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**Thermoanalytical study on the disproportionation
reaction of silicon monoxide**

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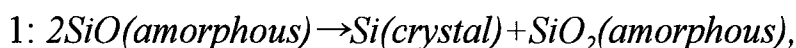
January 2000

Abstract

This work is carried out to clarify the thermal stability of silicon monoxide (SiO), and the mechanism of the decomposition reaction into Si and SiO₂, which is named “disproportionation reaction”. SiO is one of the most significant minerals for investigating space materials in fixed stars, planets, stardusts and the dark matter. For a long time, this compound has been believed to be metastable and have a tendency to decompose into Si and SiO₂ at low temperatures.

Physical, structural and chemical properties of SiO are first investigated. X-ray powder diffraction and electron diffraction analyses reveal that SiO is amorphous at room temperature. Chemical analyses show that this compound is almost stoichiometric in composition and is very stable at room temperature in air. Infrared measurements reveal that SiO has broad absorptions around 9.5 and 22 μm, which are attributed to the vibration motions of the Si-O bonds. It also shows a remarkable reflection around 7 μm, which is explained as a high polarization in the Si-O bonds. Magnetic susceptibility measurements show that this compound is completely diamagnetic and no change is observed up to 800°C. From these results, SiO is concluded to be a monomolecular compound whose bonding character is similar to carbon monoxide.

The thermal stability is investigated by heating-quenching experiments in Ar atmosphere. SiO becomes unstable above 800°C and the disproportionation reaction starts apparently at about 900°C. At high temperatures, the reaction proceeds very rapidly and finishes in a short time. The reaction process obeys the following two steps:



2: SiO_2 (*amorphous*) $\rightarrow$ SiO_2 (*cristobalite*).

Between 900 and 1300°C, step 1 occurs exclusively, whereas step 2 becomes significant above 1350°C. High-resolution electron diffraction analyses reveal that Si crystallizes in a form of five particles whose diameters vary with the annealing temperature and duration.

Thermochemical analyses of the disproportionation reaction are performed using the changes in X-ray powder diffraction intensities with the annealing temperature between 1000 and 1300°C and reaction time between 0.1 and 20 hours. The results show that Si crystallizes through a simple first-order reaction and the activation energy is decided to be 82.2 kJ·mol⁻¹ by calculating from the Arrhenius plotting of the reaction velocity vs. temperature. This value is higher than that in solid-state crystallization of amorphous Si with rearrangement of Si-Si bondings, and much lower than those of volume diffusion of Si or O in silica or silicates. This result suggests that the reaction advances in an intermediate manner between the rearrangement and diffusion.

Similar decomposition reaction is observed in high-pressure conditions above 14 GPa at room temperature.

On step 2, the resultant cristobalite belongs to the low-temperature phase. High temperature X-ray diffraction and differential thermal analyses reveal that the high-low phase transition reversibly occurs between 242 and 246°C. The powder diffraction data for the high-temperature phase are explained by the space group of $F3dm$.

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Chapter 1

General introduction

Materials science has been widely developed by investigating physical, structural and chemical properties of specimens prepared in a laboratory scale. Its application to space science, which must have an important role to investigate fixed stars, planets, stardusts and the dark matter, has been faced with difficulties in introducing such a common method. The experimental conditions are thought to be extreme in space in comparison with those on the earth, and data on space materials are actually very scarce.

For a long time, the research on meteorites has only been a way to give information for understanding the origin of the solar system or the mechanism of a star formation. In recent years, one of the remarkable results has been brought about by analyses on spectroscopic data of stars. Weak lights come from stardusts have a characteristic absorption band in the infrared (IR) region at about 10 μm , as shown in Fig. 1-1 [1-3]. Most scientists in this field have regarded this absorption as the atomic vibration between silicon and oxygen. However, there has been remained a question: what kind of materials is a cause of the absorption phenomena? A primary theory has maintained that silicon monoxide (SiO) molecules cause the IR absorption [4,5]. From the thermochemical diagram, named “Ellingham Diagram”, between free energies (ΔG_f) and temperature (T), SiO is more stable than silicon dioxide (SiO₂) above 1700°C [6]. Fig. 1-2 shows the established diagram of ΔG_f and T. Such a high-temperature condition is not unusual in space. The places where stardust or the dark

matters are concentrated so as to form new stars, could provide stable states for SiO. Furthermore, these places are states of quite low oxygen pressure, which are theoretically strong reduction conditions. In such a state, the most proper compound between Si and O atoms is the low valence compound SiO.

Recently, another theory has been proposed that the IR absorption around 10 μm is attributable to silicate minerals such as olivines or pyroxenes [7-9]. The base of the argument is that silicate minerals are commonly found in meteorites but SiO or other related compounds including low valence state of Si and O have never been observed yet.

The hypothetical phase diagram of the Si-O system is shown in Fig. 1-3 [10], where SiO is unstable below 1180°C. Above 1180°C, SiO is a stable compound. At higher temperatures, it becomes hard to study the phase relation because of the difficulty in providing a reaction system between the gas phase of Si and SiO in a common laboratory. The phase diagram contains many suspicious points, which are expressed in dotted lines and question marks.

The space materials are exposed to extremely wide conditions of temperature and pressure, which provide numerous varieties of the states in solids, liquids or gases. Common knowledge of the stability field of the earth's materials is established in the mild condition of oxygen pressure and temperature. In space, however, the possibility of existence of unusual materials in the extreme conditions should never be discarded even though they have not been confirmed on the earth yet.

SiO behaves many absorptions in the IR region and the observed space data include one of the absorption points around 10 μm , if the prediction in the astronomical theory is correct. Thus, it is important to obtain the precise optical data of SiO treated in wide conditions of

temperature and pressure. The most difficult point for elucidation of the IR absorptions is a lack of the accurate chemical data of SiO. The reported chemical properties show a many different values, and in some cases, the tabulated values are apparently far from the experimental results.

Many researchers have maintained the opinion that SiO is consisted of a mixture, Si and SiO₂. They considered that the old X-ray diffraction data of 0.36 nm was a result from silicon [11,12]. The other reports based on the patterns of X-ray spectroscopy on SiO had a conclusion that it consisted of a mixture of Si and SiO₂ [13,14]. In many old reports, SiO was synthesized by heating a mixture of Si and SiO₂ between 1200 and 1375°C under vacuum condition. It should be noted that the temperature range does not satisfy the thermochemical stability condition of SiO. Although the vacuum condition has a possibility of changing the mixture of Si+SiO₂ to SiO, it is not complete to remove a problem of remaining the starting mixture residually. As some IR or XRD results are obviously different from those of the recent reports, the specimens in the previous works are also doubtful in the state of SiO. Such circumstances may interfere the development in research of SiO applications.

Amorphous phase of SiO is produced as a by-product of the synthesis of large single crystal of Si for industrial use [15]. The most serious but important problem for the synthesis of high quality Si crystal is oxygen inclusions from the melt. The major amount of oxygen evaporates from the melt in a form of SiO and the evaporated gas is solidified at a cooled place for an amorphous phase of SiO. The residual oxygen in the melt dissolves into the Si crystal, whose mechanical and electrical properties are improved by such an oxygen inclusion.

The epitaxies of Si as well as SiO₂ are an important technique for producing semiconductor devices. There are many reports on the property

of epitaxed Si and SiO₂ [16-21], whereas the relationships between the bulk and deposited layer of SiO have not been studied. Lack of the precise chemical values, such as a thermal stability or molecular structure, in the bulk SiO may induce these saturations.

It is a well-known property that SiO decomposes into Si and SiO₂ at high temperature, where the oxidation reduction reactions of Si[II] to Si[IV] and Si[0] occur at the same time [22,23]. Such a kind of the reaction is called as “the disproportionation reaction”. The accurate analysis of the reaction in SiO will inform a new mechanism of heterogeneous nucleation and crystal growth of Si and SiO₂ where each material is completely conserved in the system.

Many studies on the solid state crystallization of Si have been performed by mainly using amorphous Si as starting materials [24]. In the initial stage of crystallization, a nucleation process by diffusion of Si atoms is not essential, because only rearrangement of Si-Si bondings initiates growth of Si crystals in the amorphous Si. In the disproportionation reaction of SiO, the produced Si atoms will migrate in the oxide medium and crystal growth, and occur in a usual way. Thus, research of the present reaction is thought to be one of the most effective ways for studying of the crystallization process of Si directly.

The construction of the present paper is as follows: In Chapter 2, the fundamental chemical values of SiO are described. The chemical behavior and process in the disproportionation reaction of SiO are mentioned in Chapter 3. In this chapter, the magnetic property, the high-pressure behavior and the relative reaction of the high-low transform in cristobalite were also studied. In Chapter 4, the thermal and crystal growth analyses in the initial stage of crystallization of Si are described. Finally, the paper is summarized as the concluding remarks in Chapter 5.

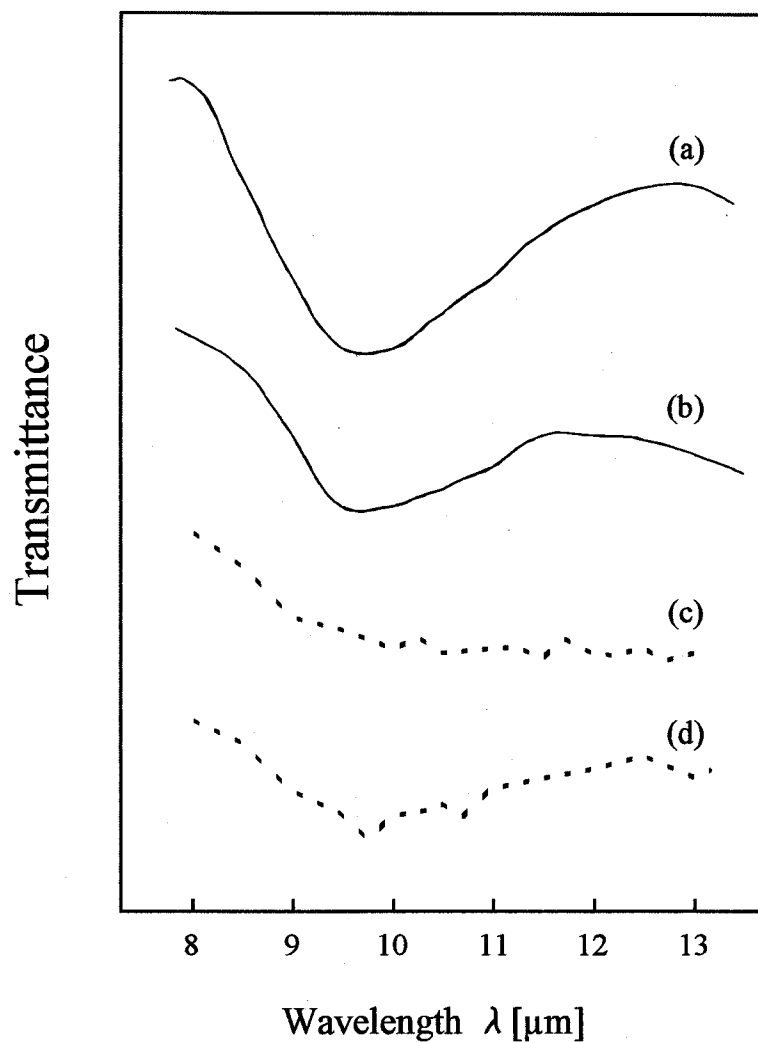


Fig. 1-1 Infrared spectra emitted from astrochemical objects.
 (a) CRL 2591 (b) Becklin-Neugebauer object (c) NGC 2264 (d) CRL 490

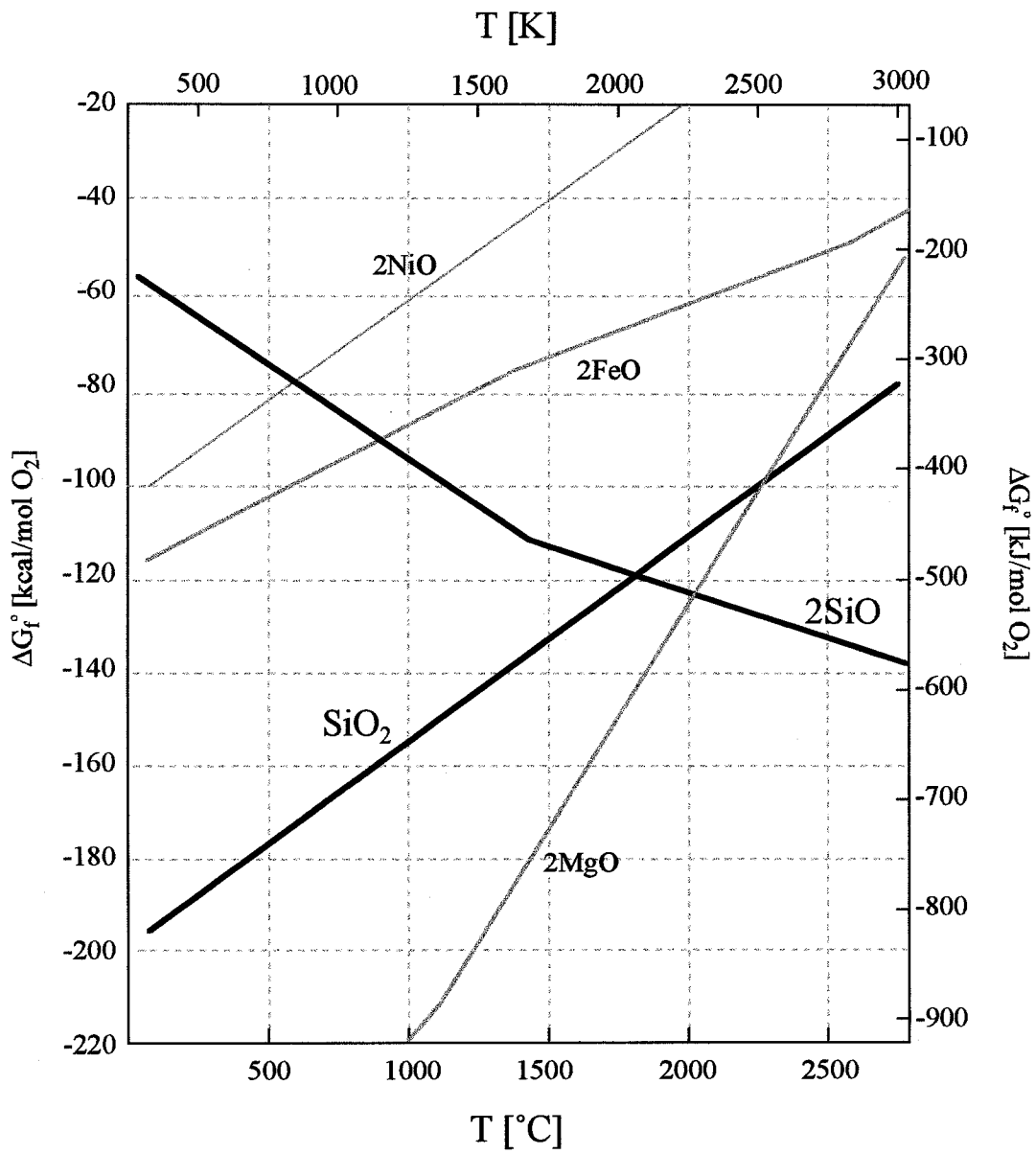


Fig. 1-2 Ellingham Diagram between free energy (ΔG_f) and temperature (T).

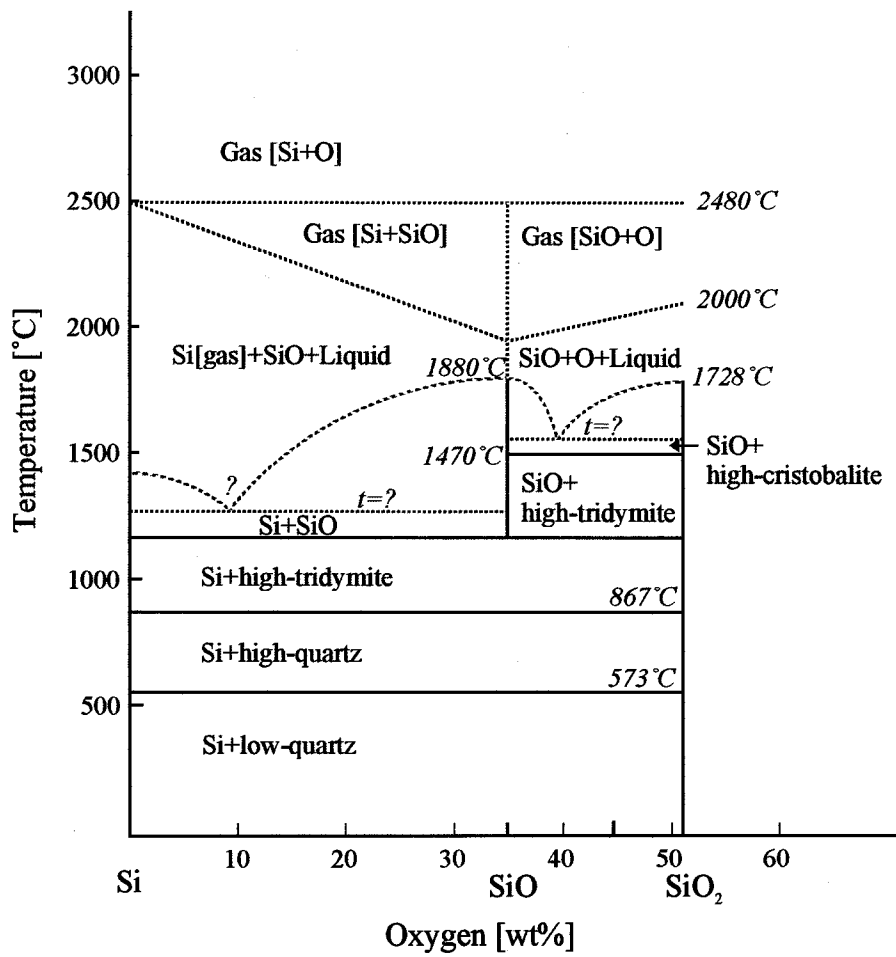


Fig. 1-3 Hypothetical phase diagram of Si-O system. [10]

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Chapter 2

Fundamental aspects of silicon monoxide

2-1 Introduction

The properties of silicon monoxide (SiO) have been first reported by Inuzuka et al [1], who prepared it by heating a mixture of Si and SiO₂ in an equimolar ratio. They concluded that the products were crystallized into a cubic structure with the cell dimension $a_0 = 6.2 \text{ \AA}$ and the specific gravity 2.2 gcm³. Several researchers have been participated in similar studies [2,3]. Kurdyumov et al [4] reported the X-ray diffraction data, where they provided the SiO specimens using a similar technique to Inuzuka's. The obtained data was filed in the JCPDS card 39-973 [4].

