Condensed Matter Physics, 2000, Vol. 3, No. 4(24), pp. 777–786

Simulation of energy states in solid solutions based on the ferroelectrics-semiconductors of $Sn_2P_2S_6$ type

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Received November 11, 2000, in final form November 28, 2000

The energy spectra of charge carriers in several models of the ordered solid solutions and virtual crystal model based on the ferroelectrics of $Sn_2P_2S_6$ type are calculated by the semiempirical pseudopotential method. It is shown that the band gap depends on the employed model of the solid solution.

Key words: *pseudopotential method, ordered solution, energy states, simulation, virtual crystal, ferroelectrics-semiconductors.*

PACS: *71, 07.05.Tp, 71.15.-m, 71.15.Hx, 71.20.Nr*

The physical property investigations of the ferroelectrics of the $(Pb_ySn_{1-y})_2P_2(S_xSe_{1-x})_6$ system [1,2] are relevant since one can look after the change of the crystal structure anisotropy and the effect of the anion and cation replacement on both the property anomalies in the critical region and the energy and phonon spectra. It was established [2,3] that the replacement of Sn by Pb in $(Pb_ySn_{1-y})_2P_2S_6$ leads to the decrease of the temperature of the ferroelectric phase transition and this transition does not change its character. The replacement of the S atom by Se in the system $Sn_2P_2(S_xSe_{1-x})_6$ leads to the splitting of the phase transition line [4]. The evolution of the phase transition peculiarities for the considered systems has been analyzed based on the investigations of temperature dependency of the heat conduction and the dielectric function [5]. The absorption edge studies of the ferroelectric solid solutions $(Pb_ySn_{1-y})_2P_2(S_xSe_{1-x})_6$ helped to establish the main conformities in the variation of the optical parameters (see table 1 from [2]). In particular, the change of the band gap with the concentration of the replacement atoms and the thermal and baric coefficients of the band gap changes were determined. Further, these important experimental characteristics can be used to compare

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the theoretical values obtained from the calculations of the energy structure under the pressure and temperature. We have already investigated the band structure of the $Sn_2P_2S_6$, $Sn_2P_2Se_6$ [6,7], $Pb_2P_2S_6$ and $Pb_2P_2Se_6$ crystals. The similarity of the crystal structures and the observed similarity of the band structures, the essential difference in the energy gap of the above mentioned crystals make it possible to create heterostructures based on them. Therefore, the theoretical simulation of the energy states in the solid solutions should precede the experimental fabrication of such heterostructures.

1. The models of the solid solution based on the $Sn_2P_2S_6$ crystals

In the paper [8] we discussed several models of the solid solution based on the CdSb and ZnSb crystals and investigated the energy states of the charge carriers. We considered the model of the virtual crystal [9] with the averaged lattice parameters and atomic positions or parameters of pseudopotential form, i.e., factors. As it is known, such a model overcomes the difficulties connected with the breaking of translational symmetry. We also proposed the model of the ordered solid solution [9,10], in which the periodic structure remains. Both models are utilized in the pseudopotential calculations. Our simulation of the energy states showed that the behaviour of the dispersion curve $E(\mathbf{k})$ slightly changes and depends on the considered model. The shift of the local extrema is possible too, but the band gap changes considerably.

Similar to [8], let us carry out the calculation of the energy spectra of the ordered solid solutions based on the crystals of $Sn_2P_2S_6$ type. We will consider the replacement solutions where the atoms of different types distribute only in the positions of the crystal lattice. The presence of many atoms in the unit cell (two formula units, 20 atoms [1]) makes it possible to choose different versions of placing the replacement atoms. The strains are known to appear in these cases. They could be compensated by the deformation of the unit cell and by the change of the atom positions. But the problem of determining the energy of the internal strains is quite complicated since these strains are defined not only by the crystallographic peculiarities but also by the magnitudes of the elastic module. So, as far as we have no information about the deformation change of the lattice parameters from the concentration of the replacement atoms we will consider several versions of the solid solution models, assuming that the replacement of the atoms of one type by the atoms of another type causes no changes in the lattice either the changes do occur, and the lattice parameters are regarded as the mean parameters.

