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Synthesis and analysis of silicon clathrate, amorphous silicon and nanocrystalline silicon from Zintl phase NaSi

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Chapter 1. Introduction

Silicon, one of the most important element, is known due to its desirable properties for industrial applications in the 20th Century, and it will also be very important in this 21st century. It is widely used for the semiconductor, solar cell, and lithium-ion battery anode. Also, it will play an important role in delivering the nanoscale medicine in the human body. Usually, the polycrystalline and monocrystalline silicon have been used for those applications. In this century, amorphous silicon, nanocrystalline silicon, and silicon clathrate will become more important due to their unique properties. Thus, the easy and cheap ways are required to synthesize those silicon materials.

Sodium-containing silicon clathrates, the type-I (Na_8Si_{46}) and the type-II ($Na_{24}Si_{136}$) with the unique framework structure attract much attention due to the particular properties, such as thermoelectric properties and superconductivity. The anode application for the lithium-ion battery will be discussed. Although the structures and those properties of the silicon clathrate were deeply researched, the way to synthesis these materials have not been well understood. Since sodium-containing silicon clathrates were found by Cros et al.,[1] the low-temperature method's for the synthesis those silicon clathrate are reported by several authors with some disagreements.

The other important compounds, a-Sis and nc-Si have also received much attention in biomedical applications, battery, sola cell and etc. Thus, the easy and cheap way to prepare these compounds was required. In order to meet this requirement, the synthesis through a solid state metathesis is one of the candidates for the a-Si and nc-Si. McMillan et al.[2] reported a solid state metathesis method using Zintl phases NaSi to synthesize these materials. They synthesized a-Si and nc-Si in a temperature range from 200°C to 500°C with metal halides (CuCl, $CoBr_2$) or ammonium salts (NH_4Cl, NH_4Br). Since then, several authors reported the SSM route for the synthesis of a-Si and nc-Si at such high temperature, such as Wang et al.[3] and Liang et al.[4] However, there are few reports about lower temperature reaction for this kind of SSM.

Therefore, the detailed study of the new synthesis methods of silicon clathrates, a-Si, and nc-Si through the precursor NaSi have been required. Besides, it is necessary for us to understand the non-equilibrium mechanism for the synthesis of that pure materials.

Chapter 2. Experiment

In this chapter, I explained the detail of synthesis method and conditions for this study. The precursor, sodium silicide (NaSi) was prepared at 630 °C for 48 hours.

Type-II silicon clathrate was synthesized through low temperature method. The temperature was changed from 270□ to 470□, to determine the appropriate condition of the type-II silicon clathrate. To obtain the pure type-II sample, the product was washed carefully to remove the impurities. The treatment with iodine was also carried out to reduce sodium in the structure.[5]

The electrochemical lithiation of the clathrate was carried out to obtain the lithiated silicon clathrate by using the anode containing 85% Na_xSi_{136}, 8% ECP, 2% VGCF, 5% PVdF (NMP 2.5ml). In charge-discharge process, the ended voltage was selected from 0.3 to 0.2 V. The lithium metal and type-II silicon clathrate was mixed by atomic ratio 24 vs 138. For the ion exchange experiment, the $LiNO_3$ and $LiAlCl_4$. The temperature for heat treatment was selected at 300□ and 180□ for the $LiNO_3$ and $LiAlCl_4$, respectively.

The a-Si and nc-Si were synthesized by a solid-state reaction of the NaSi powder with $AlCl_3$. NaSi and purified $AlCl_3$ were mixed in a range of the mole ratio 3: 1 to 3: 9.9. The tube was heated gradually after keeping for one day at room temperature, and kept at different temperature (from 180 °C to 80 °C). The nc-Si was prepared by annealing the a-Si at 600 °C for 2 hours in a vacuum-sealed quartz tube.

