PHASE STABILITY, ELECTRONIC AND OPTICAL BEHAVIOR OF PbS, PbSe AND PbTe COMPOUNDS

Y. Megdoud[1,2*], R. Mahdjoubi [1,2], L. Tairi [1], H. Bendjedou[1], S. Ghemid[1] and H. Meradji[1]

[1]Laboratoire LPR, Département de Physique, Faculté des Sciences, Université Badji Mokhtar, Annaba, Algeria.

[2]Laboratoire LESIMS, Département de Physique, Faculté des Sciences, Université Badji Mokhtar, Annaba, Algeria.

ABSTRACT

Ab initio calculations based on density functional theory using the full potential linearized augmented plane wave method (FP-LAPW) have been carried out to find the structural stability of different crystallographic phases, the electronic and optical properties of PbS, PbSe and PbTe compounds. The zinc blende (B3), rock salt (B1) and CsCl (B2). crystal structures are considered and the exchange and correlation potential is treated by the generalized-gradient approximation using the Perdew– Burke–Ernzerhof parameterization. Moreover, the modified Becke-Johnson (mBJ) scheme is also applied to optimize the corresponding potential for the band structure calculations. Results show that the rock salt phase is the stable structure in the ground state adopted by PbS, PbTe and PbSe compounds. Moreover, the band structure calculations reveal a semiconductor behavior for all the compounds. The dielectric function, reflectivity, Refractive index and absorption coefficient are calculated to investigate the optical properties.

Keywords: Ab initio, FP-LAPW**,** Structural stability, band structure and optical properties

Adresse email : yousramegdoud@gmail.com

1. INTRODUCTION

During the past decades, the lead chalcogenides, PbX (X = S, Se and Te) have been a subject of a great amount of theoretical and experimental studies, motivated by their importance in

infrared technology, and more recently, because of their utility in laser technology and as thermoelectric materials. The PbX compounds are narrow direct gap semiconductors (group IV–VI), which crystallize at ambient conditions in the cubic NaCl structure. The lead salts exhibit properties which are unusual, relative to other semiconductors. Compared for example, with the usual III–V compounds, these IV–VI chalcogens present non-typical electronic and transport properties, such as higher carrier mobilities, higher dielectric constants, narrow band gaps and positive temperature coefficients (Cowley 1965; Dalven 1973; Murase 1980) [1]. These properties make them potential candidates for different technological applications. They have been used in thermoelectronic, optoelectronic or spintronic devices, especially in long wavelength imaging (Hummer et al 2007) [2], infrared diode lasers (Preier 1979) and in thermophotovoltaic energy converters (Zogg et al 1994) [3]. The semiconductors PbS, PbSe and PbTe show a small direct gap at the L point of the Brillouin zone. In contrast to most of the semiconductors, this gap decreases with hydrostatic pressure (Andreev 1968; Besson et al 1968; Martinez 1973) and increases with temperature (Tauber et al 1966; Andreev 1968; Martinez 1973) [4]. Although, considerable progress has been made concerning theoretical description of the structural and electronic properties of lead chalcogenides compounds, there is a real lack of knowledge of their thermal properties. An accurate description of thermal properties of solids is crucial, since, it plays a significant role in determining various material properties. To the best of our knowledge, there are no theoretical reports on the thermal behaviour of these compounds in the literature.

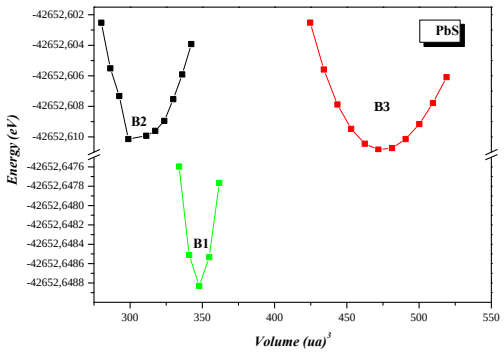
2. COMPUTATIONAL METHOD

The calculations were performed using the full-potential linearized augmented plane wave (FPLAPW) method [5] within the frame work of the DFT [6, 7] as implemented in the WIEN2K code [8], which is one of the most efficient method of simulating and calculating the ground state properties of cyrstalline materials [9]. The exchange-correlation potential for the structural properties was calculated by the generalized gradient approximation (GGA) based on Perdew et al. [10], while for the electronic properties, the Becke-Johnson (Mbj) scheme [11] was applied. In the FP-LAPW method, the wave function, charge density and potential are expanded differently in two regions of the unit cell. Inside the non-overlapping spheres around each atom of radius RMT (muffin-tin radius), spherical harmonic expansion is used and in the remaining space of the unit cell, a plane wave basis set is chosen. The convergence parameter, RMTkmax which controls the size of the basis sets in these calculations, was set to 8. RMT denotes the smallest atomic sphere radius and kmax gives the

