = 1$ ,  $s = 1$  and (b)  $n = 3$ ,  $s = 1$ .

Theoretical spectra fit experimental results very well. In Figs. 2 and 3 characteristic spectra for plasmon – phonon interaction are presented. Obtained results

describe the relationship between the results obtained on the basis of Eq. 3 and of the traditional approach presented with Eq. 2. Interactions that correspond to different Ni concentrations are represented in figures. Thus, in Fig. 2, interaction of one plasmon with PbTe TO/LO pair and one Ni local phonon is presented, and in Fig. 3 is presented interaction of plasmon – PbTe TO/LO pair and three Ni local phonons. The solid line, in all figures, represents coupled frequencies, and as it was given in [9] the positions of the coupled mode were defined as the solutions of Eq. 2 ( $\text{Re}\{\epsilon\} = 0$ ). Dashed lines, obtained experimentally as the best fit, correspond to TO phonon positions, Ni local phonon characteristic frequencies ( $\omega_{0k}$ ,  $k = 1, 3$ ) and well – known value for PbTe LO phonon [24]. Positions of coupled frequencies, obtained as the best fit using the appropriate Eq. 3, are presented as symbols: the solid circles (●) refer to Ni local frequencies and stars (\*) to PbTe TO phonon and squares (□) to PbTe LO phonons. The obtained results can be explained in the following way: Ni in PbTe substitutes the Pb, and Ni is a substitution impurity ion. The impurity mode can arise simply due to the difference between masses and force constants of the impurity ion and the ion of the host material [21], or their appearance can be caused by more complex mechanism of electron – phonon interaction [7, 8, 22]. Taking into account the change of mass and force constants between an impurity and its surrounding, we have demonstrated that this is the case of the Ni impurity local modes. That is, if the semiconductor is doped with a substitution impurity [21] (in this case Ni), when substitution of the heavier mass (Pb) is made by a lighter impurity, one gets two modes: a local mode situated above the optical band and a gap mode situated above the acoustic band but below the optical band of the host lattice. Ni impurity modes are situated above the PbTe host optical band (Figs. 2 and 3), so they are local modes.

Taking into account both the FIR and Hall measurements, we assume that in the case of very low concentration, Ni enters in PbTe lattice as a donor impurity in Ni<sup>3+</sup> state. With further increase of Ni concentration, free carrier concentration stays the same, like in the case of Cr impurities [23]. So, we can conclude that Ni enters as a Ni<sup>3+</sup> (as a donor) and as a Ni<sup>2+</sup> (as a neutral) [24]. Further Ni concentration increasing causes the appearance of another local phonon, which corresponds to Ni<sup>1+</sup> (acceptor state). The mentioned electronic behaviour of Ni dopant causes strong change in correlation between an impurity center and a lattice. A change of the electronic state of an impurity center leads to a change of a force constant between an impurity atom and a lattice, which leads to the changing of the local mode frequency. According to our results, and results for PbTe doped with III group of elements [25, 26], we concluded that mode at about 190 cm<sup>-1</sup> (which is seen for both samples) corresponds to Ni<sup>3+</sup>; mode at about 130 cm<sup>-1</sup> corresponds to Ni<sup>2+</sup> (narrow line) and mode at about 165 cm<sup>-1</sup> to Ni<sup>1+</sup>. Registered mode frequencies are between the characteristic Ga and In frequencies [25 – 27], but they do not satisfy the isotopic effect, which is consequence of the interaction between an impurity center and a lattice.

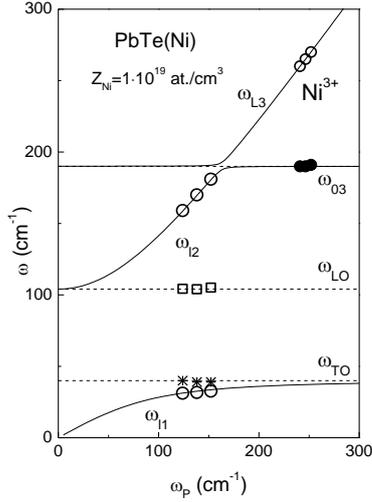


Fig. 2. The eigenfrequencies of the plasmon – phonon modes for single crystal PbTe(Ni) with  $Z_{Ni} = 1 \cdot 10^{19}$  at./cm<sup>3</sup>: the solid lines are calculated spectra [ $Re\{\epsilon\} = 0$ ;  $\epsilon$  is given by Eq. 2,  $l = 3$ ]; ● –  $\omega_{03}$ ; ○ –  $\omega_{01}$ ,  $\omega_{02}$  and  $\omega_{03}$  (Eq.3); \* – experimentally determined values for  $\omega_{TO_{PbTe}}$ ; □ –  $\omega_{LO_{PbTe}}$ . Dashed lines are visual aid.

