



# The heat capacity and entropy of the metastable lithium silicide $\text{Li}_{15}\text{Si}_4$ in the temperature range (2 to 615) K



Franziska Taubert<sup>a</sup>, Jürgen Seidel<sup>a</sup>, Regina Hüttl<sup>a</sup>, Matej Bobnar<sup>b</sup>, Roman Gumeniuk<sup>c</sup>, Florian Mertens<sup>a,\*</sup>

<sup>a</sup> Institute of Physical Chemistry, TU Bergakademie Freiberg, D-09599 Freiberg, Germany

<sup>b</sup> Max-Planck-Institute for Chemical Physics of Solids, D-01187 Dresden, Germany

<sup>c</sup> Institute of Experimental Physics, TU Bergakademie Freiberg, D-09596 Freiberg, Germany

## ARTICLE INFO

### Article history:

Received 2 March 2017

Received in revised form 7 August 2017

Accepted 28 September 2017

Available online 30 September 2017

### Keywords:

$\text{Li}_{15}\text{Si}_4$

Heat capacity

Entropy

## ABSTRACT

This contribution presents the heat capacity of metastable  $\text{Li}_{15}\text{Si}_4$  as a function of temperature in a range from (2 to 615) K. The measurements were performed using two different calorimeters depending on their specification. In the low temperature region from (2 to 300) K a calorimetric method based on a relaxation technique was used, whereas for the high temperature region from (300 to 615) K, DSC measurements applying the  $C_p$ -by-step method were carried out. The experimental data are given with an accuracy better than  $\pm 2\%$  above 5 K and up to 9% below 5 K. The measurement at low temperatures allow the calculation of the standard entropy and entropy of formation as well as temperature coefficients of electronic and lattice contributions to the heat capacity. The results represent a significant contribution to the data basis for thermodynamic calculations (e.g. CALPHAD) and to the understanding of electrochemical equilibria in the Li-Si-system.

© 2017 Elsevier Ltd.

## 1. Introduction

The abrupt shift from fossil fuels to renewable energy sources, such as wind and solar energy, leads to the development of new energy storage technologies. Electrochemical systems such as Lithium-Ion-Batteries (LIB) are brought into focus in this field. Hence, the development and thermodynamic characterization of suitable anode and cathode materials are essential. Lithium silicides are widely discussed as promising anode materials which offer, compared to the dominating graphite material, high storage capacities (e.g.  $\text{Li}_{17}\text{Si}_4$ : 4054 mAh/g<sub>Si</sub>) [1,2] and low discharge potentials [3,4]. However, the large volume changes during charging and discharging causes electrode pulverization and capacity fading [5]. Remarkable progress has been made by using thin films [6], nanotubes [7,8], or nanowires [9] of silicon to relieve mechanical stress. For a better understanding of the phase diagram and the respective phase transitions, fundamental knowledge of the physicochemical properties and especially the thermodynamic quantities, such as the heat capacity  $C_p$  and the standard entropy  $S^\circ$ , are essential.

The first thermodynamic description of the Li-Si-system was given by Okamoto [10] in 1990 based on the experimental

investigations of several authors [10–18]. This phase diagram only contained 4 stable phases ( $\text{Li}_{22}\text{Si}_5$ ,  $\text{Li}_{13}\text{Si}_4$ ,  $\text{Li}_7\text{Si}_3$  and  $\text{Li}_{12}\text{Si}_7$ ). Okamoto [10] included  $\text{Li}_{22}\text{Si}_5$  as the most lithium rich phase, even though Nesper et al. [19] already corrected  $\text{Li}_{22}\text{Si}_5$  to  $\text{Li}_{21}\text{Si}_5$  in 1987 based on X-ray structure analysis. DFT-calculations performed by Chevrier et al. [20] in 2010 confirmed that  $\text{Li}_{21}\text{Si}_5$  is more stable than  $\text{Li}_{22}\text{Si}_5$ . In 2003 Evers et al. [21] reported the existence of a new phase LiSi, which was synthesized using high pressure. One year later Obrovac and Christensen [22] performed coulometric titration experiments at room temperature and detected a single voltage plateau, which was assigned to the formation of the phase  $\text{Li}_{15}\text{Si}_4$ . Okamoto [23] published a new phase diagram in 2009 including the LiSi phase.  $\text{Li}_{15}\text{Si}_4$  was not incorporated, because of its metastable character [24]. The identification of two more phases by Zeilinger et al. ( $\text{Li}_{17}\text{Si}_4$  [2] and  $\text{Li}_{16,42}\text{Si}_4$  [25]) and the precise determination of thermodynamic quantities, such as the heat capacity and entropy of the different phases by Thomas et al. in 2013 [26] for  $\text{Li}_{21}\text{Si}_5$ ,  $\text{Li}_{13}\text{Si}_4$ ,  $\text{Li}_7\text{Si}_3$ , and  $\text{Li}_{12}\text{Si}_7$  and in 2015 [27] for  $\text{Li}_{17}\text{Si}_4$  and  $\text{Li}_{16,42}\text{Si}_4$ , led to a CALPHAD reassessment of the phase diagram by Wang et al. [28] and Braga et al. [29]. Although the high pressure phase LiSi is known for a long time, it was until recently only marginally investigated [21,30,31]. Its heat capacity was determined by Taubert et al. [32] over a large temperature range (2–673) K in 2017. This makes the  $\text{Li}_{15}\text{Si}_4$  phase the last one left for such investigations. Although  $\text{Li}_{15}\text{Si}_4$  is a metastable phase, it is of particular importance because its occurrence in