magnitude of the largest k vector in the plane wave expansion. The charge density was Fourier expanded up to Gmax = 14 (Ryd)1/2 and the maximum l quantum number for the wave function expansion inside the atomic spheres was confined to lmax = 10. The muffin-tin radius was assumed to be 2.0, 2.0, 2.2 and 2.0 atomic units (a.u.) for the Pb, S, Se and Te atoms, respectively. A mesh of 47 special k-points for these binary compounds was taken in the irreducible wedge of the Brillouin zone. Both the plane wave cut-off and the number of k-points were varied to ensure total energy convergence.

3. RESULTS AND DISCUSSION

The first step of our calculations was to study the phase stability of the PbS, PbSe and PbTe compounds. It was demonstrated theoretically that for binary solids there extends a dense spectrum of as yet undiscovered polymorphs lying in an energetically narrow range above their phase ground states, with very small total energy differences between different polymorphs [12–16]. The diverse range of materials considered indicates that this is likely to be a general phenomenon. Motivated by these findings, several possible structural phases including the rock-salt (B1), cesium chloride (B2), zinc blende (B3). The full coordinates of atoms related to all optimized structures are given in Fig1. We show the calculated total energies per formula unit at different values of the unit cell volume for all the phases studied in this work. Our GGA calculations show that the rokdsalt (NaCl) structure is the ground state stable phase adopted by PbSe, PbTe and PbS compounds with the lowest calculated total energy at zero pressure. our results are in accordance with several experimental studies [16–20] and previous theoretical results whose calculations are based on the GGA approximation [21,22].



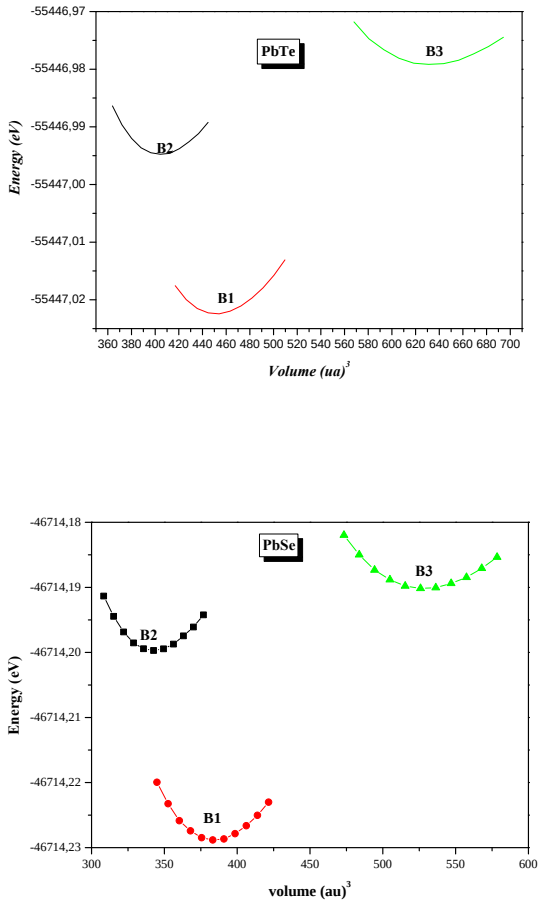


Fig.1 Total energy as a function of the volume calculated in the zinc blende phases (B3), NaCl (B1) and CsCl (B2) for the PbS, PbTe and PbSe compounds.

3.2. ELECTRONIC PROPERTIES

We have studied in this part the electronic properties of the binary compounds. In solid physics, energy bands give the possible energies of an electron in function of the wave vector k. From the dispersion equation E (k) which represents a very important property in the case of semiconductors, these electronic properties include band structures, gap energies (Eg), state densities. In our study, we calculated the energy bands of binary compounds PbTe, PbSe and PbS along the lines of high symmetry of the first Brillouin zone, in using both approximations (WC-GGA) and (mbj). The band structures obtained for each compound by the use of two approximations have almost the same pace, this is why only the curves obtained using the

(WC-GGA) are shown in Fig (2) and (3). Therefore, PbSe, PbS and PbTe have an indirect gap in the direction (L → L).