Schafer et al. [5] reinvestigated these results thermodynamically and strongly asserted that the specimens should be a mixture of Si and SiO₂ because the vapor pressure at the treating temperatures was very high and the produced SiO, if existed, should evaporate. The major XRD diffraction peaks reported in the above JCPDS card, are around 3.18, 1.93 and 1.64 Å. The diffraction peaks of Si listed also in the JCPDS card 27-1402 [6] are 3.14, 1.92 and 1.64 Å. The sets of these values are apparently quite resembled to each other. It should be noted that Schafer et al. never denied the possibility of existence of SiO itself. Their opinion is that the existence of SiO crystals is doubtful because the previously reported data of this material contain many questionable ones, which were obtained from so-called "crystallized" SiO specimens.

Coleman and Thomas [7] have investigated the structure of vacuum

deposited SiO films using a radial distribution function in electron diffractions and concluded that the films were made of very fine particles of Si and SiO₂. Kaito and Shimizu [8] have supported these conclusions from the results of their high-resolution electron microscope observations. Benyon have discussed these features in his report entitled "Silicon Monoxide: Fact or Fiction" [9]. He also asserted that there is no evidence of existing SiO in a crystalline form.

From these arguments, it has spread the impression that SiO is existable only the mixture of Si and SiO₂. However, no reports deny the existence of amorphous phase of SiO. To remove the uncertain chemical value of SiO, it is important to decide the precise characters of the amorphous phase of SiO. This work characterizes the structure of SiO, the physical and chemical properties.

2.2 Characterization of the SiO

The reagent of SiO grains was supplied from Nacalai Tesque Co. The crystallinity was analyzed by a powder X-ray diffraction (XRD) apparatus of Rigaku Rad-B. The SiO grains were pulverized and used for following measurements after they were checked the stabilities of structure and composition on leaving in air or on storing in a heated desiccator for several months.

The elemental impurities were analyzed by inductively coupled plasma mass spectrometry (ICP-MS) of HORIBA, JY138 ULTRACE. The solutions for analyses were prepared by dissolving the sample with diluted hydrofluoric acid and then neutralized by borax.

The oxygen content was first determined by a weight increase with oxidation in thermogravimetry (TG) using the apparatus of Mac Science Co. TG-DTA 2000, capabilities of which are as follows: The maximum heating rate is 20°C/min, highest temperature is 1500°C, the weight change is monitored for each one second and the maximum accuracy in weight change is 0.01 mg. The oxygen content in the starting materials was analyzed on the pulverized sample and an alumina powder was used as a reference. They were put into respective platinum crucibles, and were placed on a thermo- balance in the TG furnace. The maximum temperature was between 1420 and 1030°C and both heating rate was 10°C/min. Heating at the maximum temperature was kept until the weight increase by oxidation was finished.

The optical absorption measurements were conducted using an apparatus of FT/IR-410 supplied from JASCO for Fourier-transform infrared spectrometry (FT-IR). About 0.7 mg of the powdered SiO was mixed with 150 mg of KBr powder. The mixture was once evacuated and

pressed into a pellet form under a pressure of 7 ton/cm². Similar pellets were prepared as references of silica glass, dried silica gel, silicon crystal, quartz and cristobalite. The infrared absorption (IR) spectra were taken in the wavelength region of 2 to 25 μ m in air.

To confirm whether magnetically active material was originated during the reaction or not, measurements of magnetic susceptibilities in the specimens were performed using a vibrating sample magnetometer of model BHV-3 supplied from Riken Denshi Co. The maximum magnetic field was 10 kOe and minimum measurement range was ± 0.0005 emu with sensing time of ± 2 μ sec. The magnetometer was combined with a heater and the maximum temperature was 800°C under a flow of He gas. The specimens were placed on the magnetometer and measured both at room temperature and in an elevating condition to 800°C.

2.3 Results of characterization

Fig. 2-1 is a photograph of the starting reagent powders, which were usually obtained in a form of grains with the mean size of about 5 mm in diameter. The color of the grains was metallic gray, whereas it changed to brown by pulverization. The brown color is commonly accepted as a standard for SiO.

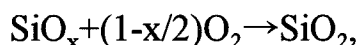
The crystal structure as well as the crystallinity of SiO was analyzed by XRD measurements. A typical pattern of SiO is shown in Fig.2-2, where no obvious peak appeared at all. As no ordered structure was detected, the supplied reagent of SiO is perfectly in an amorphous state in the XRD level.

It has been commonly accepted that SiO is a labile compound and is easily oxidized in air to SiO₂ even at room temperature. In the present experiment, however, powdered SiO is very stable at room temperature and an increase in weight by spontaneous oxidation hardly observed for several months or more. To obtain a clear evidence of the stability in SiO, the XRD patterns of the powder left for many months in air and of the freshly prepared one were compared. The result showed that the amorphous pattern of the freshly powdered SiO was not changed after 6 months, as shown in Fig. 2-2.

Fig. 2-3 shows an analytical result of the atomic impurities in the starting materials determined by ICP mass spectrometry. Major impurities are Na and K, whereas the maximum concentrations among them are still less than 0.6 ppm. The result that other atoms are much less than 0.3 ppm, indicates this reagent being in a high purity state.

The amount of oxygen in the starting materials was determined by thermogravimetric analysis (TG) in air. Changes in TG by oxidation are

shown in Figure 2-4. The weight increase was started at about 600°C on heating. When the temperature was kept at 1420°C, the change was finished after 18 hours and no further change was observed, as shown in Fig. 2-4 a. This means that the oxidation reaction was completed at 1420°C. When the starting weight was 20.70 mg, the weight increase by oxidation was +7.56 mg. As the final composition was strictly determined to be SiO₂, the oxidation reaction is written as the formula:



where the starting material is represented by SiO_x, and the oxygen content x lies between 0 and 2. From the weight change in Fig. 2-4 a, the x value was determined to be 0.994₄. This value indicates that the oxygen content in the starting material is very close to the stoichiometry of SiO.

When the temperature was kept at 1030°C, the increasing rate in weight changed to slow and after 15 hours the change was almost finished, as shown in Fig. 2-4 b. The composition at that time is calculated tentatively to be SiO_{1.4}, indicating incomplete oxidation. The result means that the reaction rate is lowered at this temperature. Such a slow oxidation should be due to a low diffusion rate of oxygen through SiO₂ layers formed around the individual SiO particle, or through the shell region of the pressed specimen produced with advancement of the oxidation. Therefore, the oxidation at low temperature is controlled by a thickness of the oxidized layers on the surface of SiO particles or specimens.

Infrared (IR) absorption spectra of SiO and the powdered Si crystal are shown in Fig. 2-5. SiO has two apparent absorptions around 9.5 and 22 μm. These absorptions correspond to the Si-O stretching and Si-O rocking modes, respectively [10]. A very weak absorption is observed around 13 μm, which is assigned as the bending mode of Si-O-Si. As

shown in this figure, a sharp transmission peak was observed around 7 μm . This peak has been explained as a scattering from the interface between SiO and KBr, which was mixed as an optical dilution reagent. The scattering is caused by a high refractive index of SiO of about 1.9, which is much higher than that of KBr of 1.5 [11]. The high refractive index of SiO is induced by polarized electron clouds in the bonding of silicon and oxygen. Details of the explanation in connection to the magnetic properties will be described in Section 3-3.

In Si crystals, however, no obvious IR absorption was observed, as also shown in Fig. 2-5. This indicates that Si is optically a good transmitting material in the infrared region between 2 and 25 μm . This leads to a thought that it will be hard to distinguish in the IR spectra whether Si is actually included or not.

IR absorption spectra of several polytypes specimens of SiO_2 are shown in Fig. 2-6. Every sample has three remarkable absorptions around 9.5, 13 and 22 μm . In quartz and cristobalite, additional peaks between 14 and 17 μm . are observed. These patterns are apparently different from that of SiO in Fig. 2-5, and the peaks are very sharp and clear. Especially, the peaks around 13 μm , corresponding to the bending mode of Si-O-Si, are much more distinctive than that in the case of SiO. This feature suggests that SiO molecules in the amorphous solid are mutually isolated and consequently, the bending mode of Si-O-Si disappears in them. The strong transmission peak around 9.5 μm in SiO is not observed in these SiO_2 specimens. This is easily recognized by the fact that the refractive indexes in all SiO_2 polytypes is lower than that of KBr, corresponding to low polarizations in the Si-O bonds.

The electronic structure of SiO molecules has not completely been clarified yet. To obtain the precise information on the electronic state of

SiO, measurements of the magnetic properties are thought to be an important way because they are reflected by the fine structures such as bonding orbital, electron densities and character of electrons.

A typical result of the magnetic hysteresis measurements is shown in Fig. 2-6, where the static magnetic field from -5 to 5 kOe were applied to the specimen. It became clear that the specimen showed a diamagnetic behavior with a susceptibility of $-0.0385 \text{ emu}\cdot\text{g}^{-1}$ at room temperature and showed no different magnetization between the back and forth fields. Thus, SiO is a diamagnetic material and consequently, it has completely closed electron shells and has no magnetic electrons, which are often observed in ESR signals in case of Si crystals grown from the vapor [12].

In this disproportionation reaction, there is a problem whether the crystallization of silicon proceeds from SiO through an electronically activated state or not. Fig. 2-7 shows the magnetization change on heating up to 800°C under an inert condition of He gas flow. The result indicates almost no change through the heating process. The magnetic susceptibility is less than $1.6 \times 10^{-5} \text{ emu}\cdot\text{mol}^{-1}$.

From the results of FT-IR analyses of SiO, the electron density and the bonding character of the orbitals between Si and O atoms are suggested to be much different from those of a usual Si-O bond in silica or silicates. The high polarization in the bonding between each element is suggested by a result of the s-p hybrid orbital in Si, which gives a higher electron density than that in O. However, SiO has no lone pair electron in each molecule because SiO is found to be completely diamagnetic up to 800°C . Namely, the states of electron poor oxygen and rich silicon in a SiO molecule may be very stable. When the molecular structure of SiO is assumed as a similar type to CO, there remain no conflicts in the experimental results. Fig. 2-8 illustrates the proposed model from the present results for the

electronic structure of SiO molecule. The molecular units are aggregated with no ordered arrangement into an amorphous solid.

The molecular structure of SiO was reported by Emons et al. [13,14], who proposed a polymer model of $(\text{SiO})_n$, as shown in Fig. 2-9. It consists of framed structures of Si-Si chains with Si-O-Si branches and the coordination number of Si is four, although the valence number is not changed from -2. Hirose et al. proposed a related model, and it was also based on such a Si-Si chain structure [15].

The results of the present work deny the polymer models even though they would have no free electron and show a diamagnetic property. The discrepancy appears in the IR patterns. The absorption of the Si-O-Si bending motion, which is necessary in the previous models, is absent in the present IR patterns. In addition, the absorptions from Si-O stretching and rocking are also unclear. Therefore, SiO should have no Si-O-Si structure, which is essential for making a long polymer chain. The present IR results are consistent with the proposed model: a random mixture of the molecular units of SiO.

From the present characterizations, it is concluded that SiO molecules in the stoichiometric form exist as an amorphous solid and is very stable at room temperature. Some scientists have maintained that the existence of SiO is a fiction and materials so-called "SiO" consist of aggregated fine particles of Si and SiO_2 . If these claims were true, the following results hardly be explained completely: First, the data of the weight increase in TG by oxidation always registered the value $\text{Si/O} \sim 1$, secondly, the IR absorption spectra of SiO were much different from those of Si and SiO_2 , and finally, no apparent peaks were observed in XRD.

The magnetic properties were measured up to 800°C in order to detect a change in the electronic state of SiO by heating. The sample was always

diamagnetic in this temperature range, discarding an origination of magnetically active substance. From the magnetic and IR results, the molecular structure of SiO was considered by analogy with the structure of CO molecules.



Fig. 2-1 SiO photographs of the reagent grains (right two) and powder (left).

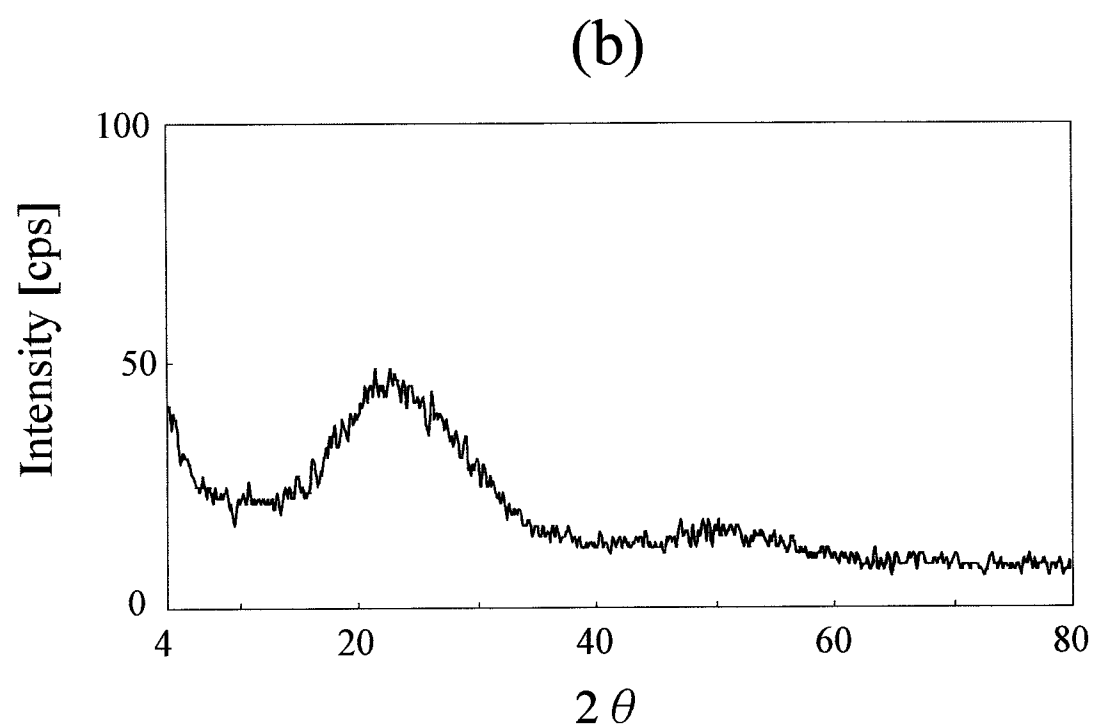
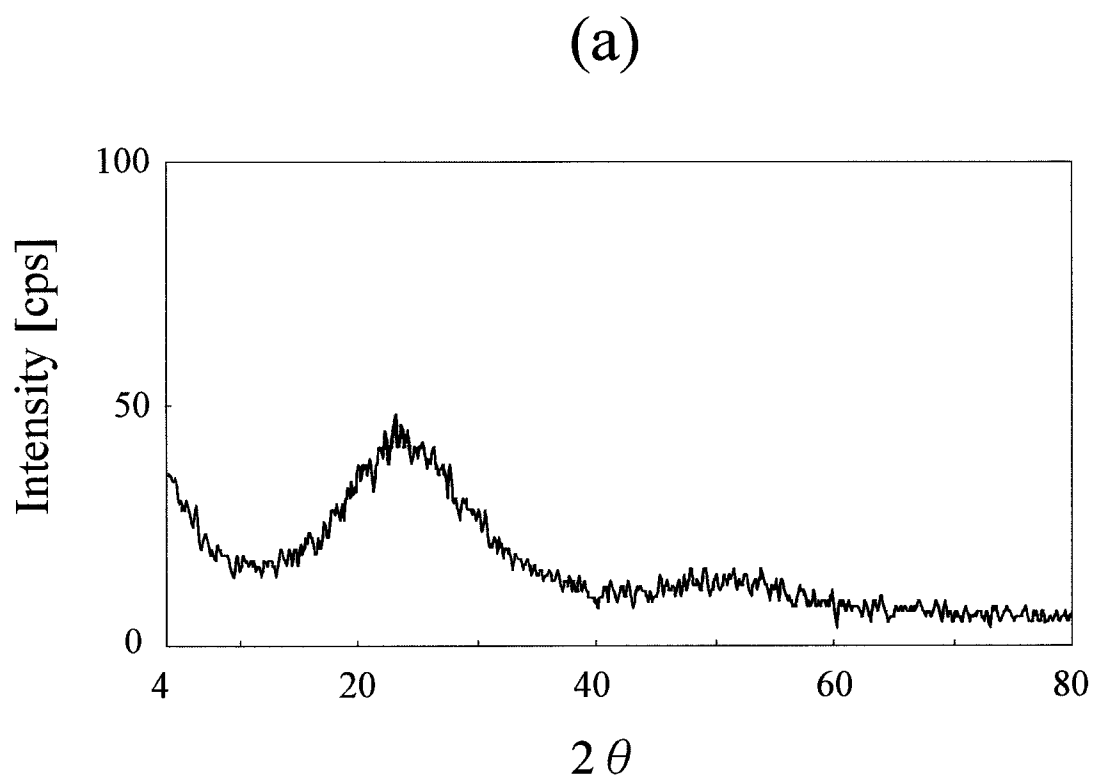


Fig. 2-2 XRD patterns of SiO.
(a) Freshly powdered.
(b) Left for 6 months in air.