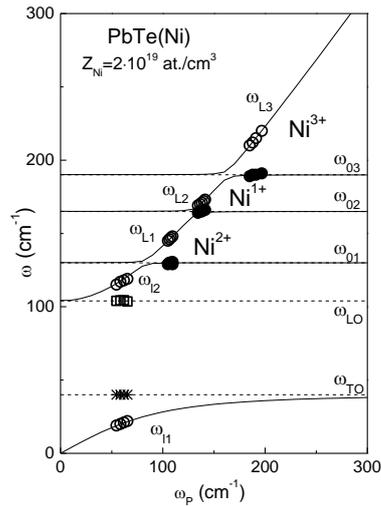


Fig. 3. The eigenfrequencies of the plasmon – phonon modes for single crystal PbTe(Ni) with  $Z_{Ni} = 2 \cdot 10^{19}$  at./cm<sup>3</sup>: the solid lines are calculated spectra [ $Re\{\epsilon\} = 0$ ;  $\epsilon$  is given by Eq. 2,  $l = 5$ ]; ● –  $\omega_{01}$ ,  $\omega_{02}$ ,  $\omega_{03}$ ; ○ –  $\omega_{01}$ ,  $\omega_{02}$ ,  $\omega_{L1}$ ,  $\omega_{L2}$  and  $\omega_{L3}$  (Eq. 3); \* – experimentally determined values for  $\omega_{TO_{PbTe}}$  and □ –  $\omega_{LO_{PbTe}}$ . Dashed lines are visual aid.

We presumed that PbTe phonons interact with plasma only, e.g. this interaction is not influenced by impurity centers directly. Therefore, we can determine the value of the LO phonon and the plasma frequency, as described in Ref. 10. Since the calculated value for the LO phonon coincides with the values from the literature, we conclude that this approach was justified. If we followed the described procedure for the local phonons of Ni also, e.g. if we join positions of the coupled phonons with, by this manner, calculated plasma, we would obtain large difference for values of coupled frequencies calculated from Eq. 2 and Eq. 3. That is the reason why we positioned coupled frequencies on the theoretical curves, and then we read the value of the plasma frequency. We observe linear shift of the plasma frequency values when the ionisation state of the impurity center increases. Hereby, the interaction between ionised center and the free carriers becomes stronger. One of the mechanisms that can describe this situation is related with changes of the density of the free carriers in the vicinity of the ionised center [3]. Besides, it is possible that near ionised centre different plasma modes are formed. In former case, the Coulomb interaction of different plasma modes forms in the limits of one energy band the single collective excitation, which is displayed in our spectra with an eigenfrequency equal to

$$\omega_P = \left[ \sum_{j=1}^m \omega_{jP}^2 \right]^{1/2} \quad (6)$$

Assume that in this case free carriers are in a some way tied to close neighbourhood around the charged impurity center. Also, we shall assume that here we have a two – component plasma around each impurity center, where one component is determined from PbTe coupling. Calculated values of the second component of the corresponding impurities centers, at  $T = 300K$ , are given in Table 1.

Table 1. Calculated values for the two – component plasma based on Eq. 6.

PbTe(Ni)	$\omega_{1P}$ [cm <sup>-1</sup> ]	Ni <sup>1+</sup> - $\omega_{2P}$ [cm <sup>-1</sup> ]	Ni <sup>2+</sup> - $\omega_{2P}$ [cm <sup>-1</sup> ]	Ni <sup>3+</sup> - $\omega_{2P}$ [cm <sup>-1</sup> ]
$1 \times 10^{19}$ at./cm <sup>3</sup>	152	—	—	187
$2 \times 10^{19}$ at./cm <sup>3</sup>	65	126	88	186

Obtained results should be understood only qualitatively. Namely, noticed plasmon – ionized impurity – phonon interaction can be described in several manners

[see for example Refs. 4, 7, 8, 19, 21]. However, in all cases the increase in the amount of interaction must be

observed, while the ionisation state of the impurity center increases, as well as its local character.

## 5. Conclusion

As a method to investigate phonon properties of Ni doped PbTe single crystals we used far – infrared spectroscopy. We obtained three local modes of Ni at about 130, 165 and 190  $\text{cm}^{-1}$ , which corresponded to the impurity atoms in different valence states. The positions of these modes depend on impurity centre charge, and their intensities depend on temperature and Ni concentration. We also revealed that in this system plasmon – ionised impurity – phonon coupling existed.