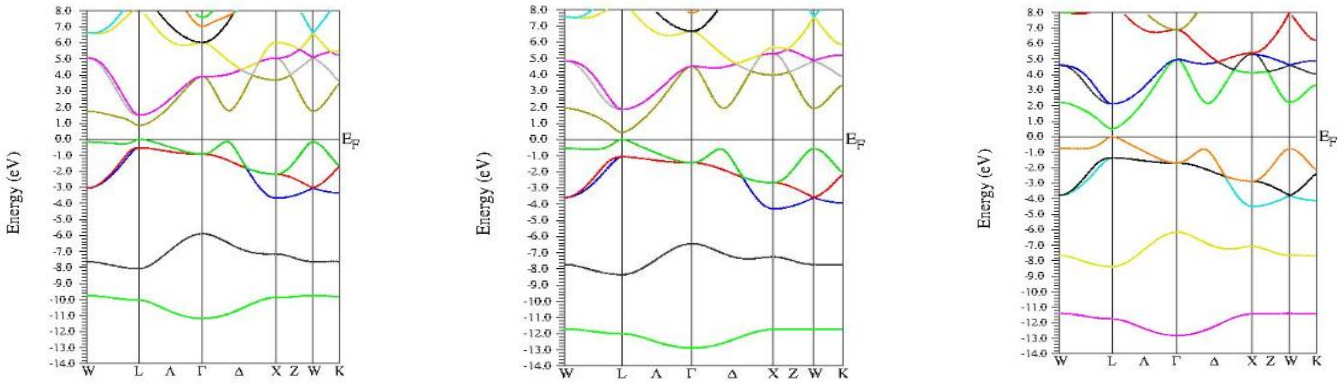


Fig2. Band structure of the PbS, PbTe and PbSe compounds in the NaCl structure using the WC-GGA in NaCl phase.

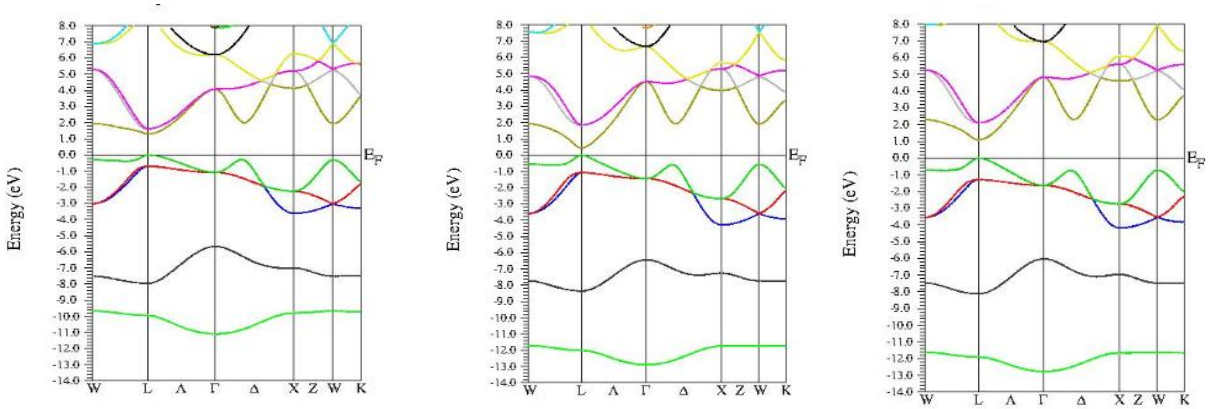


Fig3. Band structure of the PbS, PbTe and PbSe compounds in the NaCl structure using the mbj in NaCl phase

3.3 OPTICAL PROPERTIES

The optical properties in solid state physics describe the interaction of electromagnetic radiation with a material and induce polarization effects as well as the displacement of conduction electrons. These processes constitute the optical response of the material and can be characterized by the dielectric function ε (ω) which plays an important role in the study of the optical properties. We have studied and determined in this section the optical properties of our compounds PbX (X= S,Se and Te) understanding of the nature of these compounds and to give a clear idea of its applications in optoelectronic devices.

