Cluster Models and *ab initio* Calculations of Thermodynamic Parameters of Lead Chalcogenides

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Lead telluride can be used in semiconductor optoelectronics for deep infrared thermal photovoltaics as materials that works in 300-950 K temperature range. PbX (X = Te, Se, S) can be used as the components of infrared detectors and emitters of infrared lasers, photodetectors, solar cells, thermoelectric devices, field effect transistors and as telecommunication appliances. The effective using of this materials both in model studies and practical applications caused by set of unique properties of lead telluride, in particular, bocouse the small band gap, high carrier mobility and high dielectric constant.

The first step for the quantum-chemical calculation of the cluster properties was the determination of the lowest energy configuration. All calculations started with SCF (Self-Consistent Field) convergence and geometry optimization; after obtaining a stable minimum, the frequencies were calculated. The calculations of the lowest energy structure were carried out using Hartry-Fock method on the basis of the Stevens-Basch-Krauss-Jasien-Cundari (SBKJC) parameterization. In this basic set only the valence electrons which are directly involved in chemical bonding are considered.

The calculation of thermodynamic parameters have been spent using the software package Firefly (PCGamess) within the density functional theory method (DFT), using hybrid valence electrons basic set B3LYP [1]. Visualization of spatial structures was carried out using Chemcraft.

Analytical expressions for temperature dependence of the energy ΔE, enthalpy ΔH, Gibbs free energy ΔG and entropy ΔS of PbTe crystals for the temperature range from 80 to 1000 K are represented by the following expressions respectively:

$$\Delta E(T) = 0,0271 \cdot T + 64,494, \quad (1)$$

$$\Delta H(T) = 0,0243 \cdot T + 64,494, \quad (2)$$

$$\Delta G(T) = 0,0241 \cdot T + 64,54, \quad (3)$$

$$\Delta S(T) = 0,0271 \cdot \ln T - 54,11, \quad (4)$$

Obtained by us analytical expressions of temperature dependencies of heat capacity at constant volume C_v and heat capacity at constant pressure C_P are shown by the following equations:

$$C_V = 50,7 + 6,6 \cdot 10^{-3} T - 0,044 \cdot 10^5 T^{-2}, \quad (5)$$

$$C_P = 45,1 + 6,6 \cdot 10^{-3} T - 0,044 \cdot 10^5 T^{-2}. \quad (6)$$

This research is sponsored by NATO's Public Diplomacy Division in the framework of "Science for Peace" (NATO SPS 984536)).

1. S. Pashinkin, M. S. Michailova, A. S. Malkova, V. A. Fedorov, Inorganic Materials, 45 (11), (2009), 1226.