The products were characterized by the powder XRD diffractometer (Rigaku, RAD-2B with the Cu $K\alpha_1$ radiation, λ = 1.5406 Å). The data was collected in a continuous scan mode from 10° to 60° in 2θ with the step of 0.01°. The crystallite size was calculated from the Debye-Scherrer formula, using MDI jade 5 software. The RIETAN-FP program were using for the structural parameters refinements.[6] The ^{23}Na, ^{21}Al and ^{29}Si solid state MAS NMR experiments were carried out using a Bruker AVANCE III HD 300 MHz spectrometer (7 T). The resonance frequencies for ^{23}Na ^{27}Al, and ^{29}Si NMR are 59.63 MHz, 78.20 MHz, and 79.39 MHz, respectively. The Raman spectroscopy and the FT-IR spectra were measured.

Chapter 3. Synthesis of pure type-II silicon clathrate

In ***Chapter 3***, the high purity of Na_xSi_{136} was synthesized by the decomposition of Zintl compound NaSi. The appropriate synthesis temperature was different from the other references. The heating temperature and time for the decomposition were researched with other conditions. The suitable condition is about 380□ for a large evacuation tube (4.16 cm), and for 3 days. The high purity of the sodium silicon clathrate (Na_xSi_{136}) over 96 wt% was obtained with and x for Na_xSi_{136} was about 1. The pure type-II silicon clathrate through the etching by a NaOH solution at 60 □ in 2 minutes.

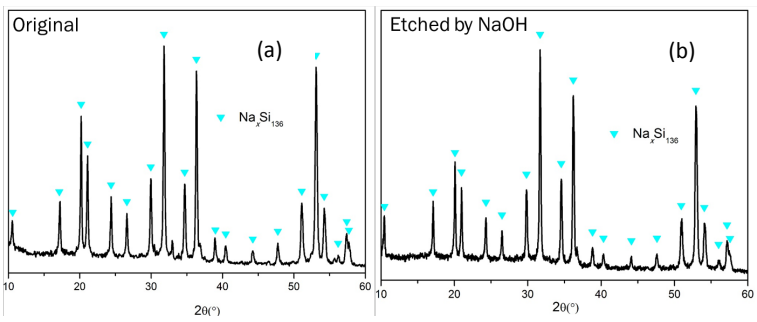

Figure 1. The XRD pattern of Na_xSi_{136} (x > 12); (a) original; (b) etched by NaOH

Chapter 4. Electrochemical, heat treatment, and ion exchange method for Li_xSi_{136}

In ***Chapter 4***, the lithium contained silicon clathrate was tried to synthesize by the electrochemical, heat treatment, and ion exchange methods. The electrochemical study was carried out in the charge-discharge process with the voltage range from 0 V to 3.2 V. The plateau appeared at 0.3 V in the initial lithiation process, suggested the lithiation of the pristine clathrate. The experiment with the charge-discharge range from 0.25 V to 3.2 V showed the reversible insertion and removed of lithium for type-II. The result of X-ray diffraction also indicated the remaining of the type-II structure after the lithiation and the delithiation process. In the reaction with metal lithium, the powder XRD results show the tendency to form lithium-silicon amorphous. The ion exchange experiments indicate that the $LiNO_3$ and $LiAlCl_4$ are not suitable for preparing lithium silicon clathrate.

Chapter 5. Synthesis and characterization of Na-containing amorphous silicon

In ***Chapter 5***, the reaction of NaSi and $AlCl_3$ was investigated. A mixture phase containing type-I, a-Si, and c-Si/nc-Si was obtained in the temperature range 90–180 °C. These serious of studies indicate the excess $AlCl_3$ and controlled heat treatment are necessary for the effective synthesis of a-Si. Both the type-I and type-II compounds were appeared with increasing the proportion of $AlCl_3$. The sodium-containing amorphous silicon (a-Si: Na) was synthesized by a reaction of NaSi and $AlCl_3$ with the 3 vs 9.9 molar ratio at 90 °C, and the nanocrystalline silicon with the particle size of 11 nm is obtained by annealing the a-Si at 600 °C under vacuum. The Raman spectrum showed both the character peaks of a-Si and nc-Si in a-Si sample. The EDX experiment indicated that 7.7 wt% of sodium contained in the a-Si. Moreover, the ^{23}Na MAS NMR spectrum indicated that 0.5 at% of sodium is doped in the a-Si. Almost all the sodium was removed by the crystallization. It is the first time to obtain the sodium-containing amorphous silicon. The electronic state of sodium in a-Si is the different from that in silicon clathrate.