To choose the solid solution model, we utilize the investigation data of the concentration rearrangement of vibrational spectra for the mixed crystals $Sn_2P_2(Se_xS_{1-x})_6$. Authors of [11,12] showed that the increase of x leads to the decrease of a number of anions $[P_2S_6]^{4-}$. It corresponds to the appearance of the additional bands in the vibrational spectra. The intensity of these bands is proportional to the probability of the appearance of the structure group $P_2[Se_kS_{6-k}]^{4-}$ (k=1...6) type. The analysis

Table 1. The atomic coordinates of the $Sn_2P_2S_6$ crystal ($P2_1/n$).

Atom number	Atom	X	Y	Z
1	Sn	0.2574	–0.3691	0.0410
2	Sn	0.2426	0.1309	0.4590
3	P	–0.0674	–0.1087	0.0605
4	P	0.4326	–0.3913	–0.4395
5	S	–0.2630	–0.0021	0.1013
6	S	0.0325	–0.1913	0.3229
7	S	0.0569	0.3023	0.1560
8	S	0.2370	–0.4979	–0.3987
9	S	0.4431	–0.1977	0.3440
10	S	0.4675	0.3087	0.1771

of the frequency of P-S(Se) valence vibrations and the calculations of the probability show us that a lot of the mixed anions in the solid solutions of $Sn_2P_2(Se_xS_{1-x})_6$ are realized at $x = 0.5$, especially in the complex consisting of three atoms of S and of three atoms of Se. Besides it was shown that other configurations of the complexes $P_2[Se_kS_{6-k}]^{4-}$ are possible too.

Let's consider the following models of the solid solution similar to the investigations of [11,12]:

Model 1: Pb atoms replace half of Sn atoms in $Sn_2P_2S_6$.

Model 2: one atom of S is replaced by Se in $Sn_2P_2S_6$ crystal. It corresponds to the presence of a structure group of PS_2Se–PS_3 type.

Model 3: the third of S atoms is replaced by Se atoms. The structure complexes PS_2Se–PS_2Se and $PSSe_2$–PS_3 are realized in this case.

Model 4: half of S atoms are replaced by Se atoms. It corresponds to the presence of the structure groups of PS_3–PSe_3 and $PSSe_2$–PS_2Se type, and besides the complex PS_3–PSe_3 is less probable according to the calculation [12].

Note that the lattice parameters of the $Sn_2P_2S_6$ crystal remain the parameters of the above mentioned models of the solid solutions: a=9.318 Å, b=7.463 Å, c=6.518 Å, $\gamma = 91.15°$ [13]. In these models, the unit cell contains the same number of atoms as in the constituent materials and the replacement is performed in such a manner that the space symmetry of the resulting crystal does not change.

Model 5: the virtual crystal.

The atomic coordinates for the $Sn_2P_2S_6$ crystal (space group $P2_1/n$, the origin is replaced on the value $r_0 = (a + b + c)/4$ [7,13]) are presented in table 1. The atoms with their coordinates are denoted as 1–10 and the atoms with the invariant coordinates are denoted as $1' - 10'$ accordingly.

In the first model of the solid solution, the choice of the versions is digit: 1, 1' or 2, 2'atoms (Sn) are replaced by Pb atoms. In the second model we considered such distribution of the atoms: 5, 6, 8 and 5', 6', 8' atoms are the S atoms and the 7, 7' atoms are the Se atoms. Model 3 assumes the following versions: the first version – 5, 6, 8, 9 and 5', 6', 8', 9' atoms are S atoms; 7, 10 and 7', 10' are the Se atoms; the second version: 5, 8, 9, 10 and 5', 8', 9', 10' atoms are the S atoms and 6, 7, 6', 7' atoms are Se atoms. We chose different versions in the fourth model of the $Sn_2P_2(S_{0.5}Se_{0.5})_6$ solid solution: the first version – 5, 6, 7 and 5', 6', 7' atoms are the S atoms; 8, 9, 10 and 8', 9', 10' atoms are the Se atoms; the second version – 5, 8, 9 and 5', 8', 9' atoms are the S atoms; 6, 7, 10 and 6', 7', 10' atoms are Se atoms. Since the latter is the most probable, we consider different cycle rearrangements of the atoms.