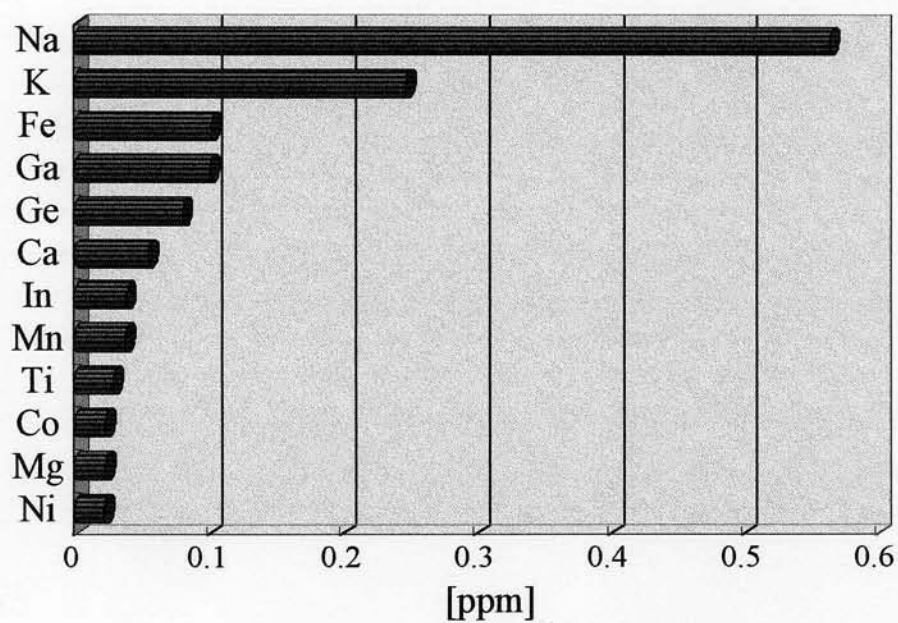
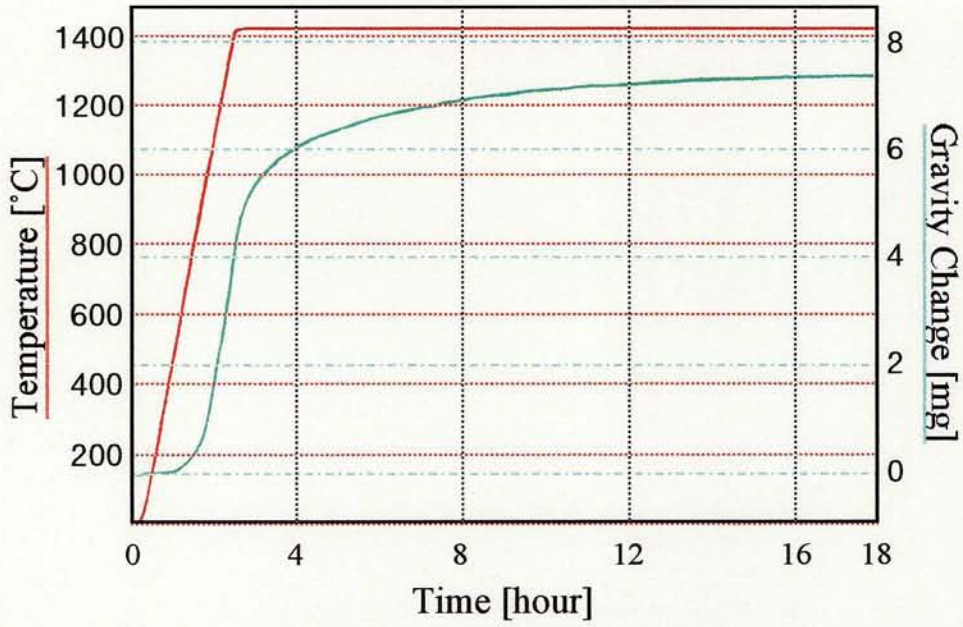


Fig. 2-3 Inductively coupled plasma mass spectrometry analysis (ICP-MS) for impurities in the reagent of SiO

(a)



(b)

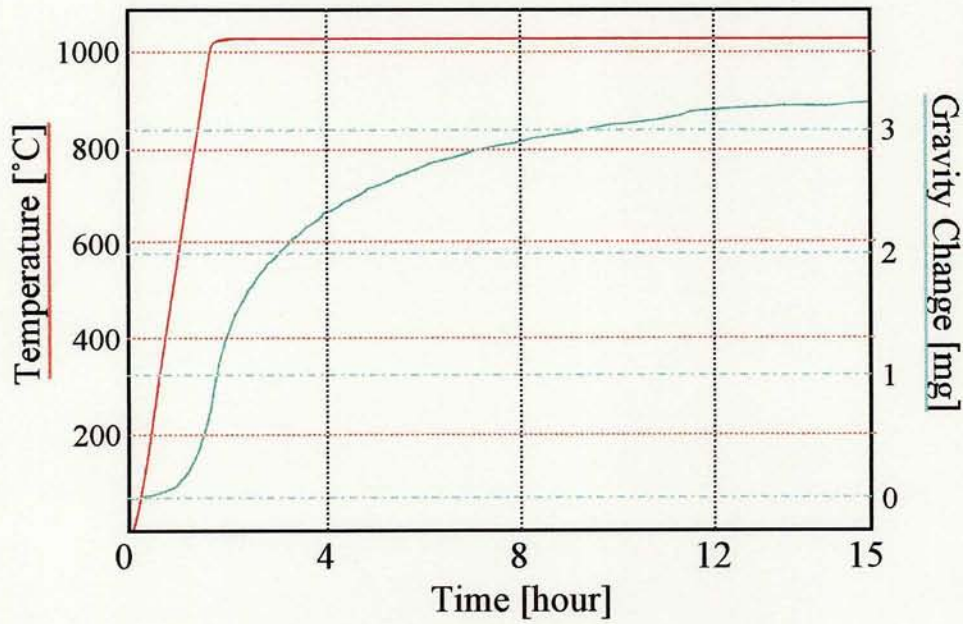


Fig. 2-4 Thermogravimetric (TG) analyses of SiO in air, at (a)1420°C and (b)1030°C

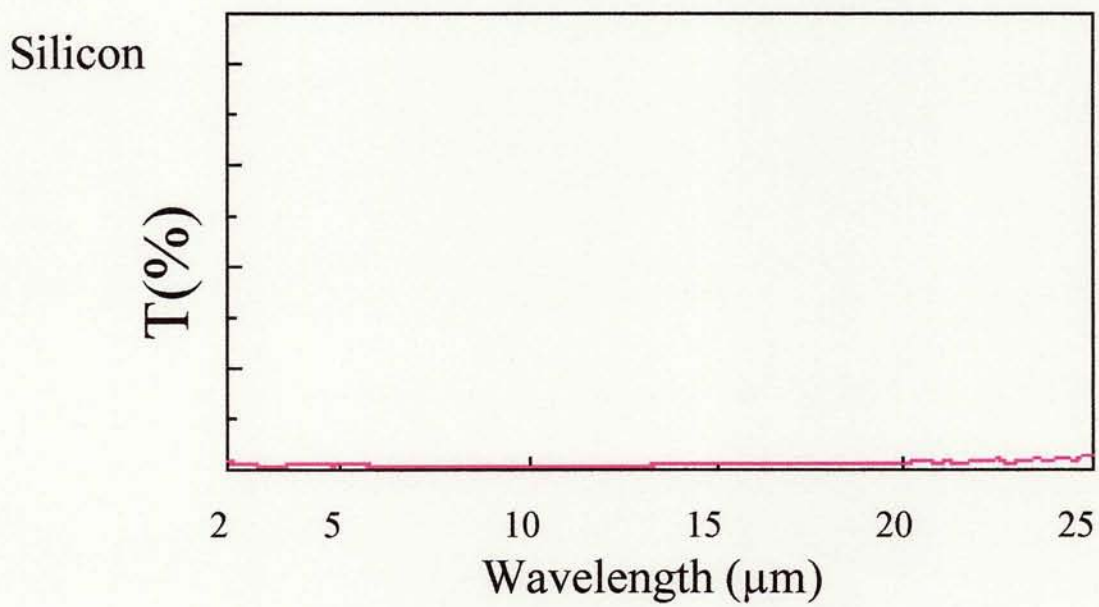
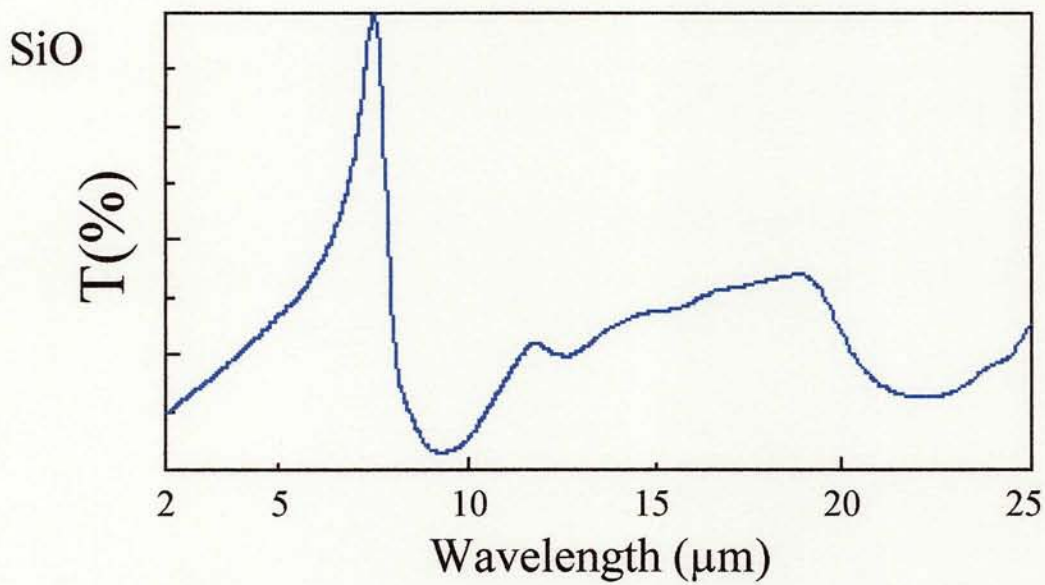


Fig. 2-5 Fourier-transform infrared spectrometry (FT-IR) patterns of SiO and Si.

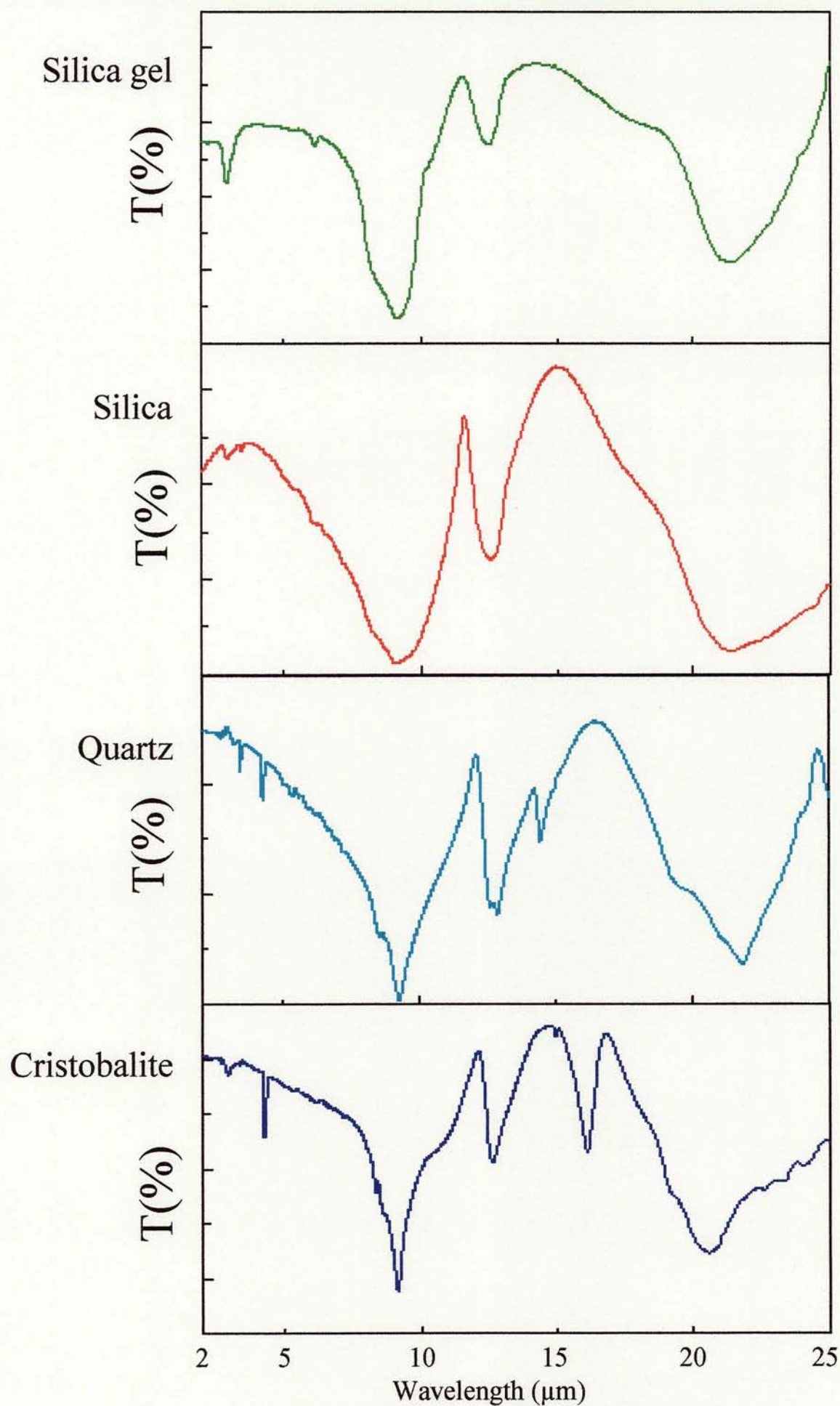


Fig. 2-6 FT-IR spectra of SiO₂ polytypes.

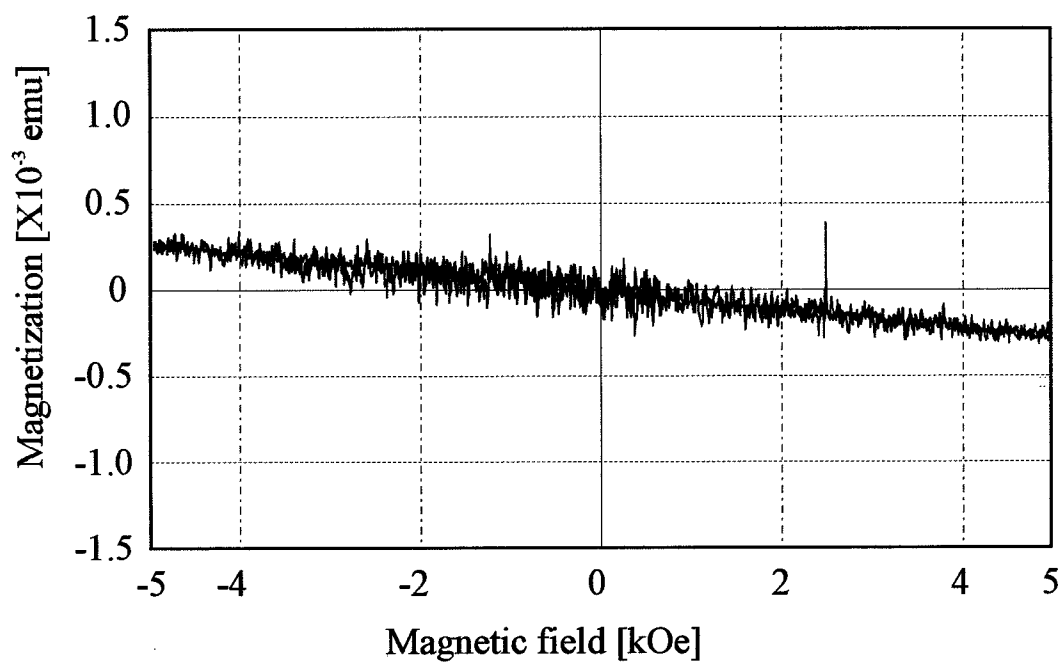


Fig. 2-7 Magnrtic hysteresis loop of SiO at room temperature, indicating a diamagnetic property.

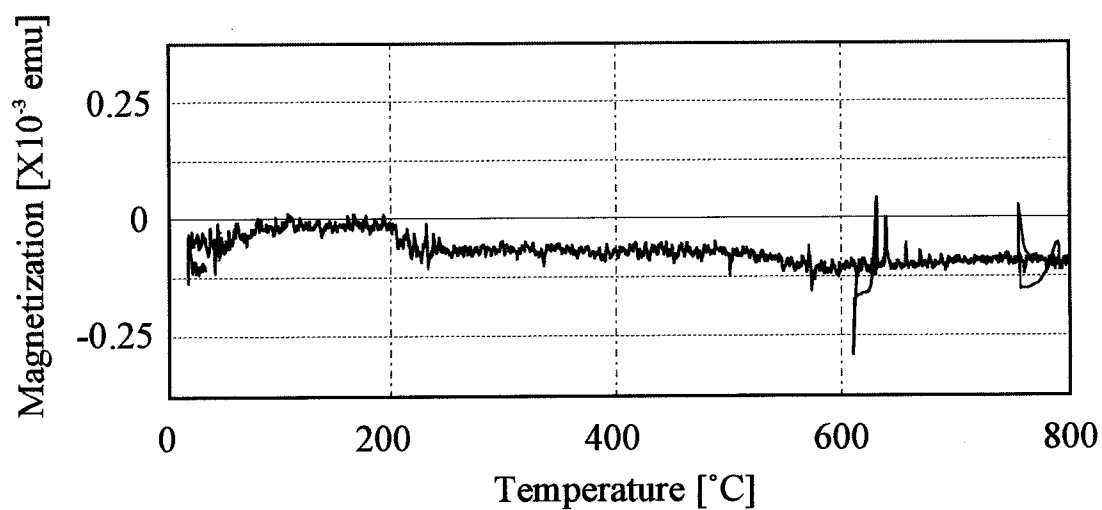


Fig. 2-8 Magnetization of SiO between RT to 800°C.

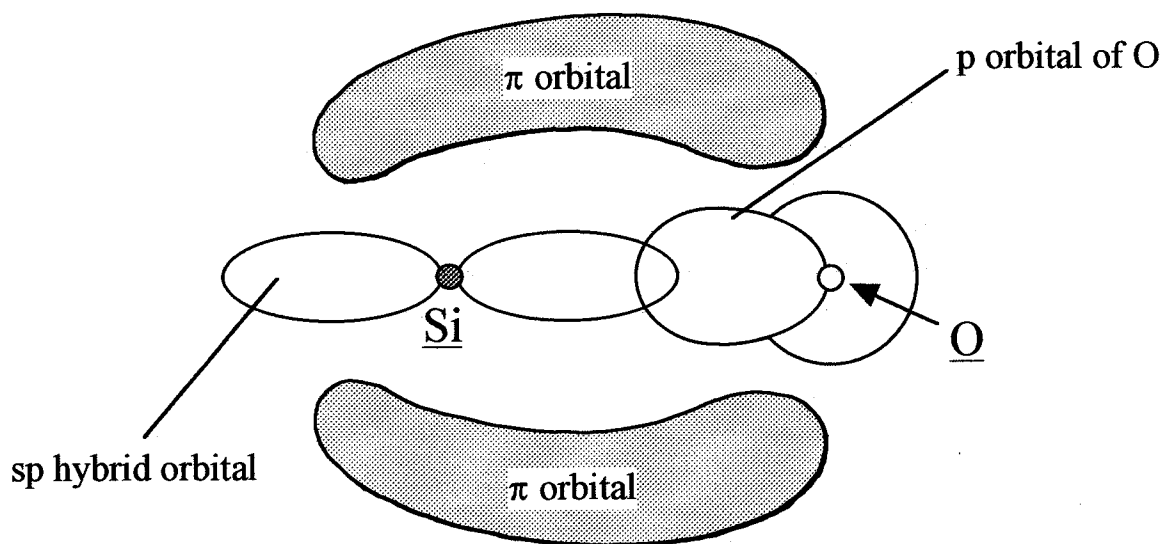


Fig. 2-9 Electronic structure model of SiO molecule.