\* Corresponding author at: TU Bergakademie Freiberg, Institute of Physical Chemistry, Leipziger Straße 29, D-09599 Freiberg, Germany.

E-mail address: [Florian.Mertens@chemie.tu-freiberg.de](mailto:Florian.Mertens@chemie.tu-freiberg.de) (F. Mertens).

electrochemically driven transformations [24]. The complete lithiation of silicon in an electrochemical reaction leads to the formation of  $\text{Li}_{15}\text{Si}_4$  [22,33,34]. In 2013 Zeilinger et al. [2,24] managed for the first time to produce  $\text{Li}_{15}\text{Si}_4$  via ball milling.  $\text{Li}_{15}\text{Si}_4$  crystallizes in a cubic unit cell with the space group  $I-43d$  [20,22,33,35]. It decomposes at temperatures above 473 K into  $\text{Li}_{13}\text{Si}_4$  and  $\text{Li}_{17}\text{Si}_4$ . Annealing experiments between (473 and 573) K yielded in amorphous weakly crystalline products [24]. The aim of this work is focused on the thermodynamic characterization of  $\text{Li}_{15}\text{Si}_4$  using calorimetry.

## 2. Experimental

### 2.1. Synthesis

The synthesis of  $\text{Li}_{15}\text{Si}_4$  was conducted via ball milling. Stoichiometric amounts of elemental lithium and silicon (suppliers and purity are referenced in Table 1) were transferred into an 8 cm<sup>3</sup> stainless steel grinding beaker in an argon filled glove box. The milling was performed in an Ardenne Vibrator for 15 h with a tungsten carbide (WC) ball ( $d = 10$  mm). Every 30 min there was a pause of 15 min to prevent the sample from overheating.

### 2.2. X-ray diffraction (XRD)

The characterization of the synthesized  $\text{Li}_{15}\text{Si}_4$  phase was carried out by means of powder X-ray diffraction using a Bruker D2 Phaser X-ray diffractometer with a Lynxeye<sup>®</sup> detector (Cu  $K\alpha$  radiation). The X-ray tube was operated at 30 kV and 10 mA. The XRD pattern was collected with a step size of 0.02° and 3 s dwell time. A polyethylene foil was applied to protect the sample against atmospheric oxygen and moisture. The reference diffractogram from the ICSD [35] database was applied to identify the material and to verify its phase purity. The unit cell parameter was refined by least-square fitting using the program package WinCSD [36].

### 2.3. Lithium content determination

The lithium content was determined by applying a volumetric titration method, according to Axel et al. [37]. About 13 mg of the sample was mixed with 1 ml of acetone and dissolved in 100 ml of 0.01 N  $\text{H}_2\text{SO}_4$ . A Titronic<sup>®</sup> auto burette from Schott (Germany) was used for the potentiometric back-titration of the unspent acid with 0.01 N NaOH. Standard solution ampoules (Titrisol<sup>®</sup> 0.1 M) were utilized for the preparation of the 0.01 N  $\text{H}_2\text{SO}_4$  and 0.01 N NaOH.

### 2.4. Thermal analysis

The DSC measurement was carried out on a SENSYS DSC (SETARAM, France) equipped with Inconel protection tubes. The sample preparation was performed in an argon filled glove box. About 50 mg of  $\text{Li}_{15}\text{Si}_4$  was filled into a tantalum crucible that was closed with a tightly fitting tantalum lid by mechanical

pressing. The sample was heated to 1073 K at a constant heating rate of 5 K min<sup>-1</sup>. Pure argon was used as purge gas at 20 ml min<sup>-1</sup>.

