X-Ray Diffraction Investigation of Lithium Silicides under High Pressure

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(Received October 1, 2019)

Lithium silicide Li₁₂Si₇ (orthorhombic) and Li₇Si₃ (trigonal), composed of Li ions and Si clusters were synthesized by heat treatment of Li and Si mixture. Their high-pressure properties were investigated by synchrotron X-ray diffraction (XRD) measurements using a diamond anvil cell (DAC). Compression was successfully made up to 16 GPa for Li₁₂Si₇ and 20 GPa for Li₇Si₃, but no phase transition was observed. The bulk modulus was obtained from the fitting by Murnaghan equation of state. The obtained bulk moduli were compared with those of other lithium silicides, Si and Li, and there were found to be correlation between the bulk modulus and the Li-Si composition ratio.

1. Introduction

Recently, lithium silicide alloys have attracted attention as alternatives to graphite anodes for Li-ion batteries, due to its specific capacity [1]. Despite the great potential of silicon anodes, enormous volume expansion and internal stress during cycling cause electrode crushing and capacity decay, and hence limit their practical application [2-3]. Thus, the knowledge of mechanical properties such as the bulk modulus is essential for future application of lithium silicide to Li-ion batteries.

Lithium silicide has been synthesized with various Li-Si ratios (Li₁₂Si₇, Li₁₅Si₄, Li₁₃Si₅, Li₁₁Si₅, Li₁₂Si₅, Li₂₂Si₅) by heat treatment of Li and Si mixture [4]. Furthermore, Li₁₁Si₄ phase that does not exist in the equilibrium Li-Si phase diagram, was realized by electrochemical insertion of Li into Si [5]. LiSi with a three-dimensional Si network was synthesized under high temperature and high pressure [6-7]. Although there are various lithium silicides with deferent composition, all are in a ratio of Li/Si ≥ 1.

Figure 1 shows the crystal structures of Li₁₂Si₇ (orthorhombic) and Li₇Si₃ (trigonal) investigated.
in this paper. Among the lithium silicides synthesized under the ambient pressure, Li₁₂Si₇ is the most Si rich. We can find Si₃ clusters and Si₄ clusters in the unit cell shown in Fig. 1 (a). On the other hand, more Li-rich Li₇Si₃ contains only Si₂ clusters [Fig. 1 (b)]. Si clusters of these lithium silicides are expected to be bonded to each other under very high pressure, leading to Si novel network. However, there are only a few high pressure experiments to clarify the bulk moduli as well as a phase transition. Most of the available information about the bulk moduli of lithium silicides are from theoretical studies, and only the bulk modulus of Li₁₅Si₄ has been experimentally demonstrated.

The aim of this paper is to clarify the structural phase transition and compressibility of Li₁₂Si₇ and Li₇Si₃ by X-ray diffraction (XRD) investigation under high pressure.

2. Experimental

The samples were prepared in a glove box, filled with Ar. Li₁₂Si₇ was prepared by heat treatment of a mixture consisting of Li and Si. A mixture of Li pieces and Si powder with a molar ratio of 12:7 is placed in a boron nitride (BN) crucible and sealed in a stainless steel tube to prevent contact with air. The stainless steel tube containing the sample was heated in a muffle furnace at 800 °C for 30 minutes followed by heating at 450 °C for 16 hours [8]. The sintered sample was grounded using a mortar pestle in the glove box.

Li₇Si₃ was synthesized in a similar manner by heat treatment of a mixture Li and Si with molar ratio of 7:3 at 780 °C. Subsequently, the sample was allowed to cool down to 720 °C in 2 hours and was maintained at this temperature for 4 hours [9].

The characterization with powder X-ray diffraction measurements using CuKα (Rigaku SmartLab) was performed by covering the sample with Kapton film to prevent reaction with air.

For high pressure XRD measurements up to 20 GPa, we used a diamond anvil cell (DAC).

![Fig. 2. XRD patterns of (a) Li₁₂Si₇ (λ = 0.61595 Å) and (b) Li₇Si₃ (λ = 0.61669 Å) measured with various pressure. The marks × indicate NaCl and the marks + indicate diamond structure Si.](image-url)
Diamond anvils with culet diameters of 300 µm or 500 µm were employed in this study. A tungsten thin plate having a hole of 150 µm or 200 µm was used for sample chamber and the sample was inserted inside this chamber together with ruby balls for pressure calibration [10] and NaCl acting as a pressure medium. All of the manipulations were conducted in the glove box. High pressure synchrotron XRD measurements were performed at BL18C in Photon Factory of KEK and the diffracted X-ray beam was collected using a flat imaging plate. The wavelengths of X ray were 0.61595 Å for Li$_{12}$Si$_7$ and 0.61669 Å for Li$_7$Si$_3$.