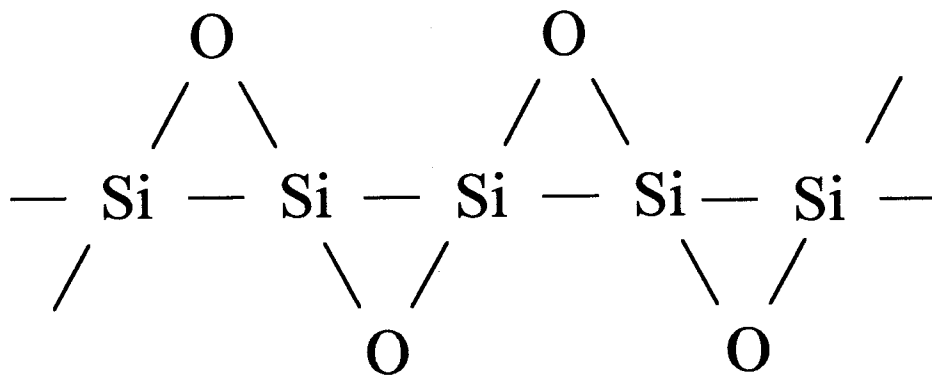


Fig. 2-10 Emons's polymer model of the SiO molecular [13].

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Chapter 3

Analyses of the disproportionation reaction of silicon monoxide

3-1 Introduction

As described in the previous chapter, the reported properties of silicon monoxide (SiO) involve many problems, and the results often lead inaccurate information. One of the typical examples is that the melting point of SiO is reported to be 1730°C. The previous reports have revealed that this material was easily oxidized above 600°C, while it decompose above 800°C into Si and SiO₂ in oxygen free conditions through the well-known “disproportionation reaction”. Thus, it may be difficult to observe the melting behavior at such a high-temperature region without any reaction. As the inaccurate information is still remained in many textbooks or in famous tables, it is important to confirm the reported values before the present investigation.

Studies of SiO have been obstructed by the difficulty of obtaining a single-phase specimen. As described above, SiO decomposes into Si and SiO₂ by the disproportionation reaction on heating at high-temperature. This reaction is suggested to be useful for preparation of Si particles in an easy way. The exact analysis of the reaction will give an important way for determination of the fundamental properties of this material. As described in Chapter 1, SiO is thought to be one of the possible constituent materials in space. Especially, the IR measurements of the bright area where stardusts are concentrated and new stars are formed, showed a

significant absorption around 10 μm [1], which was considered as a result of SiO [2]. From a viewpoint of thermochemistry, this material is possible to exist only at an extreme condition of high-temperature and very low atmospheric pressure. A similar condition can be considered in the initial stage of the earth forming. It is commonly recognized by many scientists that the young earth is covered with stardusts and meteorites whose main constituents are metallic iron and silicates, under a condition at high-temperature and low pressure. Such a condition would be adequate for producing SiO by reduction from common silicate minerals. As a result of the reaction, a great amount of SiO may be produced and dispersed to space by evaporation. Similar situations may exist in numerous young stars in space. This consideration will give a support for the recent astronomical data of the IR spectra.

The disproportionation reaction produces Si and SiO₂, the latter of which is commonly crystallized in the cristobalite form at high-temperature. This mineral has two polytypes: the low-temperature form or α -cristobalite and the high-temperature form or β -cristobalite. It was reported that the $\alpha - \beta$ phase transformation occurs rapidly and reversibly at about 240°C [3], and the high-temperature phase is unstable at room temperature. Although, the reported XRD result contains some extra peaks, which cannot be explained by the reported space groups $Fd3m$ or $P2_13$ [4,5].

In this chapter, thermal properties of SiO used in the present study are first clarified. Next, the results by heating the specimens between 900 and 1400°C in Ar atmosphere are described. After the disproportionation reaction, the products were analyzed by XRD, FT-IR and SEM-EPMA. The reaction under high-pressure was also investigated. In addition, an in-situ analysis of the high (α)-low (β) transformation of cristobalite was

performed using a high-temperature XRD technique.

3.2 Experimental

The raw material of amorphous SiO grains with 99.9% purity, synthesized by reduction of pure SiO₂ powder, was supplied from Nacalai Tesque Co. Analyzed impurity elements by an ICP method were less than 0.5 ppm. The atomic ratio Si/O was very close to the stoichiometry of 1.0 determined by the TG method. Detailed properties of the reagent were described in Chapter 2.

Heating procedure

The SiO grains, dark brown glass with a mean diameter of several mm, were pulverized, filled into a rubber tube and molded to a pellet of about 8 mm in diameter. After the tube was evacuated by an aspirator, the pellet was pressed hydrostatically under a pressure of 7 ton/cm². The pressed pellet was put into a tamman crucible of alumina and suspended in a vertical MoSi₂ furnace.

A schematic figure of the furnace is shown in Fig. 3-1. In this furnace, the sample can be transferred from the low-temperature region to the high-temperature one without breaking the atmospheric condition. The atmosphere can be controlled by changing the contents and flow rates of gas, which is introduced from the bottom part of the furnace to the top. The thermal profile of the furnace was carefully inspected before starting the experiments.

At the beginning of the experiment, the specimen was hanged at the upper part of the furnace where it was kept at room temperature. The furnace was evacuated by a vacuum pump and then filled with pure Ar gas. To remove remained air completely; the above procedure was repeated several times. Then, the sample was transferred within 5 minutes from the

upper part to the central region where the heating condition was already provided.

The heating conditions were as follows; the temperature was between 900 and 1400°C and the heating time were between 0.1 to 20 hours. Each process was carried out under a flow of 30 ml/hr of Ar gas with 99.99% purity. After the treatment, the sample was rapidly pulled up to the upper starting position and kept for more than 30 minutes without any change of the condition. The system was opened when the cooling was completely finished so as to avoid an unexpected oxidation in the quenched specimens.

Sample analysis

The amounts of crystallized materials in every sample were analyzed by an X-ray powder diffraction (XRD) using monochromatized Cu radiation. When the samples were in an amorphous state, the structure was inspected by FT-IR using an apparatus of JASCO, FT/IR-410 where the KBr method was applied. The sample for the FT-IR measurements was prepared by the same way as was already described in Chapter 2.

The microscopic features and compositions of the products were examined by a SEM-EPMA apparatus of JEOL, JSM5600.

High pressure experiment

To investigate the chemical changes of SiO under high-pressure, the experiments around 8 GPa were performed using a cubic anvil type high-pressure apparatus made by Reken Kiki Co., LTD. For higher pressures at 14 and 18 GPa, a multianvil-type high-pressure apparatus, which was settled in Okayama Univ., was used. Details of these systems as well as the operation techniques have already been described elsewhere [6,7]. Two kinds of the high-pressure cells were provided individually for each

system. The cell assemblages are illustrated in Fig. 3-2. The experiments were performed at room temperature without any control of atmosphere, and the samples were recovered after the pressure was completely released. Because of highly compact state, an undesired oxidation of the samples by air atmosphere is avoided during the compression.

The products after compression were also analyzed by XRD, FT-IR and SEM-EPMA.

In situ observation for high-low transformation of cristobalite

The high-low transformation of cristobalite was studied by an in situ system, MXP-3, of high-temperature X-ray powder diffraction (HT-XRD) supplied from MAC Sci. Co.

The main part of the apparatus is schematically shown in Fig. 3-3. The details of the system have been described elsewhere [8-11]. The powder samples of cristobalite were synthesized by heating a silica glass at 1400°C for 20 hours. The products were confirmed by XRD to be a single phase of low-cristobalite at room temperature.

The cristobalite specimens were treated by successive heating at 100, 200, 300, 500, 650 and 800°C. The temperatures between each holding point were changed with a rate of 15°C/min. The angle range and scanning rate for detection of diffracted X-rays were from 15 to 80° and 2°/min, respectively. Before heating and after cooling, the XRD measurements were also conducted in the same way. To detect the high-temperature phases more precisely, a step scanning technique was used under the conditions that the counting interval was set at 0.02° for 5 sec and the counting was repeated 3 times. All the measurements were carried out under air atmosphere.

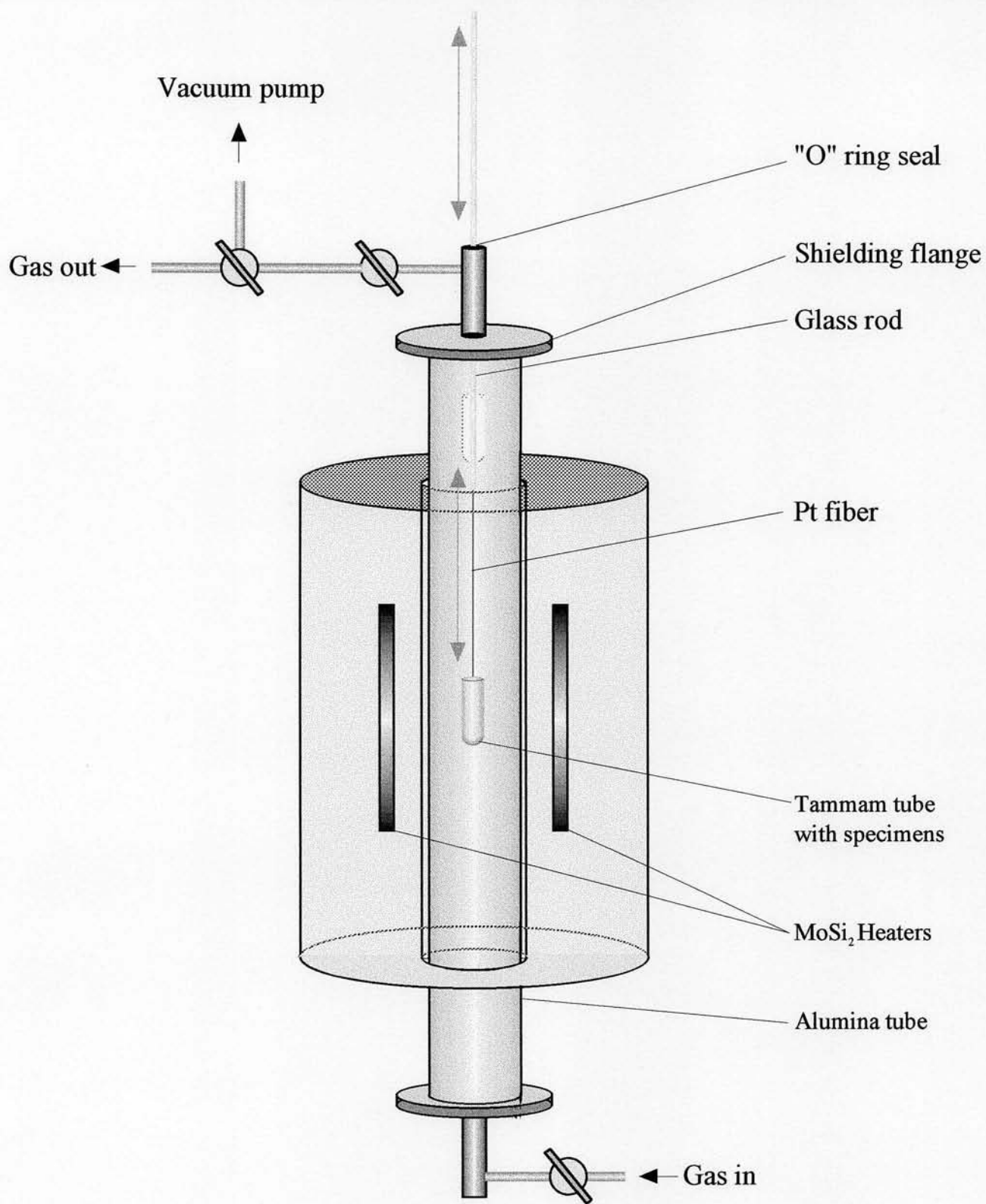


Fig. 3-1 Schematic figure for the vertical MoSi₂ furnace.

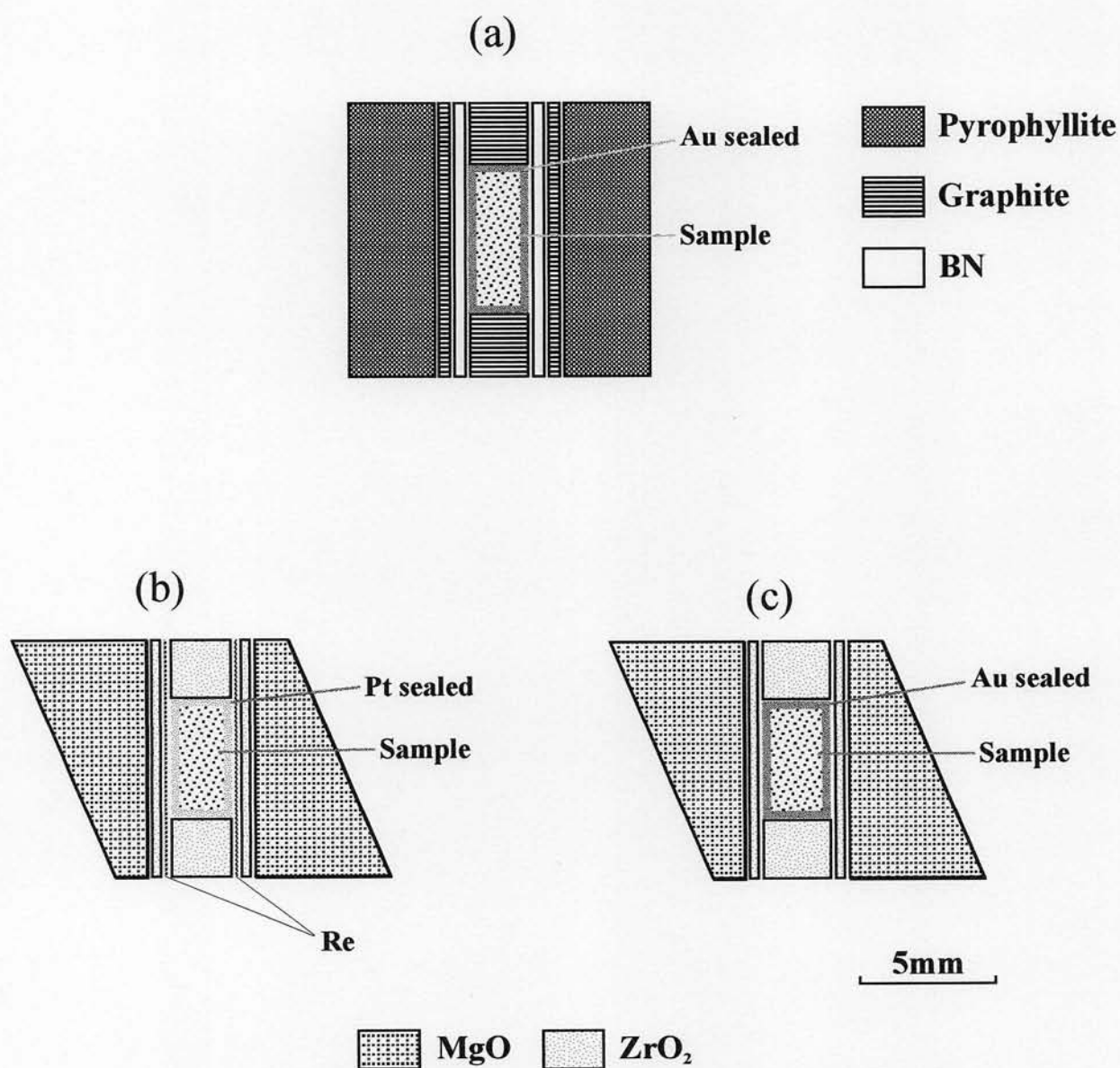


Fig. 3-2 Cell assemblages for high pressure experiments.

(a) for the cubic type used for 8 GPa

(b) for 6-8 split sphere type of multianvil used for 14 GPa

(c) for 6-8 split sphere type of multianvil used for 18 GPa

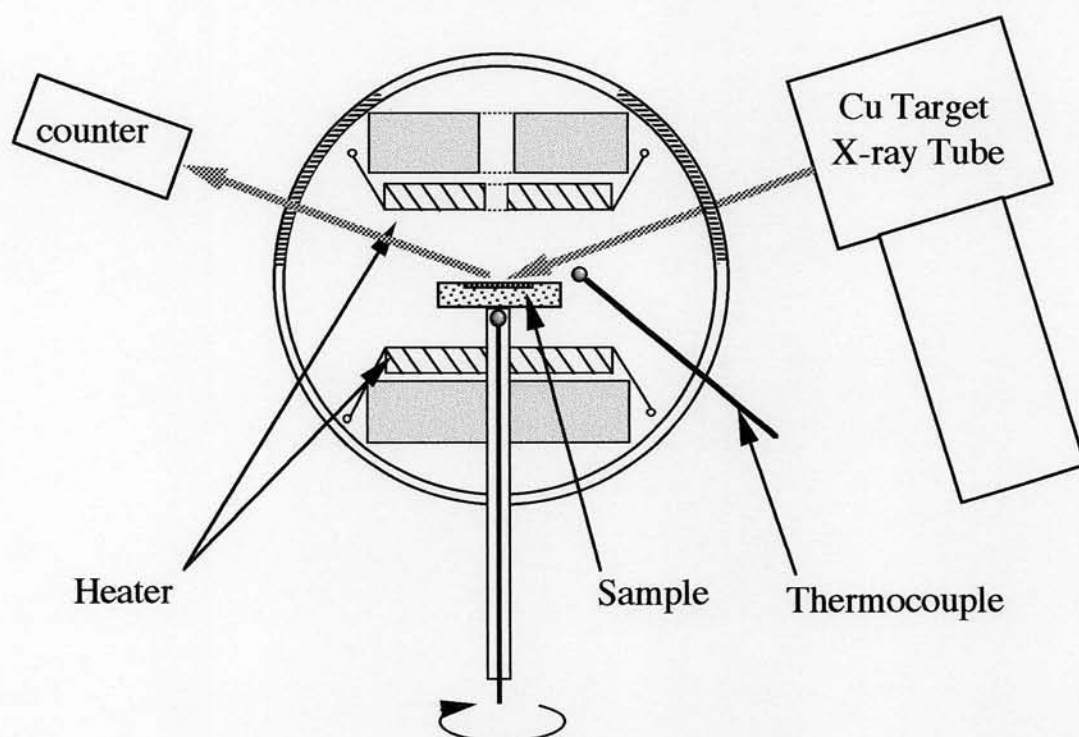


Fig. 3-3 Scheme of the in-situ observation apparatus for high-temperature X-ray diffraction

3.3 Analytical results on reaction process of the disproportionation reaction

As has been described in the earlier chapters, SiO tends to decompose into Si and SiO₂ in an oxygen free atmosphere at higher temperature than 800°C. The reaction process, in which the reaction rate and the yield of the produced Si or SiO₂ are important items, is thought to be much influenced by the condition of heating temperature and time. Furthermore, the states and the structures of obtained Si and SiO₂ will also be changed by such a reaction condition.