The complex dielectric function linearly connects the electric field E (ω) to displacement D (ω) by the equation:

$$D(\omega) = \varepsilon(\omega)E(\omega) \qquad (1)$$

The dielectric constant ε (ω) is a complex function in the case of a field dynamic [23-26]. This function is the sum of two components: ε1 (ω) component or real part and ε2 (ω) component or imaginary part such as:

$$\varepsilon(\omega) = \varepsilon_1(\omega) + i\,\varepsilon_2(\omega) \quad (2)$$

The real part ε_1 (ω) is connected to the polarization, and the imaginary part depends on the electronic transition at the origin of absorption. The two real and imaginary parts of the dielectric function can be obtained from the Kramers-Kronig relations [27,29]:

$$\varepsilon_1(\omega) = 1 + \frac{2}{\pi} P\int_0^{\infty} \frac{\omega'\,\varepsilon_2(\omega')}{(\omega'^2 - \omega_{12})} d\omega' \qquad (3)$$

$$\omega_2(\omega) = -\frac{2\omega}{\pi} P\int_0^{\infty} \frac{\varepsilon_1(\omega') - 1}{(\omega'^2 - \omega_{12})} d\omega' \qquad (4)$$

where ω is the light frequency and P is the main value of the Cauchy integral.

Among the optical properties that describe the interaction of light with the medium, finds the complex refractive index. Knowledge of the refractive index of semiconductors is important in the design and analysis of heterostructured lasers and other semiconductor waveguiding devices [33. This quantityN (□) □ n (□) □ik (□) can be obtained from the knowledge of both real and imaginary function of the dielectric function, and these can be written according to the refractive index n and the extinction coefficient k as follows:

$$\varepsilon_1(\omega) = n^2 - k^2 \quad (5)$$

$$\varepsilon_2(\omega) = 2nk \quad (6)$$

Where the actual refractive index n (ω) and the extinction coefficient, which is also called the attenuation index k (ω), can be given by the following two relations [30,31]:

At low frequency (ω = 0) and from the relation (III-9), we obtain the following relation:

$$n(\omega) = \frac{\varepsilon_{1(\omega)}}{2} + \frac{\sqrt{\varepsilon_1^{2(}(\omega) + \varepsilon_2^2}(\omega)}{2} \quad (7)$$

$$k(\omega) = \frac{\sqrt{\varepsilon_1^{2}(\omega) + \varepsilon_2^{2}(\omega)}}{2} - \frac{\varepsilon_1}{2} \quad (8)$$

In the calculations of the optical properties of PbX by approximation (WC-GGA), we used the equilibrium mesh parameter and a number of 1500 k-points in the Brillouin area, because the computation of these properties requires a large number of corresponding eigenvalues to eigenvectors.

$$n(0) = \varepsilon^{1/2}(0) \quad (9)$$

The calculation results of the imaginary part ε2 (ω) of the dielectric function in the range of energy from 0 to 25 eV for these binary compounds are illustrated in Figure (3-7). The analysis of these spectra shows that the behavior of ε2 (ω) is almost similar for all four compounds, and the first critical points of the dielectric function that corresponds to the fundamental absorption thresholds start at about 3.14, 2.19, 1.15 and 1.07 eV for PbS, PbSe and PbTe respectly. The origin of these points is due to the optical transition between the highest valence band and the lowest conduction band. Thus, we notice next to the fundamental peak the main peaks that reflect the maximum absorption, are located 6.12, 5.04, 5.35 and 4.45 eV. These peaks characterize the transitions (Lv-Lc)

From the calculated results of the real part of the dielectric function, we have determined the static dielectric constant ε1 (0) which is a larger quantity and given by the lower limit of the energy of ε (ω). The values of the static dielectric constant ε1 (0) and of the static refractive index n (0) obtained for the compounds PbX). The comparison with the theoretical data available in the literature was also made. Note that the calculated values of ε1 (0) and n (0) are in good agreement with other theoretical works.

The evolution of these spectra shows that the values of the refractive index of the PbS, PbTe PbSe compounds reach a maximum value at the energies 5.34, 4.86, 5.18, 2.63 eV, respectively.