3. Results and discussion

The high pressure XRD experiments were successfully performed up to 16 GPa for Li$_{12}$Si$_7$ and 20 GPa for Li$_7$Si$_3$. Figure 2 shows the XRD patterns of Li$_{12}$Si$_7$ and Li$_7$Si$_3$ obtained under high pressure. The horizontal axis shows d-spacing for comparison purpose of XRD patterns from different X-ray apparatus. XRD pattern at ambient pressure was measured before enclosing the sample inside the DAC. The cross marks (×) in the figure indicate NaCl pressure medium, while the plus marks (+) indicate diamond structure Si as an impurity. As shown in Fig. 2, all the peaks shift toward lower d with increasing pressure as a result of the lattice contraction under pressure. No change in peak profile suggests apparently no phase transition to be involved.

The lattice constants were calculated from the XRD peak positions and refined using the least squares method. Figure 3 shows the lattice volume normalized with the volume at ambient pressure as a function of pressure. Li$_{12}$Si$_7$ and Li$_7$Si$_3$ are more compressive than the covalently bonded diamond structure Si and less than the metallic bonded lithium [11]. This could be attributed to the ionic bonding between Li and Si. We note here that Li-rich Li$_7$Si$_3$ is more compressive than Si-rich Li$_{12}$Si$_7$, suggesting that the composition of Li and Si is related to the compressibility.

The pressure ($P$) dependence of volume ($V$) of Li$_{12}$Si$_7$ and Li$_7$Si$_3$ were fit to a Murnaghan equation of state (EOS) [12],

$$
\frac{V}{V_0} = \left(\frac{B_0 + B'P_0}{B_0 + B'P}\right)^{\frac{1}{B'}}
$$

where $P_0$, $B_0$, $B'$ and $V_0$ are the atmospheric pressure, the bulk modulus, the $P$ derivative of bulk modulus, and the zero-pressure lattice volume, respectively. The solid lines in Fig. 3 were obtained from this fitting. The bulk modulus and its $P$ derivative obtained as fitting parameters were $B_0 = 53.4\pm2.1$ GPa and $B' = 2.9\pm0.4$ GPa for Li$_{12}$Si$_7$ whereas $B_0 = 49.3\pm2.1$ GPa and $B' = 2.1\pm0.4$ GPa.

Fig. 3. Compressive curve of Li$_{12}$Si$_7$, Li$_7$Si$_3$, diamond-Si and Li.

Fig. 4. Bulk modulus $B_0$ as a function of atomic ratio of Li in lithium silicide.
for Li$_7$Si$_3$.

Figure 4 shows bulk modulus $B_0$ as a function of atomic ratio of Li in lithium silicide. The $B_0$ of Li$_{12}$Si$_7$ and Li$_7$Si$_3$ obtained in the present experiments were plotted together with those given in the literature [13-16]. The circle marks (○) indicate the only available experimental data for Si, Li, and Li$_{15}$Si$_4$ from the literatures. The other data have been obtained by theoretical calculation. The literature data suggested that $B_0$ shows almost linear trend with respect to the composition. The present data seems to be almost consistent with this trend. However, these data showed slightly higher values than the calculated ones of Li$_{12}$Si$_7$ and Li$_7$Si$_3$. Thus, it is found that $B_0$ of lithium silicide varies not linearly with the composition of Li and Si.

4. Conclusion

Lithium silicides, Li$_{12}$Si$_7$, Li$_7$Si$_3$, were synthesized and examined in high pressure synchrotron XRD measurements. The high pressure XRD experiments were successfully performed up to 16 GPa for Li$_{12}$Si$_7$ and 20 GPa for Li$_7$Si$_3$. However, absence of any change in peak profile suggests apparently no phase transition. The obtained compressibility of lithium silicide showed intermediate values between those of the covalent Si and metallic Li. The bulk modulus obtained experimentally were $B_0 = 53.4 \pm 2.1$ GPa and $B_0 = 49.3 \pm 2.1$ GPa for Li$_{12}$Si$_7$ and Li$_7$Si$_3$, respectively. Correlation between the composition and bulk modulus of lithium silicide has been well observed.

Acknowledgment

This research was financially supported by Grant-in-Aid for Scientific Research (JP17H03234, JP16K21072). This work was performed under the approval of the Photon Factory Program Advisory Committee (Proposal No. 2018G123).

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