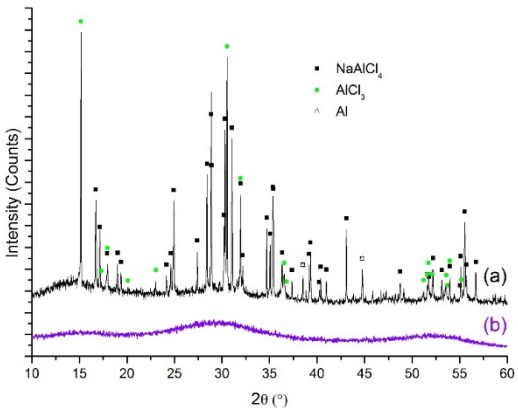

Figure 2. Powder XRD patterns for the Si sample from the solid state reaction before washing and after washed. (a) As prepared (b) After washed

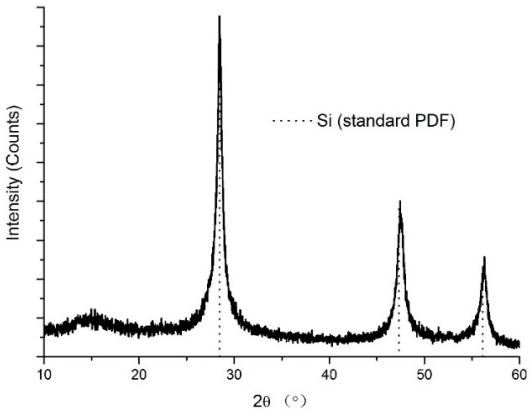

Figure 3. Powder XRD patterns for the Si sample from the solid state reaction after annealing. The standard peak for Si (ICCD-PDF # 27-1402) are provided

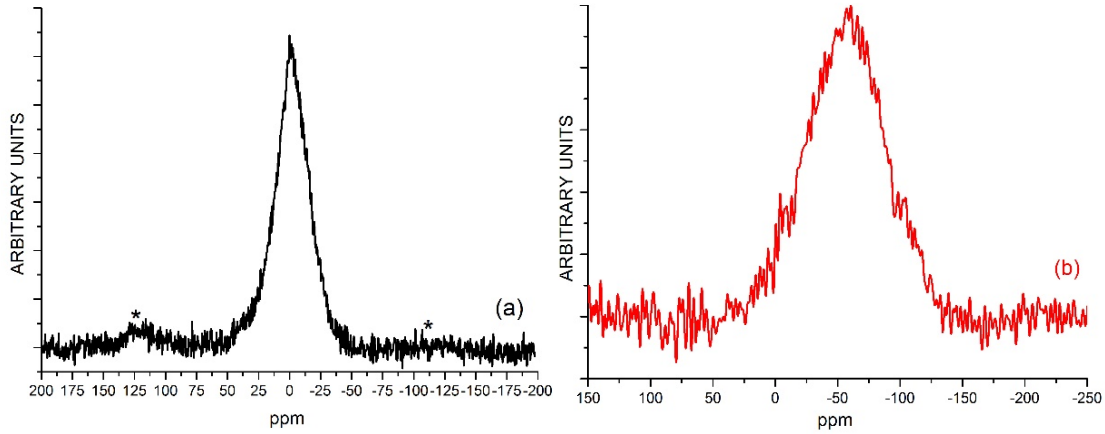

Figure 4. (a) ^{23}Na MAS NMR spectrum of a-Si from the solid state reaction before annealing. Using * to show spinning side bands. (b) ^{29}Si MAS NMR spectrum of a-Si from the solid state reaction before annealing

