Determination of thermodynamic properties of lithium monosilicide based on calorimetric and hydrogenation experiments

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The increasing demand for more efficient energy sources in portable devices and electric vehicles represents a major challenge for battery research and technology. Silicon and the lithium silicides have attracted increasing attention for use as anode material in future Lithium-Ion-Batteries (LIB) in view of costs and capacity. A consistent thermodynamic description of the Li-Si-system including phase and electrochemical equilibria is of great importance for the battery development as well as for the basic understanding of the system.

The phase diagram has been studied in literature for a very long time, but only few reliable experimental thermodynamic data was reported. Motivated by this situation we reported the heat capacities and entropies of the five stable phases $Li_{17}Si_4$, $Li_{16.42}Si_4$, $Li_{13}Si_4$, Li_7Si_3 und $Li_{12}Si_7$ [1,2] and determined recently the enthalpy of formation of Li_7Si_3 und $Li_{12}Si_7$ by linking of the hydrogen equilibrium pressures $p_{eq}(H_2)$ from hydrogenation measurements in a Sievert´s type apparatus with the precise heat capacity and entropy data of the appropriate lithium silicides[3].

The aim of this study is the experimental determination of the heat capacity, entropy and enthalpy of formation of LiSi. These measurements require a phase pure sample that was synthesized by mechanical alloying. The LiSi was characterized by means of XRD, DSC and chemical analysis. The heat capacity of LiSi was measured using two different calorimeters. In the low temperature region from 2 K to 300 K a Physical Properties Measurement System (PPMS, Quantum Design) based on a relaxation technique was used, whereas the measurements at higher temperature (300 K to 740 K) were performed in a DSC 111 (Setaram) applying the C_p-by-step method. The measurements at low temperature permit the calculation of the standard entropies, as well as electronic and lattice contributions to the heat capacity. The enthalpy of formation of LiSi was computed based on the combination of hydrogenation investigations in a Sieverts apparatus with the heat capacity and entropy data. The results of this work represent a significant contribution towards a reliable thermodynamic data set for the Li-Si-system.

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