2. The analysis of the dispersion curves for different models of the solid solutions based on the $Sn_2P_2S_6$ crystals

Now we analyze the changes which take place in the vicinity of the extrema of valence and conduction band in the resulting solid solutions based on the $Sn_2P_2S_6$ crystals at the replacement of Sn and S atoms.

As it is shown in our work [7], the band structure of the crystal $Sn_2P_2S_6$ is characterized by many valleys. The absolute extremum of the valence band is localized in the vicinity of Y point and displaces on the k_xk_y plane in the Brillouin zone. The additional extremum of the valence is localized in the vicinity of R point The absolute and additional extrema for the conduction band are localized on the R-U and Γ-Y symmetry lines [7]. More detailed calculations showed that Δk, corresponding to the difference between the localization points of the conduction band minimum and valence band maximum in the Γ-Y direction, is equal to 0.03 π/b. Energy ΔE, corresponding to this Δk, is equal to $\sim$ 0.02 eV for the conduction band and is equal to 0.004 eV for the valence band (matrix order N $\sim$ 400). The value of ΔE slightly increases with the decrease of the plane wave number. Therefore, one can consider that direct transitions are realized in the vicinity of Y point if the pseudopotential calculations are inaccurate. The direct transitions are also confirmed by the optical investigations [1]. To calculate the energy spectra in the solid solutions we will take into account only the Γ-Y and R-U directions of the Brillouin zone. We denote the first minimum forbidden gap as Eg_1 and the second minimum forbidden energy interval, connected with the additional valley in the conduction band, as Eg_2.

To calculate the energy states in the solid solutions we used the semiempirical pseudopotential method. The form-factors for different ions of α type are described by the analytical expression [9]:

$$\begin{aligned} v^{\alpha}(q) &= \beta \times v_0^{\alpha}(q); \\ v_0^{\alpha}(q) &= A_1^{\alpha}\left(q^2 - A_2^{\alpha}\right) / \left(1 + \exp A_3^{\alpha}\left(q^2 - A_4^{\alpha}\right)\right), \end{aligned}$$

where $\beta = \Omega^{\alpha}/\Omega_c$ is the normalizing parameter, Ω^{α} is the atomic volume of the type α: $\Omega^{\mathrm{Sn}} = 181.5$, $\Omega^{\mathrm{Pb}} = 203.4$, $\Omega^{\mathrm{S}} = 173.6$, $\Omega^{\mathrm{Se}} = 181.6$ atomic unit [9]; Ω_c is the volume of the unit cell; $\mathrm{A}_i^{\alpha}(i = 1-4)$ are the pseudopotential parameters. For the Sn, Pb, S, Se and P atoms, these parameters are listed in table 2. The form-factors

Table 2. The values of A_i^{α} parameters for the Sn, Pb, P, S and Se atoms.

Atom	A_1	A_2	A_3	A_4
Sn	0.4	1.916	1.05	0.6
Pb	0.33	2.16	1.05	0.6
P	0.9	2.6	0.664	–1.44
S	0.2	3.13	2.5	3.0
Se	0.155	3.13	3.1	3.2

were selected so that, on the one hand, they coincided with the form- factors of the model pseudopotential in the actual region of the wave vectors [14] and, on the other hand, they gave the real value of the energy gap. We used the same program of calculation and kept the same order of the secular matrix (~ 400) as in calculation of the band structure of the $Sn_2P_2S_6$ crystal [7].