### 2.5. Calorimetric heat capacity measurement

The measurements were carried out as described in detail by Thomas et al. [26]. All sample preparation steps were performed in an argon filled glove box to protect the sample from oxygen and moisture. The low temperature heat capacities from (2 to 300) K were measured with the Physical Property Measurement System (PPMS, Quantum Design, USA) routinely with its heat capacity option, which is based on a relaxation technique [38].  $\text{Li}_{15}\text{Si}_4$  pellets with a mass of about 10 mg were prepared by pressing. The samples showed a suitable level of thermal conductivity for the type of measurement. To ensure good thermal contact of the pellet to the sample platform, Apiezon N grease was used. The heat capacity is automatically calculated by the PPMS software, which subtracts the values obtained from the addenda measurements (sample platform and grease) from the corresponding sample (sample platform, sample and grease) ones [39]. The high temperature measurements of the heat capacities from (300 to 615) K were performed with a DSC 111 (SETARAM, France). About 80 mg of  $\text{Li}_{15}\text{Si}_4$  was placed into a standard stainless steel sample vessel, which was tightly crimped with a nickel sealing. All vessels and seals used have been adjusted to identical mass by hand polishing to avoid blank effect variations. A  $C_p$ -by-step method assisted by the instrument software (Calisto, AKTS/SETARAM) was used, consisting of a series of temperature steps (10 K, 3 K min<sup>-1</sup>), that were preceded and followed by isothermal periods of 60 min duration. These measurements were conducted for the sample, an empty vessel (blank experiment), and the reference material sapphire. The heat capacity values of the recommended reference material were taken from the NIST database [40] and were used to compute the heat capacities of  $\text{Li}_{15}\text{Si}_4$  according to Eq. (1):

$$\bar{C}_p = \frac{\int_{t_i}^{t_{i+1}} \dot{Q}_{\text{sample}} dt - \int_{t_i}^{t_{i+1}} \dot{Q}_{\text{blank}} dt}{\int_{t_i}^{t_{i+1}} \dot{Q}_{\text{ref}} dt - \int_{t_i}^{t_{i+1}} \dot{Q}_{\text{blank}} dt} \cdot m_{\text{ref}} / m_{\text{sample}} \cdot \bar{C}_{p,\text{ref}} \quad (1)$$

with  $\bar{C}_p$  the specific heat capacity of the sample at the mean temperature of the ramp,  $t_i$  and  $t_{i+1}$  the temporal limits between which the respective peak of the heat flow  $\dot{Q}$  is detected,  $m_{\text{ref}}$  and  $m_{\text{sample}}$  the masses of the reference and the sample, and  $\bar{C}_{p,\text{ref}}$  the specific heat capacity of the reference material (sapphire) at the mean temperature of the ramp.

## 3. Results and discussion

### 3.1. Characterization of $\text{Li}_{15}\text{Si}_4$

The most important requirement for the determination of thermodynamic data is a well-defined sample with respect to purity and structure. Hence,  $\text{Li}_{15}\text{Si}_4$  was characterized by means of X-ray diffraction, chemical and thermal analysis. The X-ray diffraction pattern of  $\text{Li}_{15}\text{Si}_4$ , the protective polyethylene foil, and its appropriate reference pattern [35] are presented in Fig. 1. The measured pattern fits very well to the published reference one [35]. No additional impurity phases such as tungsten carbide, remaining Si, or stainless steel are found, confirming the phase purity of the sample. All observed reflections in the measured XRD-pattern were successfully indexed to the space group  $I-43d$  with a unit cell parameter  $a = 10.729(7)$ , which is comparable to the ones reported in [2] and [20]. Additionally, a chemical analysis based on a volumetric titration technique was performed in order to check the chemical composition. The potentiometric back-titration revealed a Lithium content of  $47.84 \pm 0.29$  wt-%. There is a good agreement

**Table 1**  
Chemicals used for synthesis.

Compound	Provenance	Mass fraction purity
Silicon nano-powder	Joint Solar Silicon GmbH	>0.998 as stated by the supplier
Lithium foil	Alfa Aesar	>0.999 as stated by the supplier
$\text{Li}_{15}\text{Si}_4$	This work	>0.995 chem. analysis, Section 3.1

Download English Version:

<https://daneshyari.com/en/article/4907222>

Download Persian Version:

<https://daneshyari.com/article/4907222>

[Daneshyari.com](https://daneshyari.com)