## Acknowledgements

This work was supported by the Serbian Ministry of Education, Science and Technological Development (Project III45003).

## References

- [1] S. Takaoka, T. Hamaguchi, S. Shimomura, K. Murase, *Solid State Commun.* **54**, 99 (1985).
- [2] V. Gopal, *Infrared phys.* **18**, 121 (1978).
- [3] M. Cardona, G. Gunterodt (Eds.), *Light Scattering in Solids*, Top. Appl. Phys., **8**, Springer, Berlin, 1975.
- [4] J. Mycelski, A. Mycelski, *Phys. Rev. B.* **18**, 1859 (1978).
- [5] A. Ron, N. Tzoar, *Phys. Rev.* **131**, 12 (1963).
- [6] E–Ni Foo, N. Tzoar, *Phys. Rev.* **187**, 1000 (1969).
- [7] D. E. McCumber, *Phys. Rev.* **154**, 790 (1967).
- [8] D. E. McCumber, *Rev. Mod. Phys.* **38**, 494 (1966).
- [9] A. A. Kuharskii, *Solid State Commun.* **8**, 1275 (1970).
- [10] J. Trajić, N. Romčević, M. Romčević, V. N. Nikiforov *Materials Research Bulletin* **42**, 2192 (2007).
- [11] M. A. Kinch, D. D. Buss, *Solid State Commun.* **11**, 319 (1972).
- [12] B. A. Volkov, O. M. Ruchaiskii, *Pis'ma Zh. Eksp. Teor. Fiz.* **62**, 205 (1995) [*JETP Lett.* **62**, 217 (1995)].
- [13] D. R. Khokhlov, B. A. Volkov, in *Proc. of the 23rd Inter. Conf. On the Phys. Of Semiconductors*, July 21–26, Berlin, Vol. **4** ed., M. Scheffler Singapore: World Scientific, 1996 p. 2941.
- [14] J. Trajić, M. Romčević, N. Romčević, A. Golubović, S. Đurić, V. N. Nikiforov, *Journal of Alloys and Compounds* **365**, 89 (2004).
- [15] V. P. Zlomanov, T. A. Kuznetsova, S. G. Dorofeev, V. D. Volodin, O. I. Tananaeva, *Crystallogr. Rep.* **47**, (Suppl. 1) 128 (2002).
- [16] JCPDS card number 38 – 1435.
- [17] O. N. Krylyuk, A. M. Gas'kov, V. P. Zlomanov, *Vestn. Mosk. Univ., Ser. 2: Khim.*, **6**, 571 (1986).
- [18] E. Burstein, A. Pinczuk, R. F. Wallis, in: D. L. Carter, R. T. Bate (Eds.), *The Physics of Semimetals and Narrow–Gap Semiconductors*, Pergamon, New York, 1971, p. 251.
- [19] H. Burkhard, G. Bauer, A. Lopez–Otero, *Phys. Rev. B.* **18**, 2935 (1978).
- [20] N. Romčević, A. Golubović, M. Romčević, J. Trajić, S. Nikolić, S. Đurić, V. N. Nikiforov, *J. Alloys and Compounds* **402**, 36 (2005).
- [21] A. A. Maradudin, in F. Seitz, D. Turnbull (Eds.), *Solid State Physics*, vol. **19**, New York, Academic, 1966.
- [22] N. Romčević, J. Trajić, A. T. Kuznetsova, M. Romčević, B. Hadžić, D. R. Khokhlov, *Journal of Alloys and Compounds*, **442**, 324 (2007).
- [23] B. A. Akimov, P. B. Verteckii, V. P. Zlomanov, L. I. Ryabova, O. I. Tananaeva, N. A. Shirokova, *Phys. Techn. of Semiconductors* **23**, 244 (1989).
- [24] B. A. Volkov, L. I. Ryabova, D. R. Khokhlov, *Physics – Uspekhi* **45**, 819 (2002).
- [25] N. Romčević, M. Romčević, D. R. Khokhlov, A. I. Belogorokhov, I. I. Ivanchik, W. Konig, *Infrared Physic and Technology* **40**, 453 (1999).
- [26] M. Romčević, N. Romčević, D. R. Khokhlov, I. I. Ivanchik, *J. Phys.: Condens. Matter* **12**, 8737 (2000).
- [27] N. Romčević, Z. V. Popović, D. R. Khokhlov, *J. Phys.: Condens. Matter* **4**, 4323 (1992).

\*Corresponding author: jelena@ipb.ac.rs