Besides, the investigations of the energy spectra were carried out for different parameters β.We consider the cases when α is Pb or Sn for the Pb "impurity atoms" in the crystal $Sn_2P_2S_6$ or $Pb_2P_2S_6$, and α is Se or S for the Se "impurity atoms" in the $Sn_2P_2S_6$ or $Sn_2P_2Se_6$ crystal. The values of β are presented in the table 3 only for the cases: $\beta = \Omega^{\mathrm{Sn}}/\Omega_{\mathrm{Sn_2P_2S_6}} = 0.059$, $\beta = \Omega^{\mathrm{Pb}}/\Omega_{\mathrm{Pb_2P_2S_6}} = 0.065$, $\beta = \Omega^{\mathrm{S}}/\Omega_{\mathrm{Sn_2P_2S_6}} = 0.057$, $\beta = \Omega^{\mathrm{Se}}/\Omega_{\mathrm{Sn_2P_2Se_6}} = 0.053$.

The obtained dispersion curves $E(\mathbf{k})$ for both the valence and the conduction bands in the extrema vicinity for the solid solutions of $(Pb_{0.5}Sn_{0.5})_2P_2S_6$ and $Sn_2P_2(Se_xS_{1-x})_6$ are presented in figures 1–3. For the purpose of revealing the changes in the energy spectrum we also present the fragment of the energy structure in the Γ–Y and R–U directions in the Brillouin zone for the $Sn_2P_2S_6$ crystal.

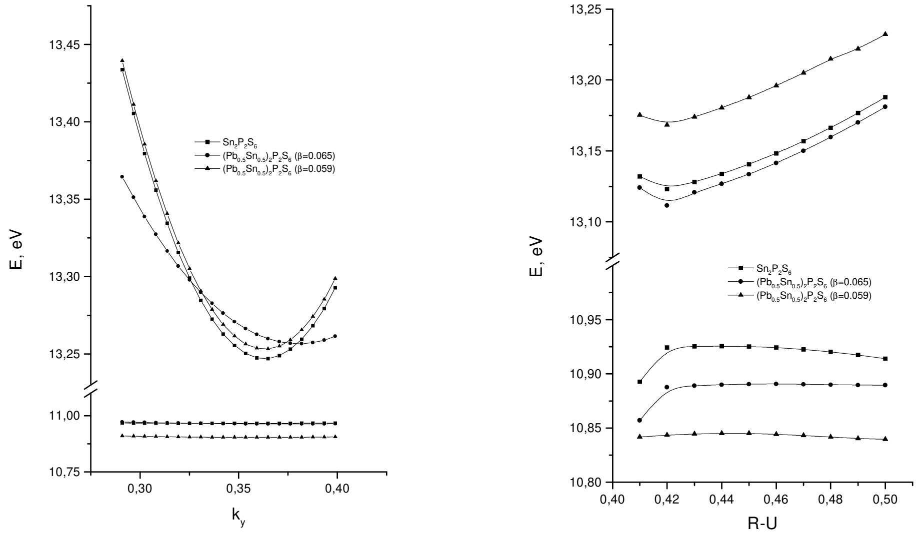

Figure 1. Dispersion curves $E(\mathbf{k})$ in the vicinity of the absolute extrema for the model 1 and for $Sn_2P_2S_6$ crystal.