Fig. 3-4 typically shows a time dependence of the XRD patterns at 1350°C. Apparent halo patterns around $2\theta \sim 22^\circ$ were observed in the figure. These are attributed to the amorphous phase of SiO₂. When the SiO specimen was held at this temperature only for 0.1 hour, the XRD peaks of crystallized Si appeared clearly, and almost all changes in the patterns were finished in this short time, as shown in the figure. Above 2 hours, no further change in the patterns of Si was observed. Details of the relationships between the intensities of XRD peaks and the particle size of crystallized Si will be described in Chapter 4.

When the sample was kept over 1 hour, the crystallization of amorphous SiO₂ to the cristobalite phase was detected. In contrast to the case of Si, the XRD peaks were quite sharp even at a beginning of the crystallization at 1 hour. That is, the crystalline sizes of the precipitated cristobalite were not smaller than scores nanometer. From the peak intensity analyses, the total amount of cristobalite was much smaller than that of Si. The typical appearance of cristobalite is shown by a SEM image in Fig. 3-5, where many squarish materials are observed. The EPMA revealed that the composition was close to SiO₂, suggesting that

these were single crystals of cristobalite.

The above-expressed experiments were conducted on the specimens which were pressed and formed into the spheres, as previously described in Chapter 2. On the unpressed powder specimens, however, the crystallization did not advanced rapidly and smoothly, and the yields as well as the crystallinity of the react; on products were considerably scattered in each treatment. One of the examples is shown in Fig. 3-6, where the pressed spheres and the unpressed powders were annealed simultaneously at 1400°C for 1 hour. The XRD patterns of the both samples showed crystallization of Si and cristobalite, whereas there is a clear difference between the two. In the pressed spheres, the reaction progressed smoothly and almost finished within 1 hour, and no halo patter was observed in XRD. On the other hands, the product of the unpressed powder contained amorphous SiO₂, because the XRD showed remarkable halo pattern around $2\theta \sim 22^\circ$, whereas the sharp peaks of Si and cristobalite were also observed. The result indicates that the crystallization of cristobalite was enhanced in the reaction product of amorphous SiO₂ by a compressed state which would induce a stress field, close adherent and so on, between each particle.

The unpressed powder specimen contains another problem of unexpected oxidation with slight amount of residual oxygen in the flow of Ar. It is difficult in the present annealing system to exclude oxygen completely from the controlled flow of Ar gas. It should be emphasized that Si is a very oxidative material against oxygen at high-temperature. As the unpressed samples have large surface areas having open interstices in comparison with the pressed ones, the produced Si may be exposed with remaining oxygen atoms in the flowing gas. Consequently, the effect of atmosphere in the unpressed powders may become significant in

comparison with the pressed ones.

Optical absorption data in the IR region is useful for settling the fine molecular structures of the annealed specimens. Note that common XRD measurements give information on gross and average structures of the resultant materials or amounts of the produced crystals, while IR data are generally used only for analyzing the fine structures.

The FT-IR patterns were measured in order to inspect the changes in the fine structures by annealing, as shown in Fig. 3-7. When the specimen was held at 1350°C for 1 hour, the high-transmission peak slightly shifted its peak position from 7.5 μm in pure SiO to 7.0 μm . The IR transmission phenomenon in SiO has been reported to be visionary and explained by the reflection effect from the high refractive index of SiO in this IR region [12]. The high index value is due to a high polarization of SiO molecules. Details of the transmission behavior in relation to the molecular structure have been explained in the previous chapter, where the IR data were compared with those of quartz crystal, silica glass and dried silica gel, in which they do not show such a pseudo-transmission peak.

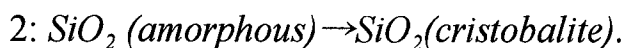
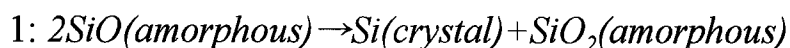
The blue shift from 7.5 to 7.0 μm in Fig. 3-7 is explained by a structural change in the amorphous SiO phase, where a considerable amount of excess oxygen was supplied by the disproportionation reaction, and formed a metastable bonding of O-Si-O, suggesting a formation of SiO_x glass. These bonds would lower the polarization of SiO molecule itself and consequently, the optical properties should be constricted to those of SiO_2 by annealing.

When the specimens were held at 1350°C for 2 hours, the high transmission peak around 7 μm became slightly weak and two obvious absorption peaks at 12.6 and 16.3 μm appeared. As the absorptions correspond to those of cristobalite, the amorphous oxide tended to

crystallize in this annealing condition. From the XRD results, the 2 hours-annealed sample consists of Si, cristobalite and a very few amount of amorphous phase. The remaining IR transmission is tentatively explained by the effect from the SiO_x glass, whose strong reflection around $7\ \mu\text{m}$ is thought to be comparable to that of SiO . It is difficult to estimate the amount of the remaining amorphous phase from the XRD halo pattern.

The unchanged IR patterns were obtained on the specimens annealed at 1350°C for more than 4 hours. This result indicates an ending of the disproportionation reaction at this temperature. Comparing the IR absorption of standard cristobalite crystals with the present data, the present peaks are still broad. Though these phenomena may be explained by crystallinity of the resultant cristobalite, it is not easy to estimate the exact quality of crystals.

From these results, the disproportionation reaction proceeds in the following two steps;



These two-step reactions show the different characters for crystallization of Si and cristobalite. In the XRD results, crystallized Si first appeared in the XRD patterns as broad and weak peaks and these peaks became sharp and strong in progress of the crystallization. Crystallized cristobalite first appeared with weak but sharp XRD peaks and only the peak intensity became strong with the reaction time. The results suggest that the crystallization of Si starts first with forming quite fine particles and in the next stage, these particles grow by agglutination of the fine ones.

In the case of cristobalite, a small amount of the large, well-developed crystal units appears even at the beginning of the reaction, and

then the crystallization follows by increasing the total amount of the unit. Such a situation implies that there are different crystallization mechanisms between Si and cristobalite. Nucleation of the Si crystals will occur very easily, and there will be many nucleated particles of Si in the initial stage. Nucleation of cristobalite is suggested to be not easy because of the large crystallization energy. Details of the crystallization mechanism will be described in the next chapter.

Fig. 3-8 shows the observed reaction times needed for the first appearance of crystallized cristobalite at each temperature, where the data indicate the times taken until the second step reaction starts. The temperature range below 1300°C, the second step reaction starts after annealing of more than 2 hours. On the other hand, the first and second reactions proceed simultaneously above 1350°C.

Such a high-temperature range, cristobalite exists in the high-temperature form. Detailed feature of the phase change behavior in cristobalite will be described in Section 3-6.

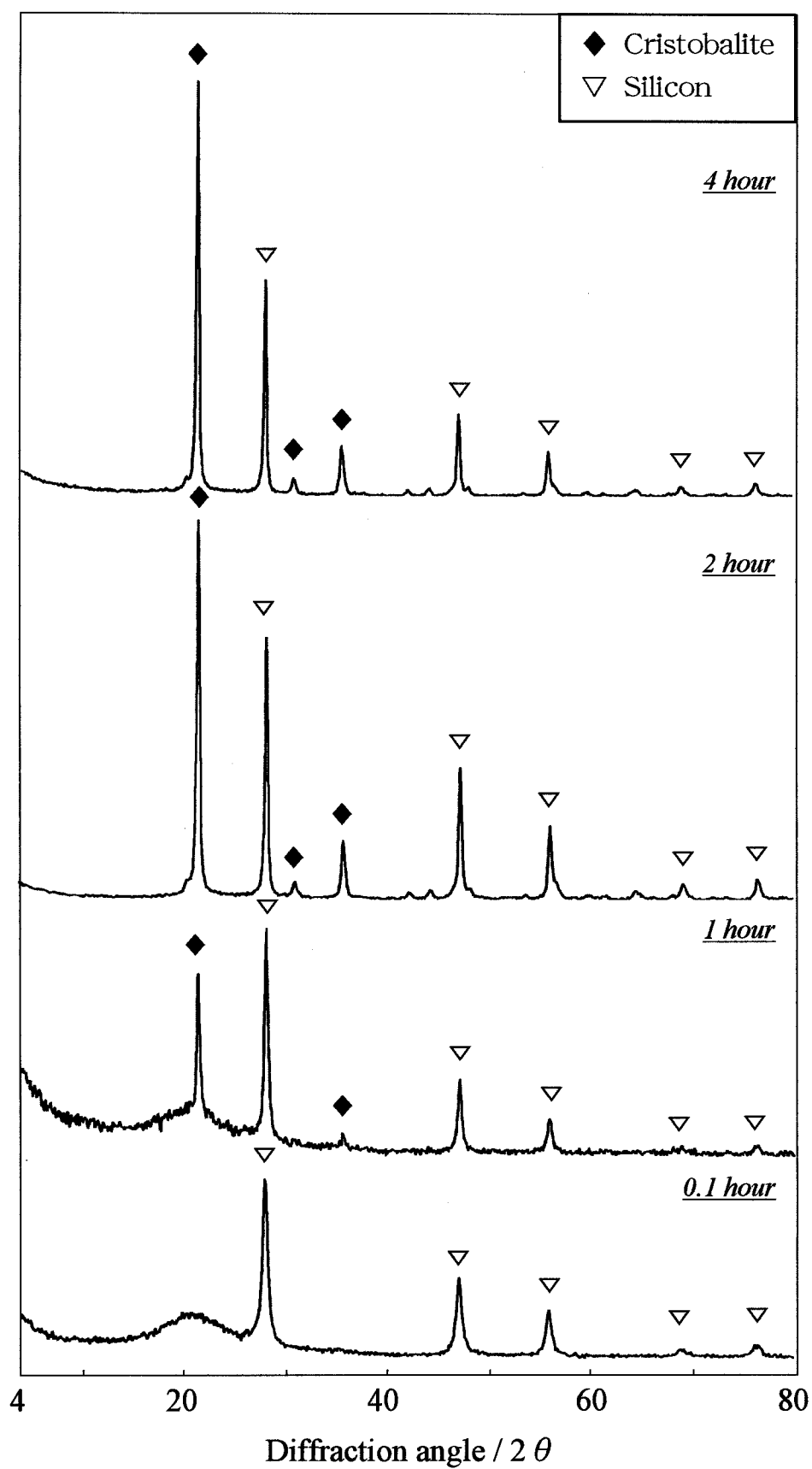


Fig. 3-4 Time dependance of XRD changes in SiO at 1350°C.

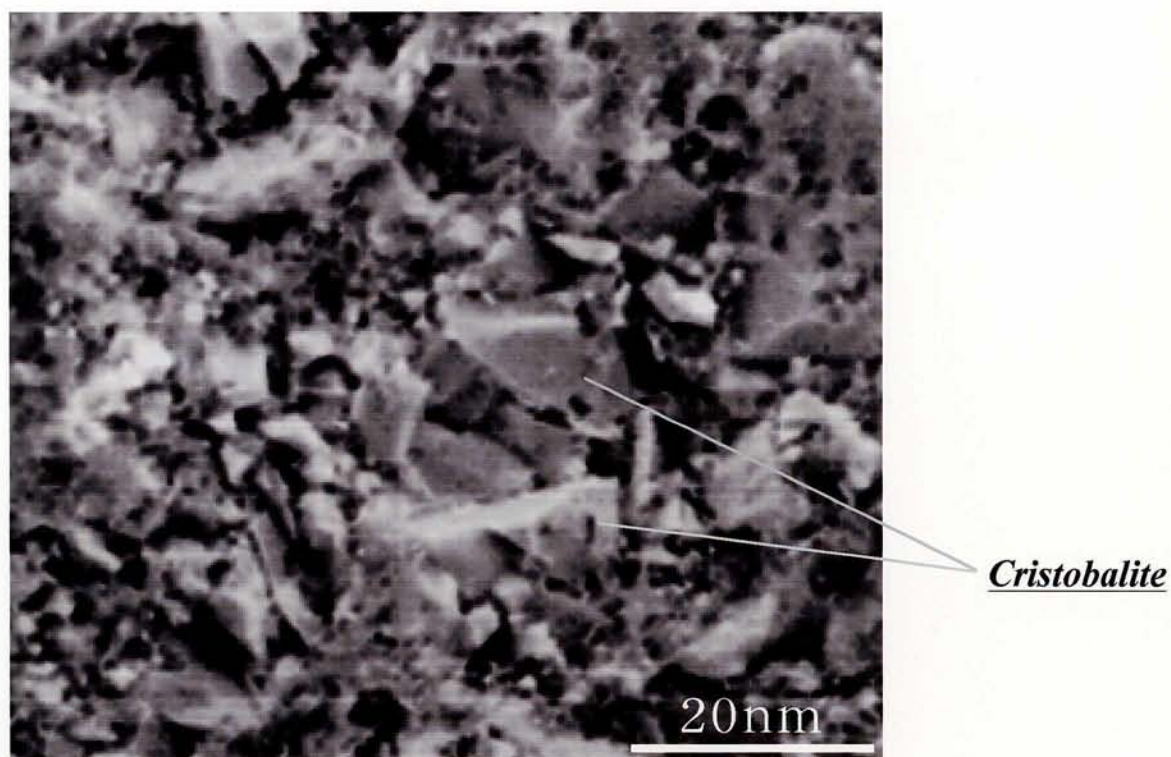


Fig. 3-5 SEM image of cristobalite, heated at 1400°C for 10 hours.

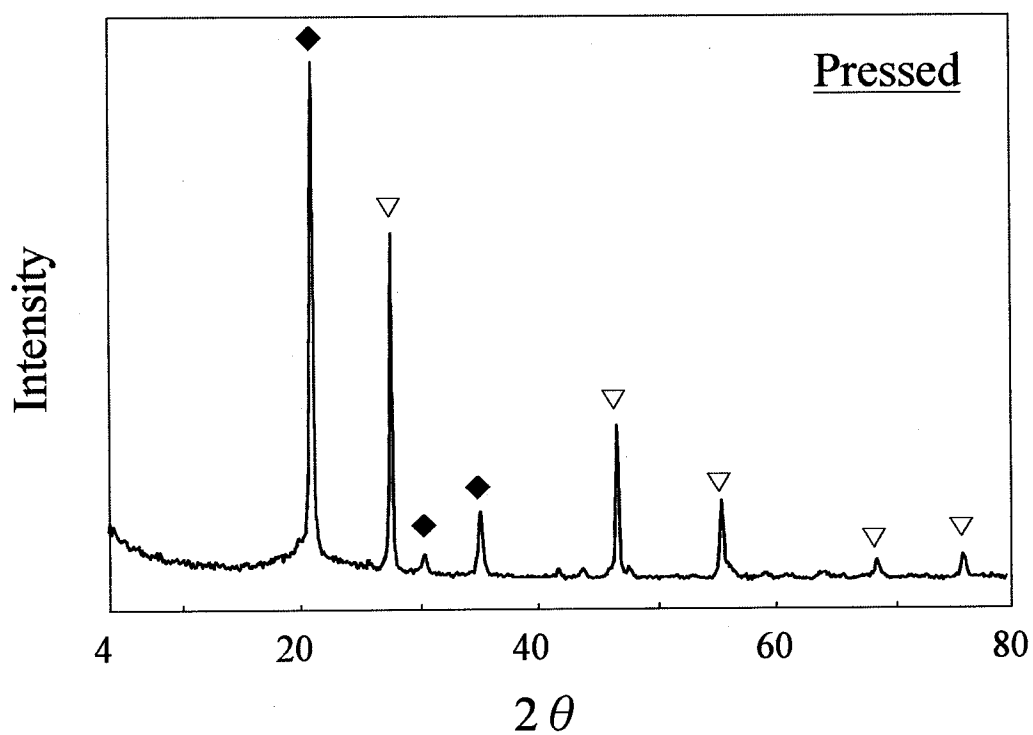
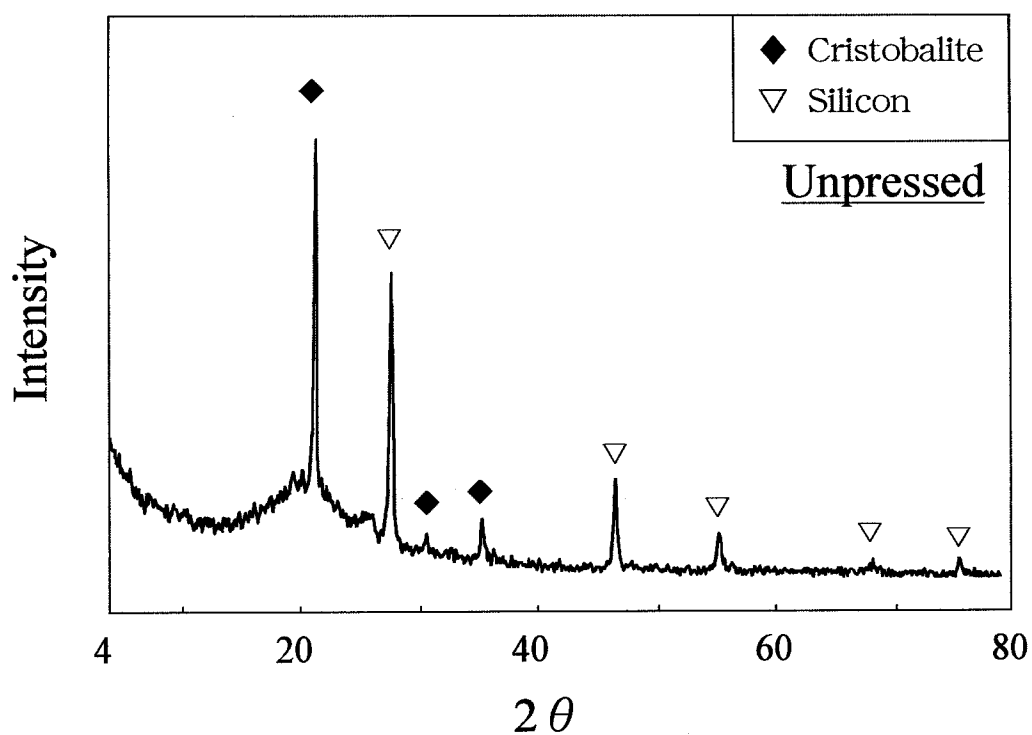


Fig. 3-6 Comparison for XRD results between the unpressed and the pressed specimens, annealed at 1400°C for 1 hour.

