First Empirical Investigations of The Thermodynamic Properties in II-VI Chalcogenide Crystals

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In this paper the cluster approaches for calculations of thermodynamic parameters of zinc chalcogenides have been proposed. Specifically there were determined formation enthalpy ΔH, formation energy ΔE, entropy ΔS, Gibbs free energy ΔG, heat capacity at constant volume C_V and constant pressure C_P of crystals. On the base of temperature dependences of Gibbs free energy for sphalerite and for wurtcite phases there were determined the transition temperatures between these phases. And on the base of temperature dependences of heat capacity at constant volume were determined the temperature dependences of Debye temperature θ_D. The calculation was carried out within the cluster approximation with using of DFT-method with the valence basic set B3LYP. All calculations have been spending in quantum-chemical computer packet PCGamess (FireFly).

For the calculation of sphalerite we used two cluster models of zinc chalcogenides: clusters A and B. The model A includes a zinc atom which is surrounded by two ligands, and has the general formula $ZnC_2H_2X_4$. The general formula of the cluster B is $Zn_4C_6H_6X_{13}$, contains a Zinc atom which is surrounded by four chalcogen atoms, it can be corresponded to a real crystal, all these atoms are four-coordinated. We used six HCX_2-ligands, which had saturated the dangling bonds.

Wurtzite structure was studied by using three models: C, D and E. Cluster C (general formula $Zn_{15}X_{15}$) was the base for the calculation of the spatial and electronic structure and the thermochemical quantities. This model consists of 30 atoms and contains two pairs of four-coordinated, eight pairs of three-coordinated and five pairs of two-coordinated couples of atoms. Cluster D (the general formula $Zn_{11}X_{11}$) consists of 22 atoms. It contains one four-coordinated, six three-coordinated and four two-coordinated pairs of atoms. Cluster E of wurtzite modification (with the general formula $Zn_{10}X_{10}$) consists of 20 atoms. It contains one four-coordinated, four three-coordinated and five two-coordinated pairs of atoms.

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