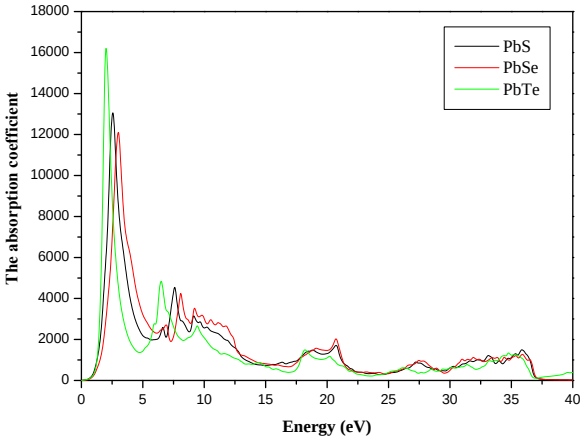


Fig3. The variation of the absorption coefficient as a function of energy for the compounds PbS, PbTe and PbSe.

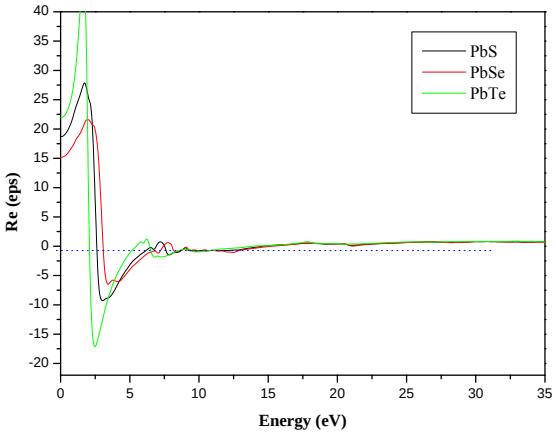


Fig4. Variation of the real part of the dielectric function according to the energy for compounds PbS, PbSe and PbTe.

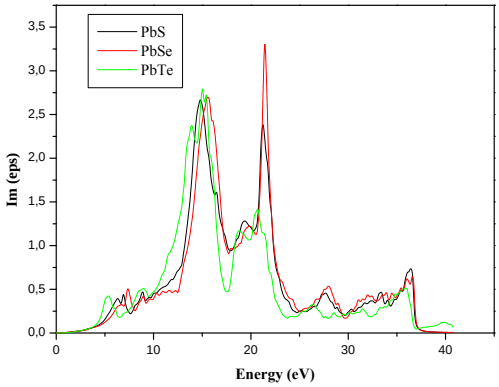


Fig5. Variation of the imaginary part of the dielectric function as a function of energy for the compounds PbS, PbSe and PbTe.

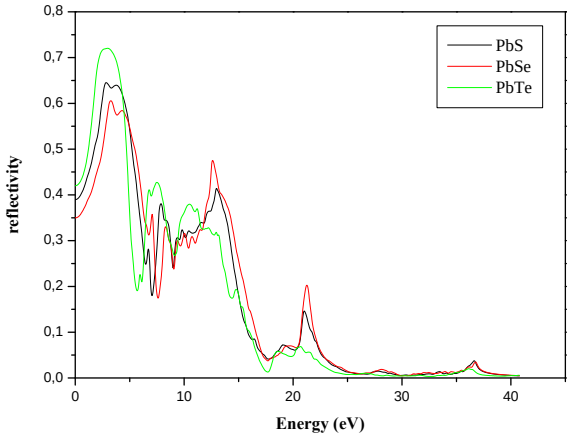


Fig6. The variation of the reflectivity as a function of the energy for the compoundsPbS, PbSe and PbTe.

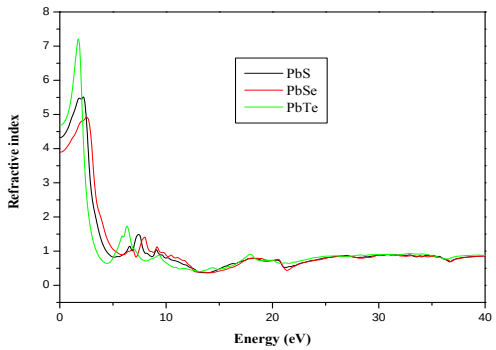


Fig 7. Refractive index variation as a function of energy for compounds PbS, PbSe and PbTe.

4. CONCLUSION

Employing the FP-LAPW method within the DFT in the framework of GGA and mBJ, we have studied the phase stability, pressure-induced phase transition, structural and electronic properties of the PbS, PbSe and PbTe compounds. A summary of our results is as follows: at zero pressure, the Rocksalt NaCl phase is found to be the most stable for PbSe, PbS and PbTe compounds. The calculated structural properties in our work are in good agreement with the available data and our band gaps, using GGA are lower than the experimental ones. The band gaps calculated with the mBJ functional are much better than the GGA and are closer to the experimental results.

