Summary. Parashchuk T.O. Thermodynamic properties of II-VI chalcogenide crystals: modeling and calculation. – Manuscript.

Thesis for the Candidate Degree in Physics and Mathematics. Speciality 01.04.07 – Solid State Physics. – Yuriy Fedkovych Chernivtsi National University, Chernivtsi, 2015.

Thesis is devoted to the theoretical calculations and experimental study of important thermodynamic parameters of II-VI crystals and their own defect subsystem. The cluster models of polymorphs of cubic sphalerite and hexagonal wurtzite for stoichiometric II-VI (ZnX, CdX; X = S, Se, Te) crystals have been offered. There was carry out the calculations of values of thermodynamic parameters under normal conditions and defined the analytical expressions of temperature dependences for energy ΔE, enthalpy ΔH, Gibbs free energy ΔG, entropy ΔS for sphalerite phase stoichiometric crystals of zinc and cadmium chalcogenides.

Using the results of DFT-calculations of the molar heat capacity at constant volume for stoichiometric crystals of zinc and cadmium chalcogenide of sphalerite phase was calculated the temperature dependence of Debye temperatures Θ_D and using the equality of Gibbs free energy for sphalerite and wurtzite phases ($\Delta G_S = \Delta G_W$) of zinc chalcogenides crystals was defined phase transition "sphalerite-wurtzite" temperatures, which are decreased in the line ZnS(1454 K) – ZnSe(1427 K) – ZnTe(1382 K) and was found the specified region of stability for polymorphs.

It was established the correlation between thermodynamic (ΔE, ΔH, ΔG, ΔS) and heat (C_V, C_P, Θ_D) parameters of ideal crystals ZnX, CdX and their basic fundamental characteristics (band gap E_g, contribution of ionization δ, electronegativity ΔX, band energy D, comprehensive compression module B).

Using crystal-quasi-chemical approaches and expressions for chemical potentials of ionized defects was defined type and charge state of point defects for undoped zinc (cadmium) tellurides, calculated the dependence of the equilibrium concentration of defects and free carriers from stoichiometric composition and technological factors of two-temperature annealing (annealing temperature T, the vapor pressure of zinc P_{Zn} and cadmium P_{Cd}), specified the homogeneity region of the ZnTe and CdTe compounds under conditions of saturation by the metal and chalcogen respectively.

It is shown that in p-ZnTe crystals the dominant point defects are doubly charged zinc [V_{Zn}^{2-}] and tellurium [V_{Te}^{2+}] vacancies and interstitial tellurium atoms [Te_i^{2-}]. After annealing of p-ZnTe in the zinc vapor $P_{Zn} = (10^3\text{-}10^5)$ Pa and annealing temperature T = (1000-1250) K the dominant point defects are doubly [V_{Zn}^{2-}] and singly [V_{Zn}^{-}] ionized zinc vacancies. Annealing in a couple of tellurium leads to dominance of [V_{Zn}^{-}] and [V_{Zn}^{0}] because of the displacement of the Fermi level toward the valence band and the increasing of the concentration of holes.

Keywords: first principe calculations, II-VI semiconductor crystals, sphalerite, wurtzite, defect concentration, thermodynamic parameters.