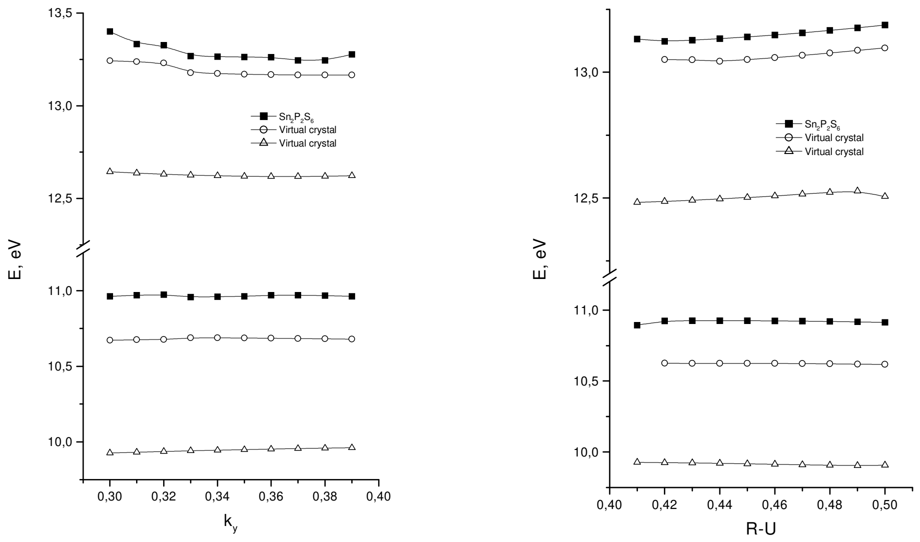

Figure 2. Dispersion curves $E(\mathbf{k})$ in the vicinity of the absolute extrema for the virtual crystal model.

The results of our calculations show that the replacement of Sn by Pb (independently on the position of Sn atom in the cell) in the $Sn_2P_2S_6$ crystal does not lead to essential changes in the energy spectrum (figure 1). The localization points of the absolute and additional extrema in the solid solution of the first model $(PbSn)P_2S_6$ coincide with those for the $Sn_2P_2S_6$ crystal. The deviation of Eg_1 for the case $\beta = 0.0653$ (α is Pb) equals $\sim$ 0,4% and for the parameter β=0.059 this deviation equals $\sim$ 5% (α is Sn). Note that the second subband, localized in the R-U direction, is more sensitive to atomic replacements. An insignificant change takes place for Eg_2 as well (figure 1). The experimental investigations regarding the fundamental absorption of the $Sn_2P_2S_6$ materials at the cation replacement suggest a small change of the energy gap in the crystals $(Pb_xSn_{1-x})_2P_2S_6$ [2].

The calculations of the energy structure for the virtual crystal model are presented in figure 2. We used the form-factors of the pseudopotentials averaged over the pseudopotential parameters A_i. The lattice parameters, atomic coordinates and angles were also averaged over $Sn_2P_2S_6$ and $Pb_2P_2S_6$ crystals (model 5, the first version) and $Sn_2P_2S_6$ and $Sn_2P_2Se_6$ crystals (model 5, the second version). As follows from the analysis of the dispersion curves $E(\mathbf{k})$ in figure 2, the Eg_2 changes unessentially in comparison with the ideal crystal $Sn_2P_2S_6$ and equals 2.35 eV, besides the shift of the local extremum for the valence band toward the little wave vector $\mathbf{k}$ in the Γ-Y direction of the Brillouin zone is observed. The value of Eg_1 equals 2.45 eV for the second version of the virtual crystal. A slight shift of the bottom of the conduction band takes place in this case.

Let's analyze the dispersion curves $E(\mathbf{k})$ for the models 2–4 of the solid solution $Sn_2P_2(Se_xS_{1-x})_6$ (figure 3). Note that the following replacement of S atoms by the Se atoms from 1 to 3 in the structure complex $[Se_kS_{6-k}]^{4-}$ leads to the decrease of Eg_1 and Eg_2. The most sharp changes are observed at the parameter β=0.053 (α is Se). It is interesting that the energy gap Eg_1 is equal to 0.6 eV for the solid solution