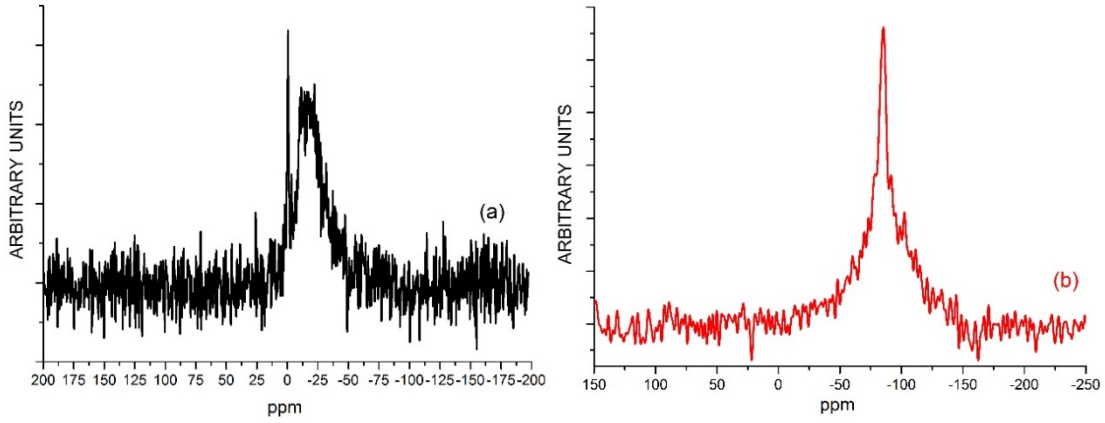

Figure 5. ^{23}Na MAS NMR spectrum of nc-Si from the solid state reaction after annealing. (b) ^{29}Si MAS NMR spectrum of nc-Si from the solid state reaction after annealing

Chapter 6. Summary

In this chapter, the results of the present study are summarized as below.

1. The suitable temperature for heat treatment to obtain the high-purity type-II was about 380□, and the period of heating is 4 days. The purity of the sodium silicon clathrate (Na_xSi_{136}) reached to 96% by the heat treatment. The pure type-II silicon clathrate was obtained by washing the sample with the NaOH solution at 60 □. The less amount of sodium in the silicon clathrate (Na_xSi_{136}) can be decreased to x = 0.7

2. The reversible lithiation and delithiation were observed in type-II silicon clathrate. The type-II structure is stable with the charge-discharge range from 0.25 V to 3.2 V. The solid state reaction with metal lithium, and the ion exchange method with $LiNO_3$ and $LiAlCl_4$ are not suitable for preparing lithium silicon clathrate.

3. The reaction of NaSi and $AlCl_3$ leads to a mixture of type-I, a-Si, and c-Si/nc-Si in the temperature range of 100–180 □. The sodium-containing amorphous silicon (a-Si: Na) was synthesized by a reaction of NaSi and $AlCl_3$ at 90 □, and the nanocrystalline

silicon with the particle size of 11nm is obtained by heating the a-Si at 600 □ under vacuum. The ^{23}Na MAS NMR shows 2.16 at% of sodium is containing in the a-Si sample and it removed by the crystallization. The sodium-containing a-Si firstly synthesized through solid state metathesis with Zintl phase NaSi.

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This research reveal a new synthesis method for sodium-containing a-Si. The silicon clathrate was synthesized through a systematic study for synthesis silicon clathrate. The pure type-II silicon clathrate was obtained firstly by the etching method. The electrochemical, heat treatment, ion exchange method was applied for synthesis lithium contained silicon clathrate, the negative results were obtained with the heat treatment and the ion exchange methods.

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