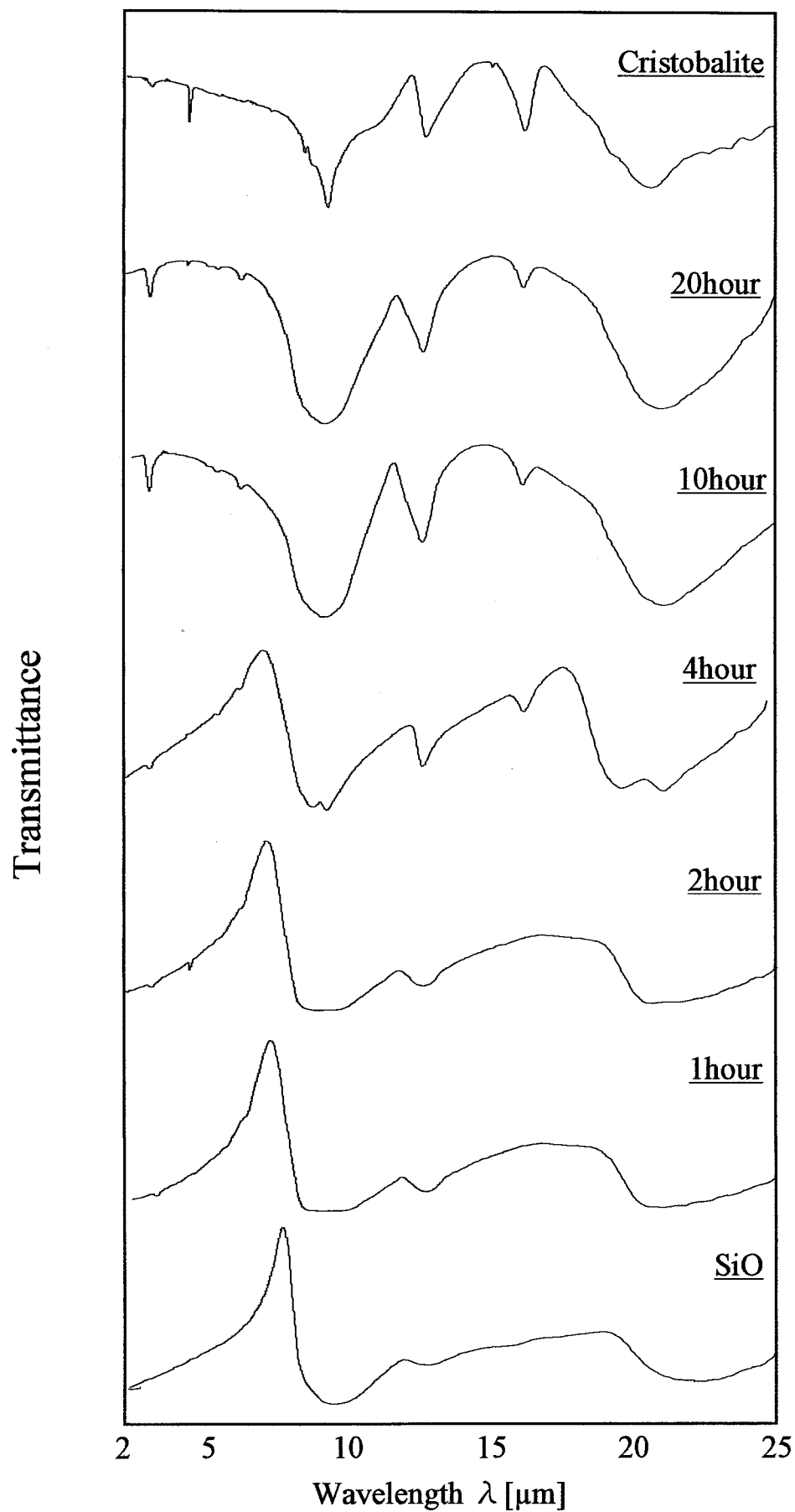
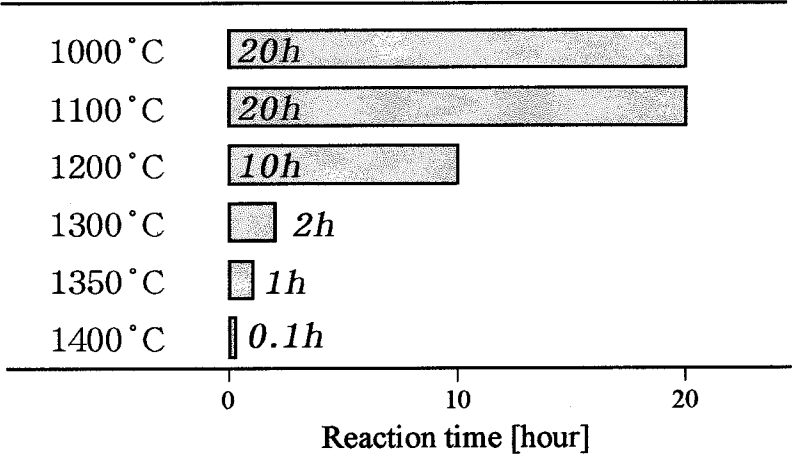


Fig. 3-7 Time-dependent IR pattern changes at 1350°C. The SiO and cristobalite patterns were added as references.

Fig.3-8 Reaction times needed for crystallization of cristobalite at each temperature.



3.4 High pressure reaction

It is commonly accepted that chemical reactions are enhanced by pressure when the molecular volumes are decreased after the reactions. Table 3-1 shows the densities of Si, SiO and the SiO₂ polytypes. Although the density of SiO has not exactly defined, it averaged about 2.2 g·cm⁻³, which is apparently smaller than those of others. Therefore, SiO is expected to be unstable by compression and has a tendency to decompose into Si and SiO₂.

Fig. 3-9 is the XRD patterns pressed at 8, 14 and 18 GPa. Below 14 GPa, no apparent peaks are observed. At 18 GPa, there are obvious peaks of crystallized Si and a broad peak around at 2.1 nm. Fig. 3-10 shows the ED pattern of the 18 GPa sample. Broad diffraction circles for crystallized Si appear in this picture, suggesting a deposition of Si particles with low crystallinity.

Fig. 3-11 is the FT-IR patterns for the pressurized specimens of SiO. They show almost the same patterns in the specimens treated at 8 GPa and in the starting ones, indicating no change below 8 GPa. At 14 GPa, there appeared slight absorption around 13 and 15 μm, which were attributable to the Si-O-Si bending motion. It should be noted that such a movement is impossible in monomolecular SiO because the Si-O-Si bond never exists. The IR results imply that the decomposition of SiO starts under the compression at 14 GPa.

As was mentioned in Chapter 2, the high transmission around 7 μm observed in IR measurement is characteristic of SiO, which is caused by the reflection from the SiO-KBr interface. In the pressurized specimens up to 14 GPa, the transmission peak positions were almost unchanged. That is, the molecular structure of the samples is essentially conserved after

compression. This agrees with the XRD results that there are no peaks in the patterns, suggesting that the structure unit is still so short in the compressed state that it is not regarded as a crystal.

At 18 GPa, the FT-IR pattern was changed, as shown in Fig. 3-11. The IR absorptions related to the motions of Si-O-Si become apparent. The XRD peaks of Si and an unknown crystal appeared, as shown in Fig. 3-9. These lead to the conclusion that the decomposition becomes significant around 18 GPa at room temperature.

The IR absorption pattern for the 18 GPa specimens is similar to that of quartz rather than that of cristobalite, as shown in Fig. 3-12, where the patterns of quartz and cristobalite are presented as references. On the other hand, the maximum absorption peaks are slightly shifted from 8.5 to 8 μm . The blue shift of the peak is supposed to be due to an increase in the stretching energy in Si-O.

The IR results are, however, in a conflict state with the XRD patterns. The difference between the IR and XRD results may be caused by a difference in the sensitivity for measuring physical properties of target materials. The IR spectrometry is sensitive for an electronic state of elements or molecules, while the XRD measurement is favorable to analyzing a stacked structure of molecules or atoms in a crystallized state. In such a condition, it is reasonable to understand the difference in the present IR and XRD results in the amount of precipitated phases by compression. At 18 GPa, for example, the amount of cristobalite is suggested to be not so much as that of the amorphous SiO_2 .

Table 3-1 Densities of Si, SiO and SiO₂ polytypes.
[g·cm⁻³]

SiO	2.18	[18]	Silicon	2.33
	2.2	[19]		
	2.24	[20]	Quartz	2.65
	2.24	[21]	Cristobalite	2.33
			Tridymite	2.26
			Coesite	2.93 [22]
			Stishovite	4.35 [23]

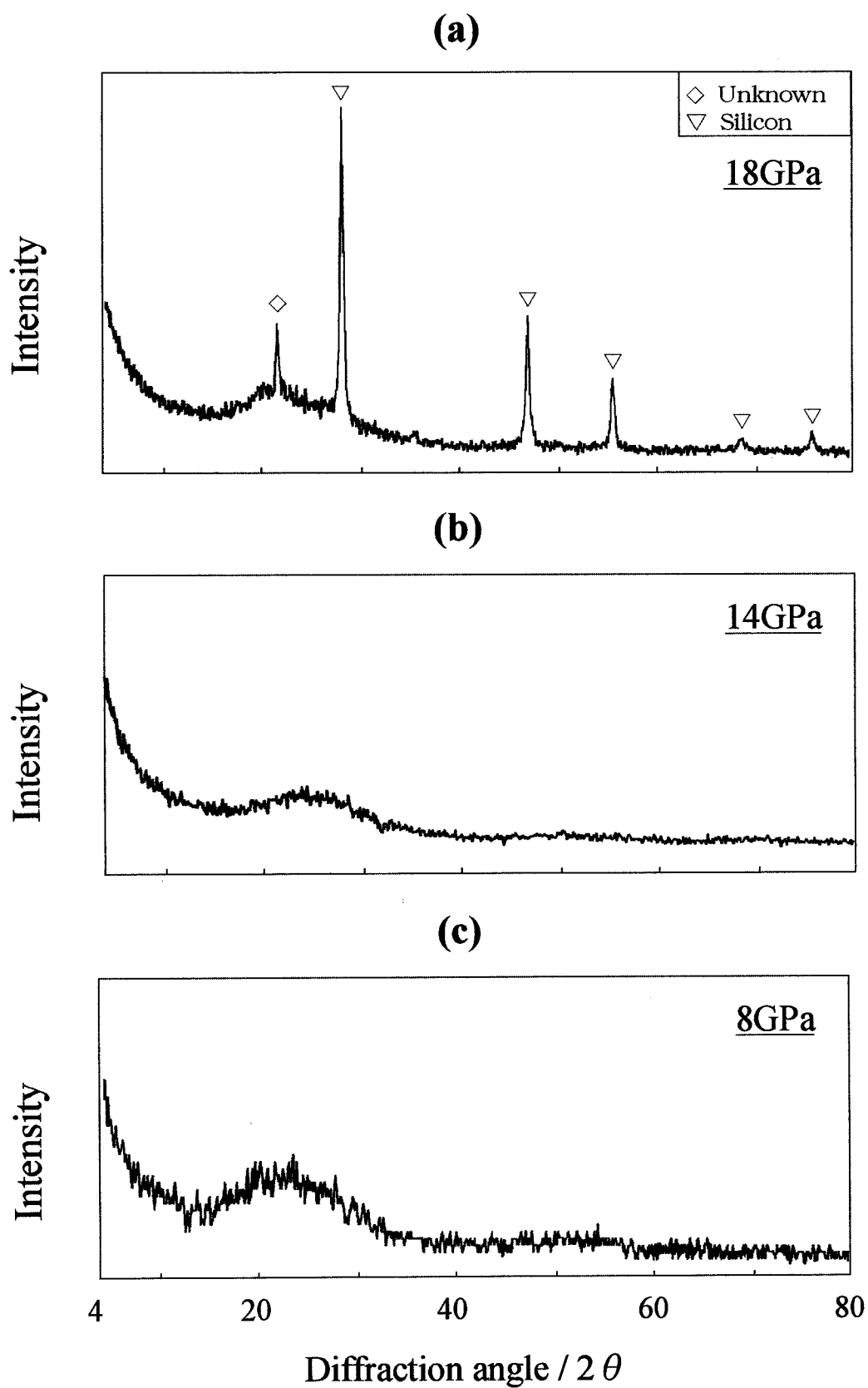


Fig. 3-9 XRD patterns of compressed specimens.



Fig. 3-10 ED image for the 18 GPa-pressed specimen .
The broad rings correspond to the diffractions of crystallized Si.

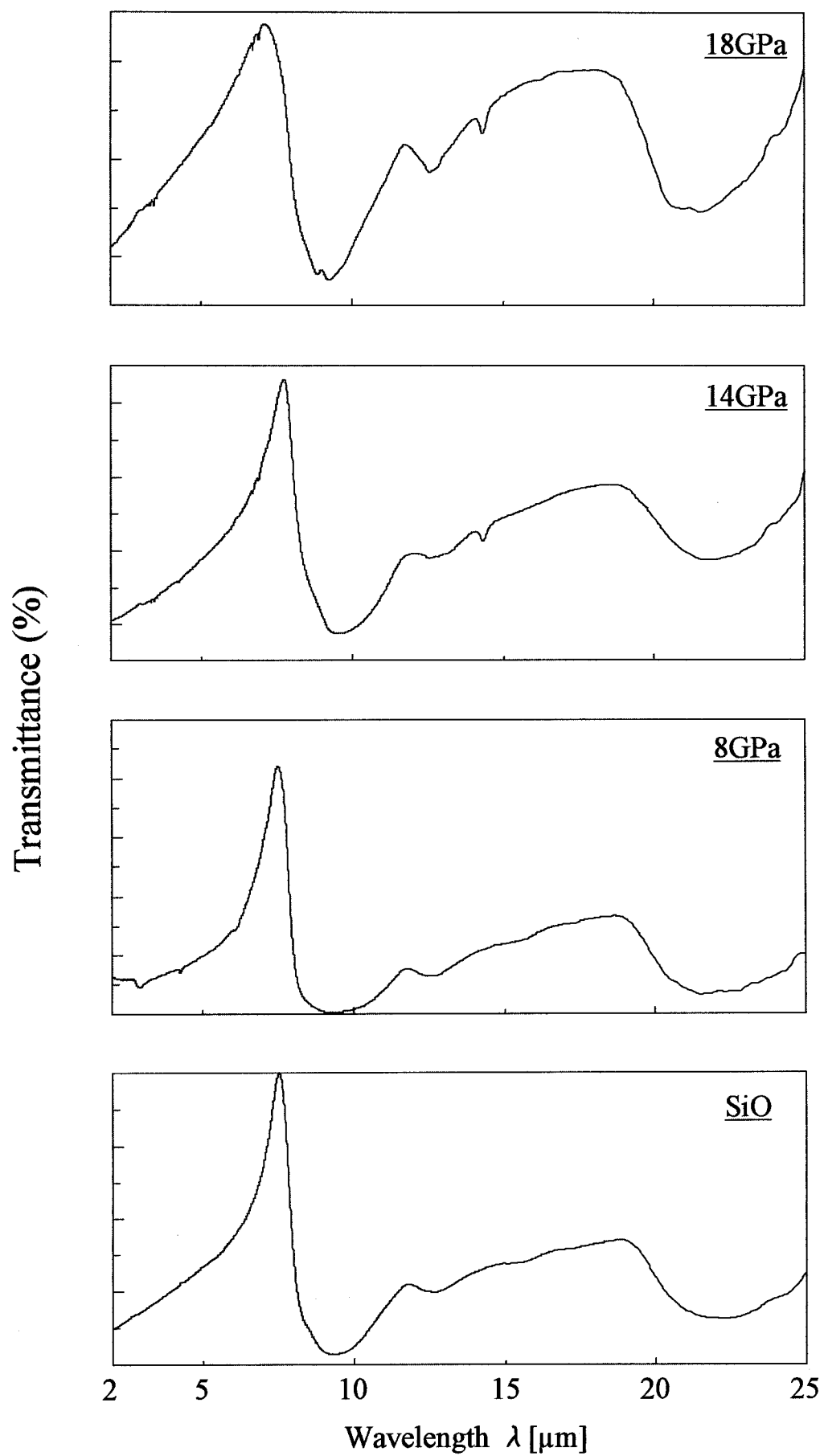


Fig. 3-11 IR patterns for compressed specimens and standard SiO.

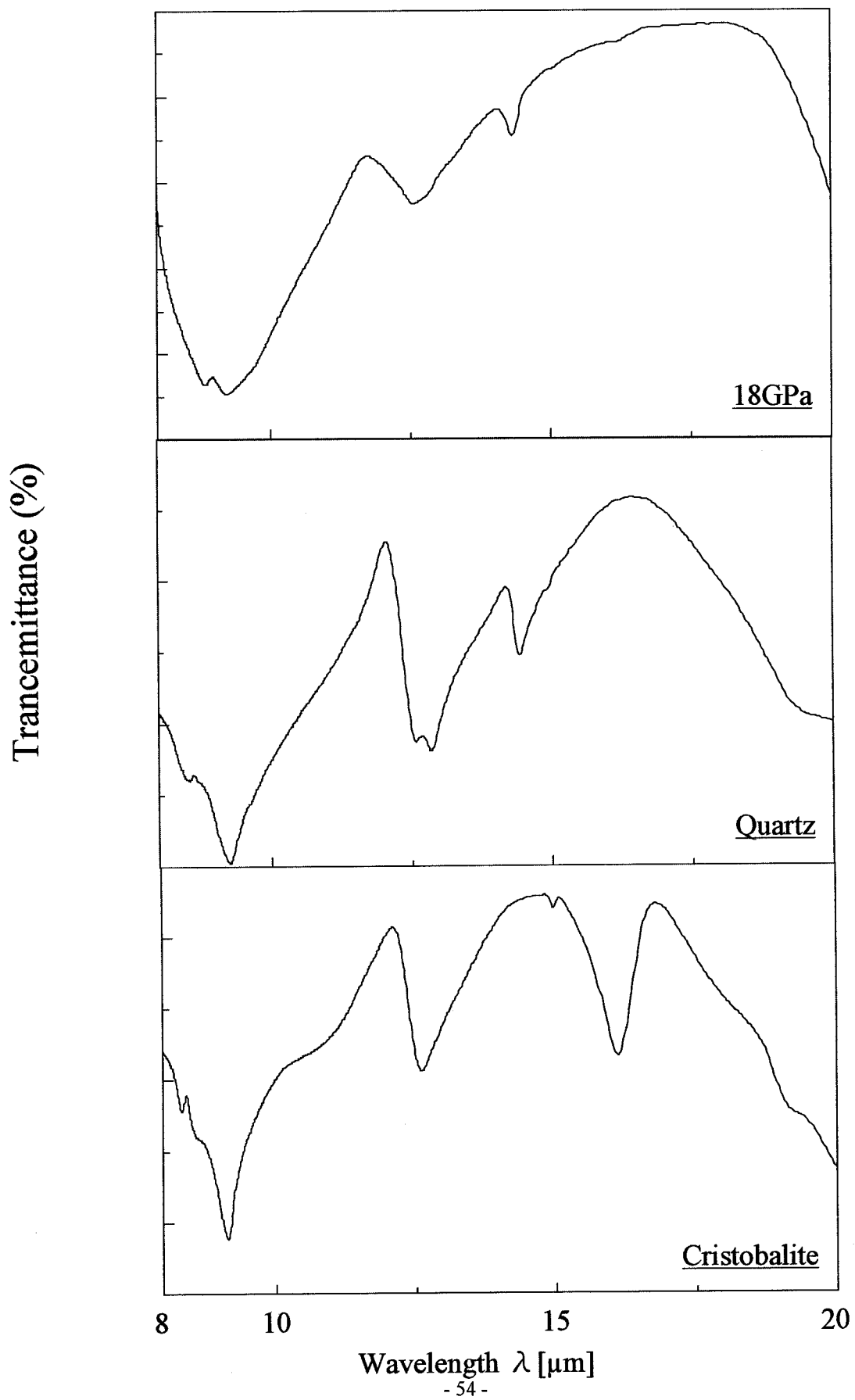


Fig. 3-12 The comparison of IR patterns between the 18GPa

3.5 In situ observation of the high-low transformation in cristobalite

The disproportionation reaction occurs at higher temperatures above 800°C. In this temperature range, it is known that the polymorphs of crystallized SiO₂, such as quartz, tridymite and cristobalite, will change from low-temperature phases to high-temperature ones, respectively. Such a polymorphic transformation can be detected by structural, thermal or other physical changes crossing the transition temperatures. A high-temperature XRD technique is useful for analyzing the structure of an unquenchable, high-temperature phase and the process of transformation.