5. REFERENCES

[1] Ahuja R et al 1996 Phys. Rev. B54 10419.

[2] Albanesi et al 2000 Phys. Rev. B61 16589.

[3] Anderson O K 1975 Phys. Rev. B42 3060.

[4] Andreev A A 1968 J. Phys. C4 50.

[5] Anderson OK. Linear methods in band theory. Phys Rev B. 1975;12:3060–3083.

[6] Hohenberg P, Kohn W. Inhomogeneous electron gas. Phys Rev. 1964;136:864–871

[7] Kohn W, Sham LJ. Self-consistent equations including exchange and correlation effects. Phys Rev A. 1965;140:A1133.

[8] Blaha P, Schwarz K, Madsen GKH, et al. WIEN2K, an augmented plane wave plus local orbitals program for calculating crystal properties. Vienna; 2008.

[9] Wong KM, Alay-e-Abbas SM, Fang Y, et al. Spatial distribution of neutral oxygen vacancies on ZnO nanowire surfaces: an investigation combining confocal microscopy and first principles calculations. J Appl Phys.2013;114:034901.

[10] Perdew JP, Burke S, Ernzerhof M. Generalized gradient approximation made simple. Phys Rev Lett. 1996;77:3865–3868.

[11] Tran F, Blaha P. Accurate band gaps of semiconductors and insulators with semi local exchange-correlation.

[12] Schon JC. Enthalpy landscapes of the earth alkaline metal oxides. Z Anorg Allg Chem. € 2004;630:2354–2366.

[13] Doll K, Schon JC, Jansen M. Structure prediction based on € ab initio simulated annealing for boron nitride. Phy Rev B. 2008;78:144110.

[14] Zwijnenburg MA, Bromley ST. Structural richness of ionic binary materials: an exploration of the energy landscape of magnesium oxide. Phys Rev B. 2011;83:024104–024109.

[15] Zwijnenburg MA, Illas F, Bromley ST. Apparent Scarcity of low-density polymorphs of inorganic solids. Phys Rev Lett. 2010;104:175103.

[16] Zachariasen W. On the crystal structure of magnesium-telluride. Z Phys Chem. 1927;128:417–420.

[17] Klemm W, Wahl K, Anorg Z. Note on magnesium telluride. Allg Chem. 1951;266:289–292.

[18] Kuhn A, Chevy A, Naud MJ. Preparation and some physical properties of magnesium telluride single crystals. J Cryst Growth. 1971;9:263–265.

[19] Parker SG, Reinberg AR, Pinnell JE, et al. Preparation and properties of Mgx Zn1¡ xTe. J Electrochem Soc. 1971;118:979–983.

[20] Waag A, Heinke H, Scholl S, et al. Growth of MgTe and Cd1¡ xMgxTe thin films by molecular beam epitaxy. JCryst Growth. 1993;131:607–611.

[21] Li T, Luo H, Greene RG, et al. High pressure phase of MgTe: stable structure at STP. Phys Rev Lett. 1995;74:5232–5235

[22] Goko € ————————————glu G, Durandurdu M, Gulseren O. First principles study of structural phase stability of wide-gap semicon- € ductors MgTe, MgS and MgSe. Comput Mater Sci. 2009;47:593–598.

[23] J.S. Tell, Phys. Rev. 104, (1956) 1760.

[24] L.D. Landau, E.M. Lifshitz, Electrodynamics in Continuous Media, Pergamon Press, Oxford, (1960).

[25] H.A. Kramers, Collected Science Papers, North Holland, Amsterdam, (1956) 333.

[26] R.De.L. Kronïg, J. Opt. Soc. Am. 12, (1926) 547.

[27] C. A. Draxl, R. Abt, ICTP lecture notes, unpublished, (1998).

[28] P. Y. Yu, M. Cardona, Fundamentals of Semiconductors, Physics and Materials Properties. Berlin: Springer-Verlag, (1999) 233.

[29] A.Pourghazi, M. Dadsetani, Physica B 370 (2005) 35.

[30] S. M. Hosseini. Physica B 403 (2008) 1907.

[31] D. Lee, A.M. Johnson, J.E. Zucker, C.A. Burrus, R.D. Feldman, R.F. Austin, IEEE Photon. Technol. Lett. 4 (1992) 949