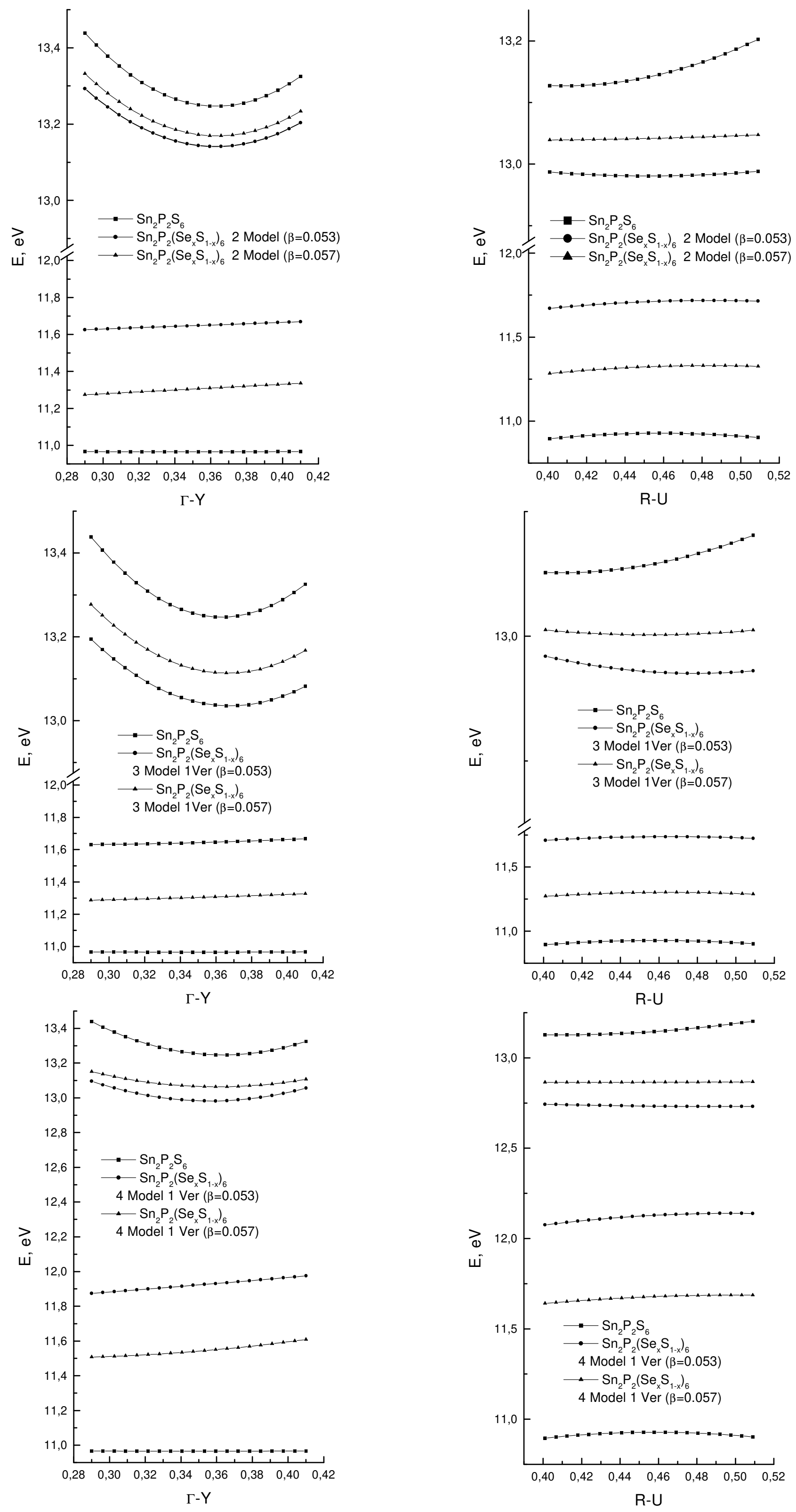

Figure 3. Dispersion curves $E(\mathbf{k})$ in the vicinity of the extrema for the solid solutions of the models 2–4.

Table 3. The results of the band structure calculations in the different models of the ordered solid solution and the virtual crystal model on the base of the ferroelectrics of the $Sn_2P_2S_6$ type.

