X-Ray Diffraction Investigation of Lithium Silicides under High Pressure

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Lithium silicide $Li_{12}Si_7$ (orthorhombic) and Li_7Si_3 (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 $Li_{12}Si_7$ and 20 GPa for Li_7Si_3, 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 ($Li_{12}Si_7$, Li_7Si_3, $Li_{13}Si_4$, $Li_{21}Si_5$, $Li_{22}Si_5$) by heat treatment of Li and Si mixture [4]. Furthermore, $Li_{15}Si_4$ 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 $Li_{12}Si_7$ (orthorhombic) and Li_7Si_3 (trigonal) investigated

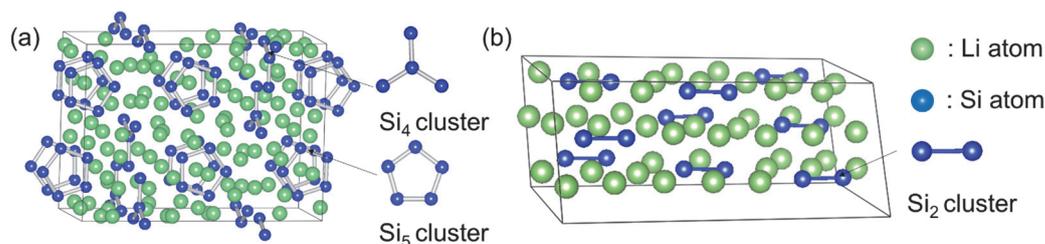**Fig. 1.** Crystal structure of (a) $Li_{12}Si_7$ and (b) Li_7Si_3.

in this paper. Among the lithium silicides synthesized under the ambient pressure, $Li_{12}Si_7$ is the most Si rich. We can find Si_5 clusters and Si_4 clusters in the unit cell shown in Fig. 1 (a). On the other hand, more Li-rich Li_7Si_3 contains only Si_2 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 $Li_{15}Si_4$ has been experimentally demonstrated.

The aim of this paper is to clarify the structural phase transition and compressibility of $Li_{12}Si_7$ and Li_7Si_3 by X-ray diffraction (XRD) investigation under high pressure.

2. Experimental

The samples were prepared in a glove box, filled with Ar. $Li_{12}Si_7$ 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.

Li_7Si_3 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.

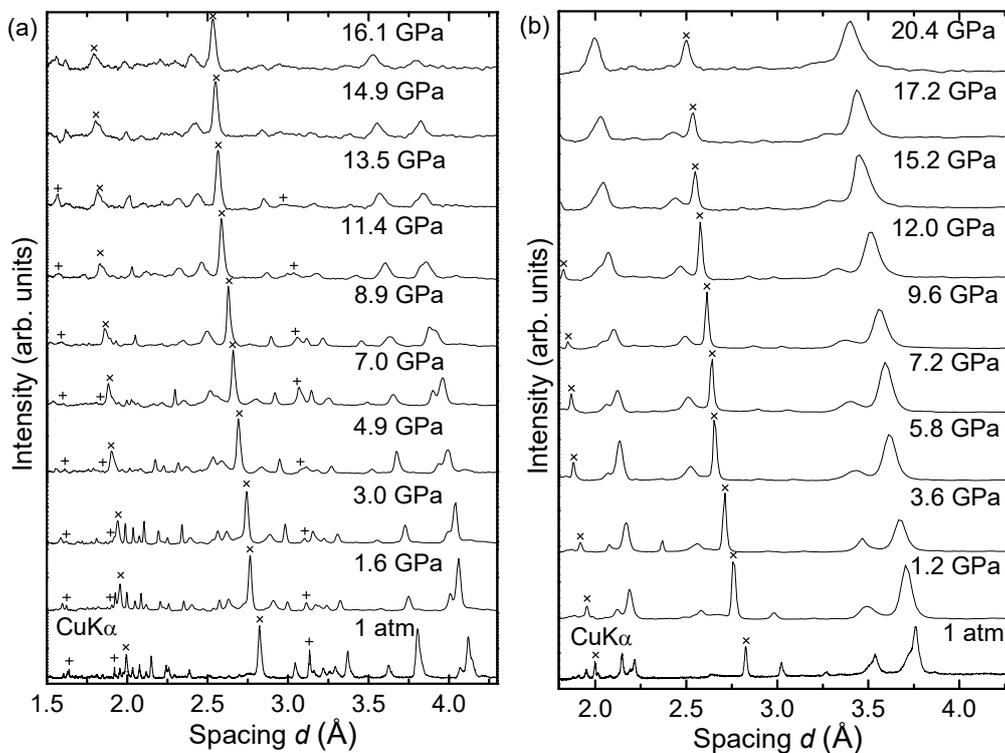For high pressure XRD measurements up to 20 GPa, we used a diamond anvil cell (DAC).

Fig. 2. XRD patterns of (a) $Li_{12}Si_7$ ($\lambda = 0.61595$ Å) and (b) Li_7Si_3 ($\lambda = 0.61669$ Å) measured with various pressure. The marks × indicate NaCl and the marks + indicate diamond structure Si.

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_7Si_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_7Si_3. Figure 2 shows the XRD patterns of $Li_{12}Si_7$ and Li_7Si_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_7Si_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_7Si_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_7Si_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 $B_0 = 53.4 \pm 2.1$ GPa and $B' = 2.9 \pm 0.4$ GPa for $Li_{12}Si_7$ whereas $B_0 = 49.3 \pm 2.1$ GPa and $B_0' = 2.1 \pm 0.4$ GPa
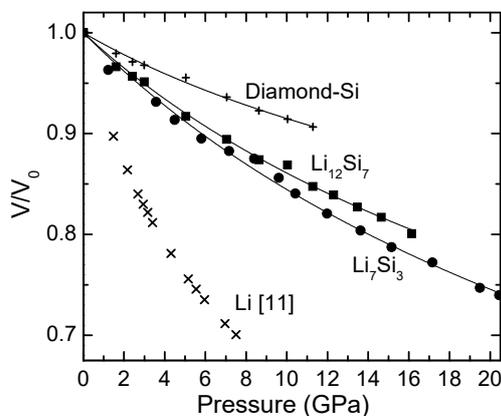

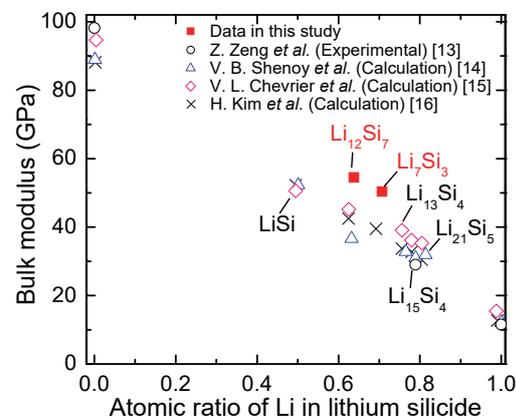**Fig. 3.** Compressive curve of $Li_{12}Si_7$, Li_7Si_3, diamond-Si and Li.

Fig. 4. Bulk modulus B_0 as a function of atomic ratio of Li in lithium silicide.

for Li_7Si_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_7Si_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_7Si_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_7Si_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_7Si_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 $B_0 = 53.4\pm2.1$ GPa and $B_0 = 49.3\pm2.1$ GPa for $Li_{12}Si_7$ and Li_7Si_3, respectively. Correlation between the composition and bulk modulus of lithium silicide has been well observed.

Acknowledgment

References

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