The high-low transformation in quartz was first described by Le Châtelier in 1889 [13] and after that, numerous studies have been done. The transition temperature was reported to be 573±1°C on rising temperature [14]. The transition proceeds by changing only the bond angles between each SiO₄⁴⁺ tetrahedra without any recombination of the bond chains. However, the precise mechanism of the transition remains to be clarified. Although all the transitions in SiO₂ polymorphs are regarded as a first order phase change, unquenchable, reversible changes are reported in some materials. Recently, studies on this field revealed an existence of the intermediate phase and suggested a more complex phase change mechanism [15-17].

In the case of cristobalite, there have been few studies for the high-low transition. The crystal data of low-temperature phase is decided for tetragonal $P4_12_12$, and $a=4.732\text{\AA}$, $c=6.9236\text{\AA}$. The crystal structure of the high-temperature phase was first determined by Wyckoff [4], where it belongs to the space group $Fd3m$. He has pointed out that the Si-O-Si bonds are arranged in a linear chain. However, the reported diffraction

pattern includes some additional peaks whose indexes are not allowed by this space group. Recently, Barth et al [5] have proposed a different space group of $P2_13$, and the structure consists of a distorted framework from the ideal close-packed structure.

As the reported two space groups do not obey the usual symmetry rule between the mother and transformed phases, the phase transition should be regarded as a first order. The high-low transition in cristobalite has been conflicted and has not been completely explained in a common diffraction rule. Therefore, it is needed in the present study to reconfirm the high-temperature phase.

In this work, the high-low transition measurements were carried out by an in situ observation technique of high-temperature X-ray powder diffraction (HT-XRD). Fig. 3-13 shows a HT-XRD pattern change of cristobalite on a heating process. Below 200°C, the patterns were not changed. Between 200 and 300°C, the pattern was changed considerably and then no further change was observed above 300°C.

Fig. 3-14 shows the HT-XRD patterns of the samples in an elevating-cooling cycle between room temperature, 800°C and room temperature. There are no different peaks in the XRD patterns before and after the treatment. Thus, the transition is concluded to be reversible. The precise experiments revealed no apparent hysteresis during the heating-cooling cycles.

To compare the present results with those in the previous reports more precisely [5], the HT-XRD measurements by the step scan counting technique were carried out at 500°C. Fig. 3-15 shows the result whose peak values were tabulated in comparing with that of the previous report, as listed in Table 3-2, where the indexed spacings of each peak are referred to the previous one.

The lattice parameters of the high-temperature phase calculated from the data in the table are almost similar to each other. For example, the lattice constant for the cubic system at 500°C is $a=7.134\text{\AA}$ and the reported one is $a=7.16\text{\AA}$ at 500°C. However, the previous XRD data involves some additional peaks, which may correspond to those of the low-temperature phase, and the reported space group became $P2_13$ with lower symmetry. On the other hand, the present data contains no additional peaks and is reasonably explained as the high symmetry space group $Fd3m$. At present, this space group derived from the HT-XRD results should be more similar to the ideal structure and reasonable for explaining the powder data than $P2_13$ reported by Barth.

As described above, the phase change in cristobalite proceeds rapidly and reversibly with no hysteresis during the heating-cooling cycle, inducing some doubt about a first-order phase transition. To clear the problem, TG-DTA analysis was performed. Because of no chemical reaction in this material, the TG pattern was not changed, whereas the DTA curve displayed clear changes, as shown in Fig. 3-16. In this result, an endo- and exothermic peaks were observed at 246 and 242°C on heating and cooling processes, respectively. That is, the phase change belongs to the first-order. As the both peaks are close in transition temperature between the heating and cooling runs, there would be a small rearrangement of the constitutional atoms in this process.

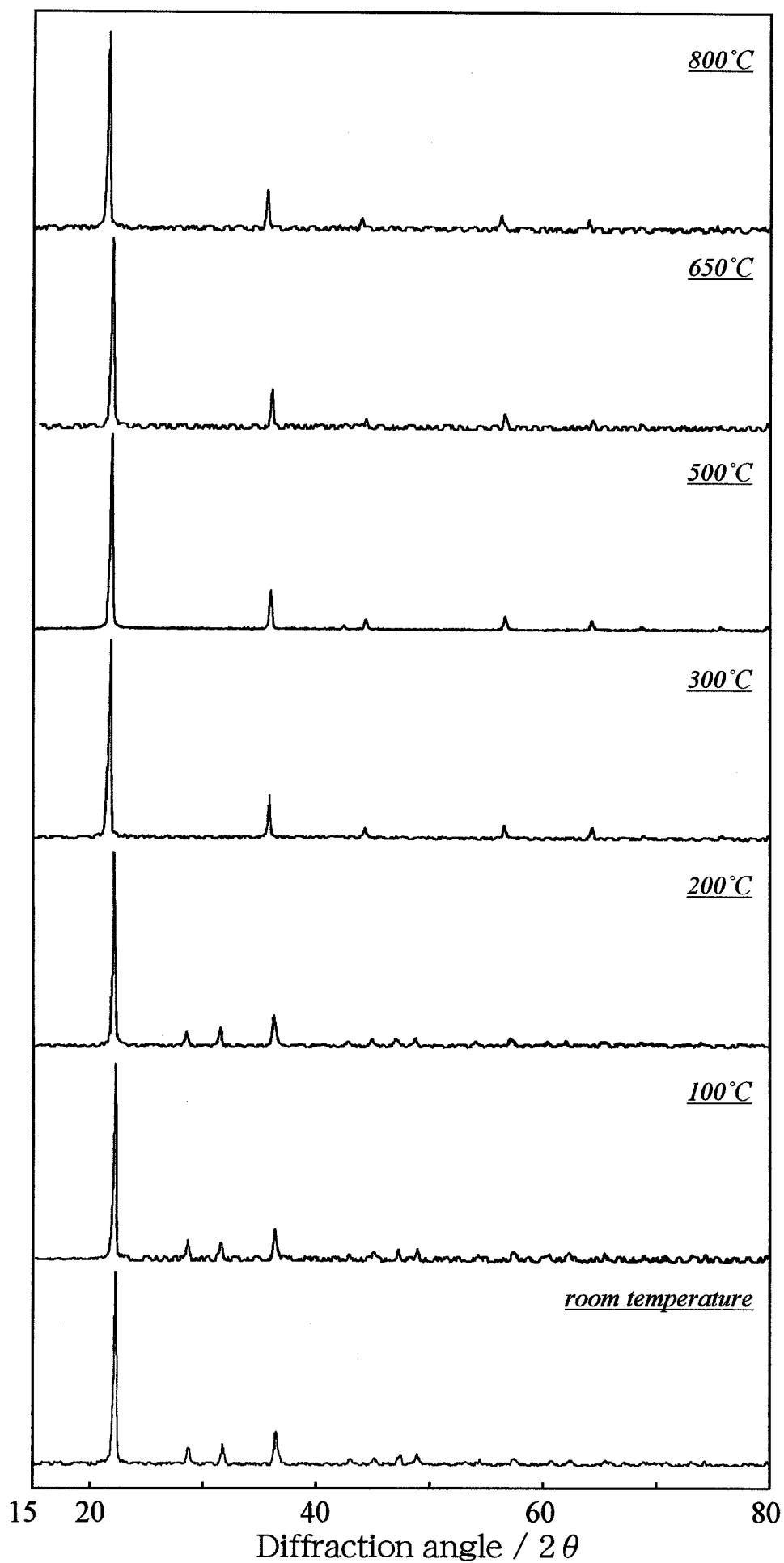


Fig. 3-13 Time-dependant HT-XRD change in cristobalite.

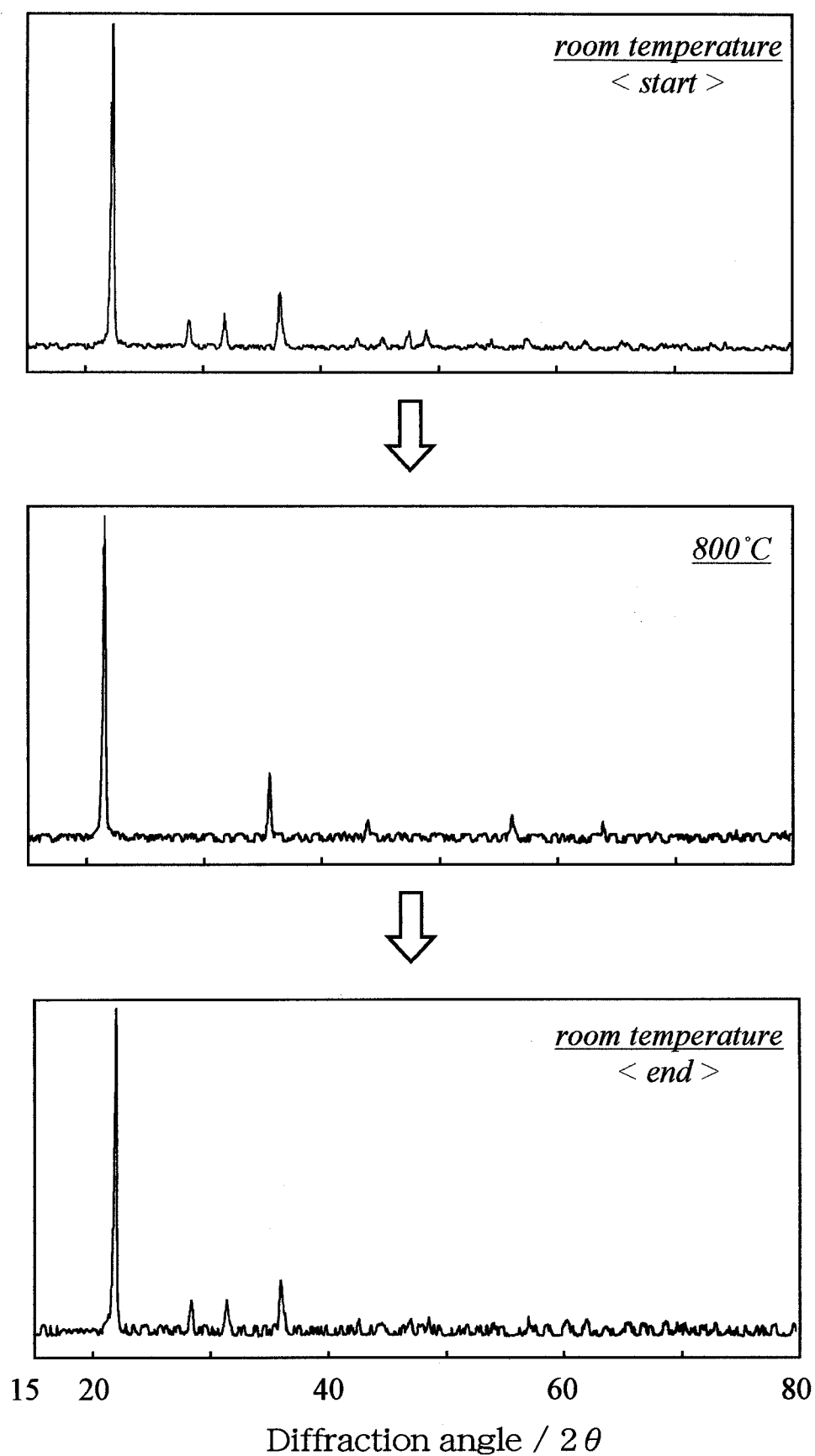


Fig. 3-14 XRD pattern changes for thermal hysteresis in cristobalite.

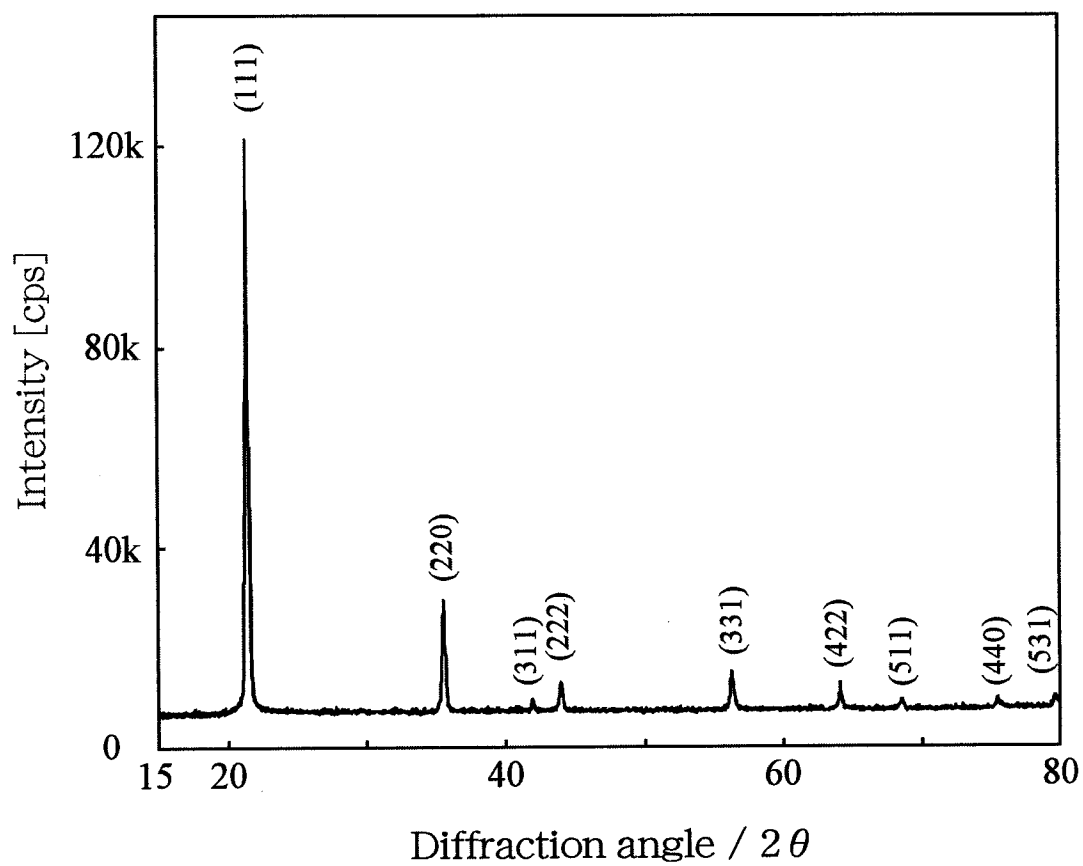


Fig. 3-15 HT-XRD pattern of high-temperature cristobalite at 500°C

Table 3-2 X-ray powder diffraction data for high- and low-cristobalite

High-cristobalite (Barth) [5] [500°C]			High-cristobalite (present work) [500°C]			Low-cristobalite [room temperature]		
<i>d</i>	<i>I</i>	<i>hkl</i>	<i>d</i>	<i>I</i>	<i>hkl</i>	<i>d</i>	<i>I</i>	<i>hkl</i>
4.15	100	111	4.111	100	111	4.040	100	101
						3.136	8	111
2.92	5	211				2.841	9	102
2.53	80	220	2.521	20	220	2.487	13	200
						2.467	4	112
2.17	10	311	2.150	2	311	2.118	2	211
2.07	30	222	2.058	5	222	2.020	2	202
1.99	5	320				1.929	4	113
						1.872	4	212
1.793	5	400						
1.688	5	411						
1.639	60	331	1.636	7	331	1.612	3	301
						1.601	1	213
						1.534	2	311
						1.495	2	302
1.469	50	422	1.456	5	422	1.432	2	312
						1.421	1	204
						1.399	1	223
1.379	20	511	1.373	2	511	1.366	2	214
						1.334	1	105
						1.300	1	313
1.265	30	440	1.262	2	440	1.281	1	322
1.209	30	531	1.206	3	531	1.206	1	410