Substance	β	Eg_1, eV	Eg_2, eV
$Sn_2P_2S_6$	–	2.15	2.25
Model 1	0.065	2.14	2.24
$(SnPb)P_2S_6$	0.059	2.25	2.34
Model 2	0.053	1.26	1.43
	0.057	1.65	1.79
Model 3			
Version 1	0.053	1.18	1.30
	0.057	1.62	1.74
Version 2	0.053	0.80	0.96
	0.057	1.36	1.48
Model 4			
Version 1	0.053	0.59	0.84
	0.057	1.17	1.37
Version 2	0.053	0.91; 0.88	1.19; 1.10
	0.057	1.41; 1.31	1.55; 1.57
Virtual crystal (model 5)			
Version 1		2.35	2.48
Version 2		2.45	2.60

$Sn_2P_2(Se_{0.5}S_{0.5})_6$ where the structure complex $P[Se_kS_{3-k}]$ consists of the Se atoms in one trigonal pyramid (such groups are less real according to the calculations [11]). The maximum for the valence band is localized in the point R of the Brillouin zone. The rapprochement of the certain and additional valleys in the model 4 of the solid solution is observed as well.

The estimations of the values Eg_1 and Eg_2 for the above mentioned ordered solid solutions of the $Sn_2P_2(Se_xS_{1-x})_6$ system are listed in table 3.

3. Conclusion

Thus the pseudopotential calculations of the energy states in different ordered solid solutions based on the $Sn_2P_2S_6$ crystals show that the energy gap essentially changes depending on the model employed. In spite of the simplicity of the above considered models we obtain (at a fixed value of β) that the replacement of S atom by Se in the anion sublattice of the $Sn_2P_2S_6$ crystal leads to a decrease of the energy gap Eg, simultaneously the replacement Sn$\rightarrow$ Pb increases Eg (at $\beta = 0.059$). Analogical results have been obtained for the solid solutions of $Sn_2P_2(Se_xS_{1-x})_6$ and $(Pb_xSn_{1-x})_2P_2S_6$ in the paraelectric phase [15] but the concentration dependencies of Eg (as it is follows from figure 1, table 1 [15]) have got a less sharp character in comparison with our calculations. One can explain the unessential change of the minimum forbidden gaps at the replacement Sn$\rightarrow$ Pb and more essential changes at the replacement S$\rightarrow$ Se using the functional dependencies of the form-factor of the pseudopotentials (see formula) for the atoms Sn and Pb and the atoms S and Se. It has been found that the values of the normalizing form-factors for Sn and Pb atoms at $\beta = 0.059$ almost coincide in the actual region of the wave vectors q. The normalizing form-factors for atoms S and Se have got different values in the same region of the wave vectors, and as a consequence the change of the extrema of the conduction band and of the valence band occurs. Varying the parameter β we change the value $v^{\alpha}(q)$ and obtain different values for Eg_1 and Eg_2. It is possible that the oscillated character of the change of the energy gap (see table 3) testifies that the considered models are only the extreme limits of all variations, which really take place in the ordered solid solution in comparison with the pure crystals. Such a simulation of the energy states in the solid solutions based on the $Sn_2P_2S_6$ crystals may stimulate the investigations and fabrication of the heterostructures and the materials with the control physical properties.

4. Acknowledgement

Authors are very grateful to Prof. Dr. D.M.Bercha for her help in the analysis of the results obtained.

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Моделювання енергетичних станів у твердих розчинах на основі сегнетоелектриків-напівпровідників типу $Sn_2P_2S_6$

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Отримано 11 листопада 2000 р., в остаточному вигляді – 28 листопада 2000 р.

Методом напівемпіричного псевдопотенціалу розраховані енергетичні спектри носіїв заряду в деяких моделях впорядкованих твердих розчинів і моделі віртуального кристала на основі сегнетоелектриків-напівпровідників типу $Sn_2P_2S_6$. Показано, що ширина забороненого зони суттєво залежить від вибраної моделі твердого розчину.

Ключові слова: *метод псевдопотенціалу, енергетичні стани, впорядковані тверді розчини, віртуальний кристал, моделювання, сегнетоелектрики-напівпровідники*

PACS: *71, 07.05.Tp, 71.15.-m, 71.15.Hx, 71.20.Nr*