P-T-x Phase Diagram of the Ga-Se System: Thermodynamics and Nonstoichiometry of Gallium Elenides

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Gallium selenides are perspective optoelectronic and thermoelectric compounds which are formed in the Ga-Se system. P-T-x diagram of this system is of interest for growing from the melt and vapor of bulk and film gallium selenides with a definite deviation from stoichiometry.

P- T-, T-x- and P-x- projections of the three-dimensional P-T-x diagram are discussed. It is important that at the maximum melting point the compositions of the coexisting solid, melt and vapor are not identical: x(solid) not equal x(melt) not equal x(vapor). Congruent and incongruent phases and phase processes are considered.

The heat capacities, c_p= f(T), of gallium selenides were determined in a adiabatic calorimeter in the temperature range 10-325K based on 88 c_p values for GaSe and 103 values for Ga_2Se_3. Uncertainty in c_p is 0.25% in the temperature range of 50-300K, and more substantial (up to 2%) in the temperature range 14.15-50K. The smoothing of the c_p =f(T) was made using a spline- approximation and software of the IVTANTHERMO Databank. By using the obtained values of c_p, isochoric heat capacity, c_v, and Debye temperatures (q) of gallium selenides were calculated. The thermodynamic functions (entropy, thermodynamic potential and enthalpy) were calculated in the 10- 320K temperature range according to the spline coefficients.

The new selective chemical transport reaction (SCTR) technique was employed to control the nonstoichiometry of gallium selenides. The basic approach of this method is the introduction (or extraction) of gallium into solid gallium selenides using chemical transport reaction: Ga(in condensed phase) + GaI_3(gas) = 3GaI(gas), where Dr H > 0- enthalpy of the reaction. This equilibrium strongly depends on the temperature conditions: shifts to the right or left with an increase or decrease in temperature, respectively. Such a shift decreases or increases the Ga content in a condensed phase. Controlling the temperature makes it possible to control the nonstoichiometry of gallium selenides. X-Ray diffraction and cathodoluminescence spectroscopy have been used for the nonstoichiometry characterization.