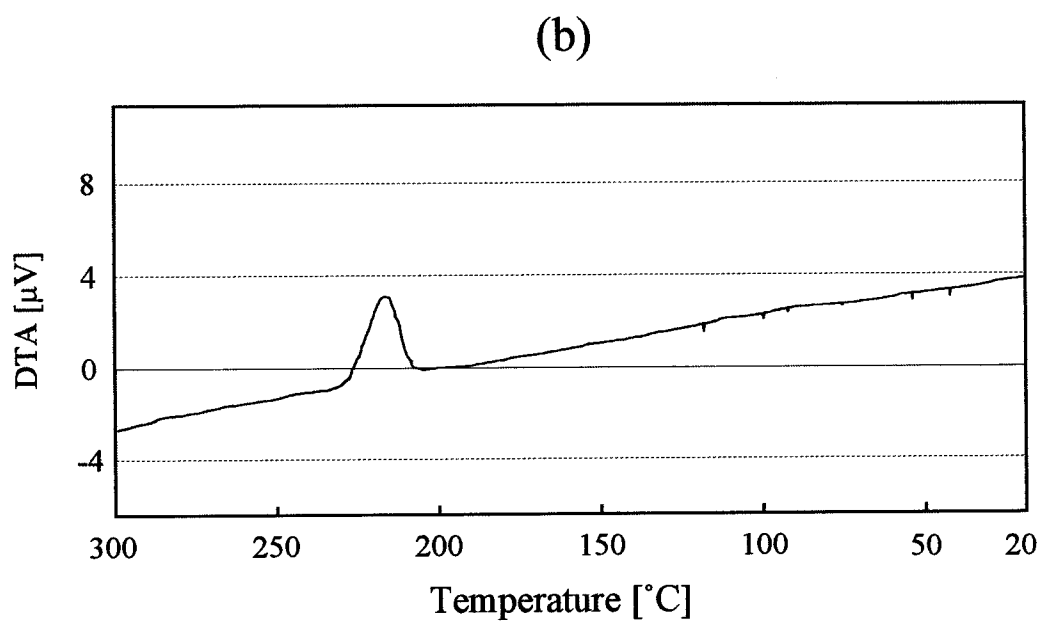
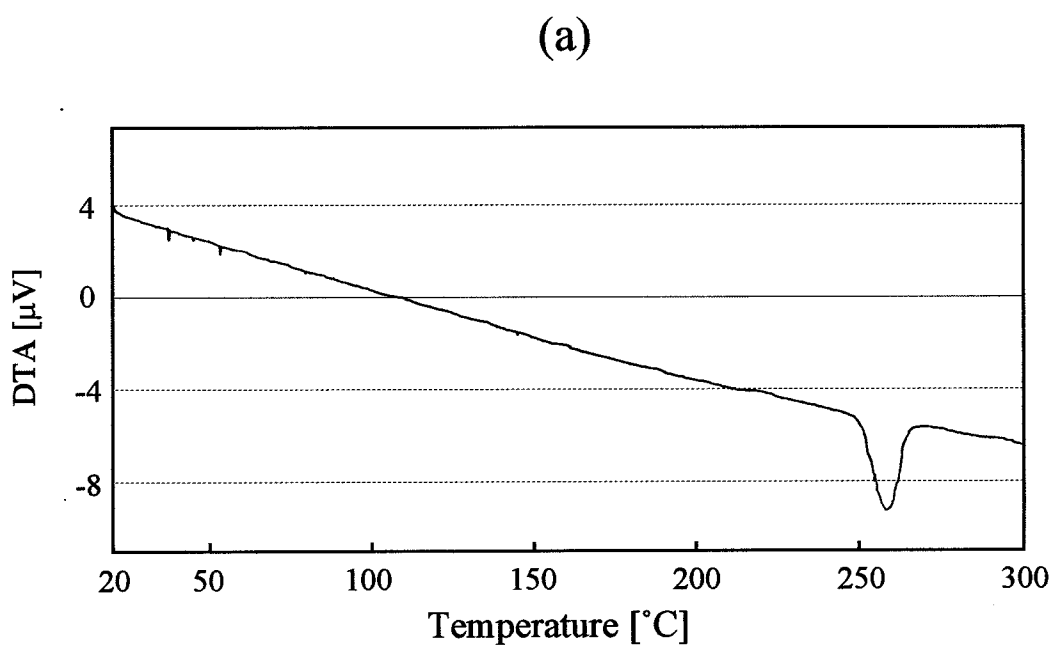
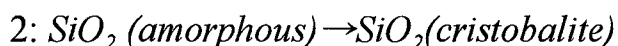
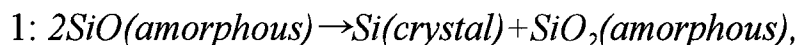


Fig. 3-16 DTA analysis for high-low transeformation in cristobalite.
(a) heating process ; (b) cooling process

3.6 Summary

The disproportionation reaction in SiO was analyzed by XRD, ED, SEM-EPMA and FT-IR. The results revealed that the reaction proceeds in the following two steps;



When the annealing temperature was above 1300°C, both steps proceeded simultaneously. It was generally observed that the FT-IR pattern was changed more gradually than the changes in XRD. The high IR reflection of SiO around 7 μm remained during heat treatments below 1300°C, suggesting a formation of SiO_x glass. Very fine particles of Si crystals were obtained through the above reaction 1. By the reaction 2, cristobalite crystallized in a well-habited form.

When SiO was compressed above 14 GPa, the disproportionation reaction started even at room temperature and at 18 GPa, the crystallized Si, and the unknown crystal phase were obtained. The reaction was thought to be enhanced by the difference in the density between SiO and Si and/or SiO₂. This suggests that SiO becomes unstable at high-pressure conditions.

Cristobalite was obtained in the low-temperature form after the high-low phase transition around 265°C. The space group of the high-temperature phase was decided by HT-XRD to be *Fd3m*. The results suggested that the high-temperature phase has a higher symmetry than the reported ones. It was confirmed by the DTA analysis that the high-low transition belonged to the first order in a very rapid and reversible manner.

The present results imply a low possibility for the existence of solidified SiO under the condition where new stars are forming, because

SiO would become unstable by the disproportionation reaction at high-temperatures. Thus, the most reasonable explanation for the IR absorption around 10 μm from stardusts should be caused by the SiO gas. If the temperature in the space where SiO exists were not so high, SiO will be solidified in an amorphous form.

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Chapter 4

Crystallization of silicon nanocrystals by the disproportionation reaction of silicon monoxide

4.1 Introduction

Fine particles of Si have attracted considerable attention to their strong photoluminescence (PL) and electroluminescence (EL) at room temperature [1-5]. These luminescent properties are strongly related to the size and the surface structure of Si particles [6]. A lot of attempts have been reported for preparation of Si particles such as, gas evaporation [1, 3, 7], magnetron sputtering [2], electrochemical deposition [4], and laser ablation [8, 9]. However, there exist many problems among these techniques: difficulty in particle size control, low deposition rate, low yield of objective particles and needs of highly sophisticated apparatus for preparation. To overcome the problems of size control and low yield, it is essential to understand the growth mechanism of Si particles in gas, liquid or solid media.

The crystallization of Si from its amorphous state is difficult to observe directly; because the crystallization proceeds only by rotation and rearrangement of Si atoms and it needs no nucleus formation process. Thermodynamic analysis of the amorphous-to-crystal process of Si has done by Csepregi *et al* [10]. The results showed that the activation energy of the reaction process is used for addition of the Si-Si bond as well as rearrangement of Si crystals to the diamond structure.

The present work is performed to understand the mechanism of the

disproportionation reaction of amorphous SiO to Si and SiO₂. Although this reaction is so popular as has been described in many textbooks of inorganic chemistry, details of the reaction mechanism and the structures of the products of Si and SiO₂ have remained to be investigated. The reaction proceeds with the following chemical formula; $2\text{SiO} \rightarrow \text{Si} + \text{SiO}_2$, where both the oxidation of Si[II] to Si[IV] and the reduction to Si[0] simultaneously occur on heating. As a result, crystalline Si is expected to be precipitated in a form of fine particles in SiO₂. Furthermore, the reaction regards as a “first order” chemical reaction, so that simple thermal analyses have easily been done.

This chapter describes the thermal and crystal growth analyses in the initial stage of crystallization of Si. As described in Chapter 3, the disproportionation reaction process analysis proposes a simple method for observation of initial state of Si crystallization, which is applicable to preparation of Si nanocrystals. The products were characterized by X-ray and electron microscope analyses.

4.2 Experimental

The degrees of crystallizations of Si and SiO₂ by the disproportionation reaction were estimated by electron diffraction (ED) and X-ray powder diffraction (XRD) studies. The nanoscopic behaviors of the crystallization were inspected by high-resolution transmission electron microscopy (HR-TEM), which has an ability to observe directly the reaction process in an atomic scale.

The specimens for analyses were synthesized by the same way as described in Chapter 3. The heating conditions were 1000°C, 1300°C and 1350°C for 1 hour in Ar gas flowing. The additional three specimens were made by annealing at 900°C for 1, 4 and 10 hours.

In the TEM observations, electron microscopes of JEOL 2000EX and 3010 were used. The ED patterns were first measured, and then the high-resolution micrographs were taken with a direct magnification of 4×10^5 , where the accelerating voltage was set at 300kV.

The averaged particle size was determined by calculating the values of full width at half maximum (FWHM) in the XRD peaks. The amount of the crystallized Si and SiO₂ were roughly estimated from intensities of the XRD peaks in comparison with those of 10 wt% NiO powders added as an internal standard.

4.3 TEM approach for the Si nanocrystals formation

Fig. 4-1 and Fig. 4-2 show results in the ED and XRD analyses of the specimens annealed between 900 and 1350°C for 1 hour.

In the ED patterns, apparent changes were observed with raising the annealing temperature, as shown in Fig. 4-1. The ED spots were obscure at 900°C and clear above 1000°C. The spots were explained by the diffractions of Si crystals having the complete diamond lattice, and the crystallization of Si progressed above 1000°C. It is noted that no diffraction spot without Si was observed. This indicates that the other materials without Si are in an amorphous state. Diffused diffraction spots were observed on the specimens annealed at 900°C, suggesting an incomplete crystallization having imperfect crystal units. Additional ED spots were detected on the specimens annealed at 1350°C. The diffraction analysis revealed that these spots were due to the diffraction of cristobalite, which was crystallized from amorphous SiO₂.

Fig. 4-2 shows changes in the XRD patterns with the annealing conditions. At 900°C, the crystallization of Si was not confirmed in the patterns of the specimens and only a slight increase in the base line intensity was detected around 28°, where the strongest diffraction peak of Si(111) exists. This increase in the base line is equivalent to the ED observation of the incomplete crystallization of Si at 900°C. The result that broad but clear XRD peaks were observed in the specimens annealed at 1000°C indicates a beginning of Si crystallization. The broad peaks mean that the crystals were not easy to grow enough in size at this temperature range. Details of the relationship between XRD peaks and the crystal size will be described below. Above 1300°C, the crystallization proceeded completely and the peaks became quite sharp. A

mixed pattern of Si and cristobalite appeared at 1350°C, corresponding to the ED results in Fig. 4-1.

Fig. 4-3 shows high-resolution electron microimages of the specimens annealed at 1000 and 1300°C for 1 hour. The areas encircled by the white lines are those of crystallized Si where the lattice images of Si (111) are apparent. When the samples were annealed below 1000°C, no obvious crystal images were detected.

The images of the specimens annealed at 1000°C revealed that there are many crystallites whose sizes are 4~5 nm in diameter. The stripes in the nanocrystal particles mean stackings of 10 to 17 layers of Si(111) planes. There are no other lattice images than the Si(111) plane, indicating that other areas than Si are in an amorphous state. From the XRD data, the whole amounts of the crystallized Si were suggested to be over 90 % in weight of the starting SiO. Details of the crystallization mechanism of Si will be described in Section 4-5.

In the 1300°C-annealed samples, relatively large crystallites whose sizes are around 11 nm were found. Sometimes, much larger particles of about 30 nm in diameter were discovered. The feature of crystallization is also shown in the shape of the XRD peaks, as will be presented in the later section.

To analyze the crystallization of Si more precisely, it is easy to measure the structural changes at 900°C because the crystallization rate is expected to be low enough to be investigated. Fig. 4-4 and Fig. 4-5 show changes in the ED photographs and the XRD patterns, respectively, in the samples treated at 900°C for 1, 4 and 10 hours. As shown in Fig. 4-4, the diffraction rings of the specimens kept for 1 hour are broad and weak. However, the patterns became clearer with increasing the soaking time. After 10 hours, the diffraction rings became sharp and able to be analyzed,

although the diffraction pattern is still in a form of rings, which are made of the numerous diffraction spots of many tiny crystals. Thus, it is concluded that the heat treatment at 900°C arranges an insufficient energy for growing Si crystals in the oxide media.

Fig. 4-5 shows the XRD pattern changes with annealing time of 1, 4 and 10 hours at 900°C. Although all the patterns have broad peaks, the intensities became strong with annealing time. However, the growing rate was quite low in comparison with those in the other high-temperature cases.

For the specimen annealed at 1000°C only for 1 hour, weak but clear spots, which are due to diffractions of many tiny finely dispersed Si particles, became apparent. The diffraction was much sharper in comparison with that of the specimen annealed at 900°C for 10 hours. The crystallization rates at 900°C have not been exactly decided yet, but the amount of Si was estimated to be below 50 % in weight even after the 10 hours.

Fig. 4-6 shows high-resolution electron microimages of the specimens annealed at 900°C for 4 and 10 hours. These photographs revealed that there existed small particles with clear lattice images, indicating an initial stage of crystallization. In the former specimen, a few ordered patterns were observed, whereas many particles existed in the latter. When the annealing time was below 4 hours, no ordered pattern was observed.

In these images, the size of the smallest particles was found to be about 1.3 nm in diameter with four stripes of the stacked lattice. The stacking distance approximately equals to that of four Si(111) layers. Consequently, the unit of such a particle consists of the stacking for four Si(111) layers. In a few cases, images having smaller units were observed on these photographs. However, it is difficult from the ED

images to distinguish exactly whether they are in an initial state of crystallization or not. The major particle size is about 3.6 nm, which means a stacking of nearly twelve Si(111) layers.

The microimages in the annealed specimens at 900°C for 10 hours showed that the mean size of the Si particles was 5 nm, which was apparently larger than those for 4 hours. However, the amorphous areas around the particles still remained widely, suggesting an incomplete crystallization of Si after 10 hours.

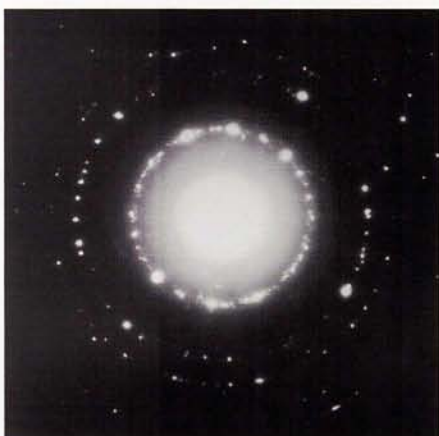
(a)



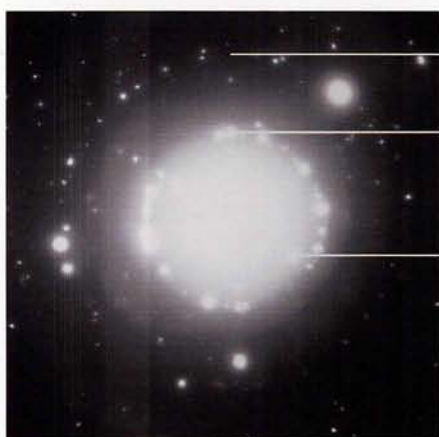
(b)



(c)



(d)



Si(220)

Si(111)

Cristobalite(101)

Fig. 4-1 Electron diffraction pattern change on heating SiO.
Cricle patterns are results from crystallized Si.
(a) 900°C (b) 1000°C (c) 1300°C (d) 1350°C

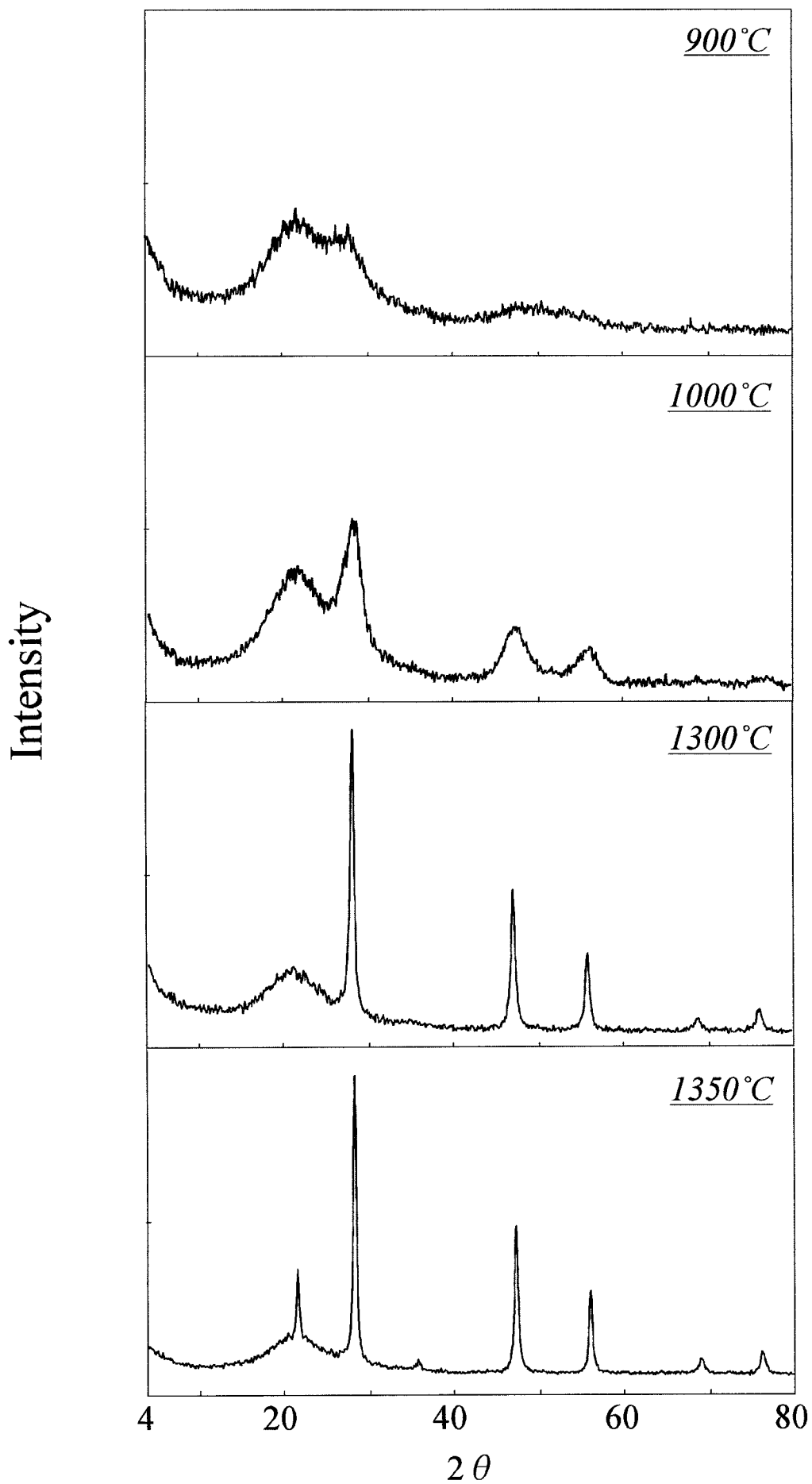


Fig. 4-2 XRD patterns annealed at 900, 1000, 1300 and 1350°C for 1 hour.

(a)



Fig. 4-3 (a) Electron microimage of the SiO specimen annealed at 1000°C for 1 hour.

(b)

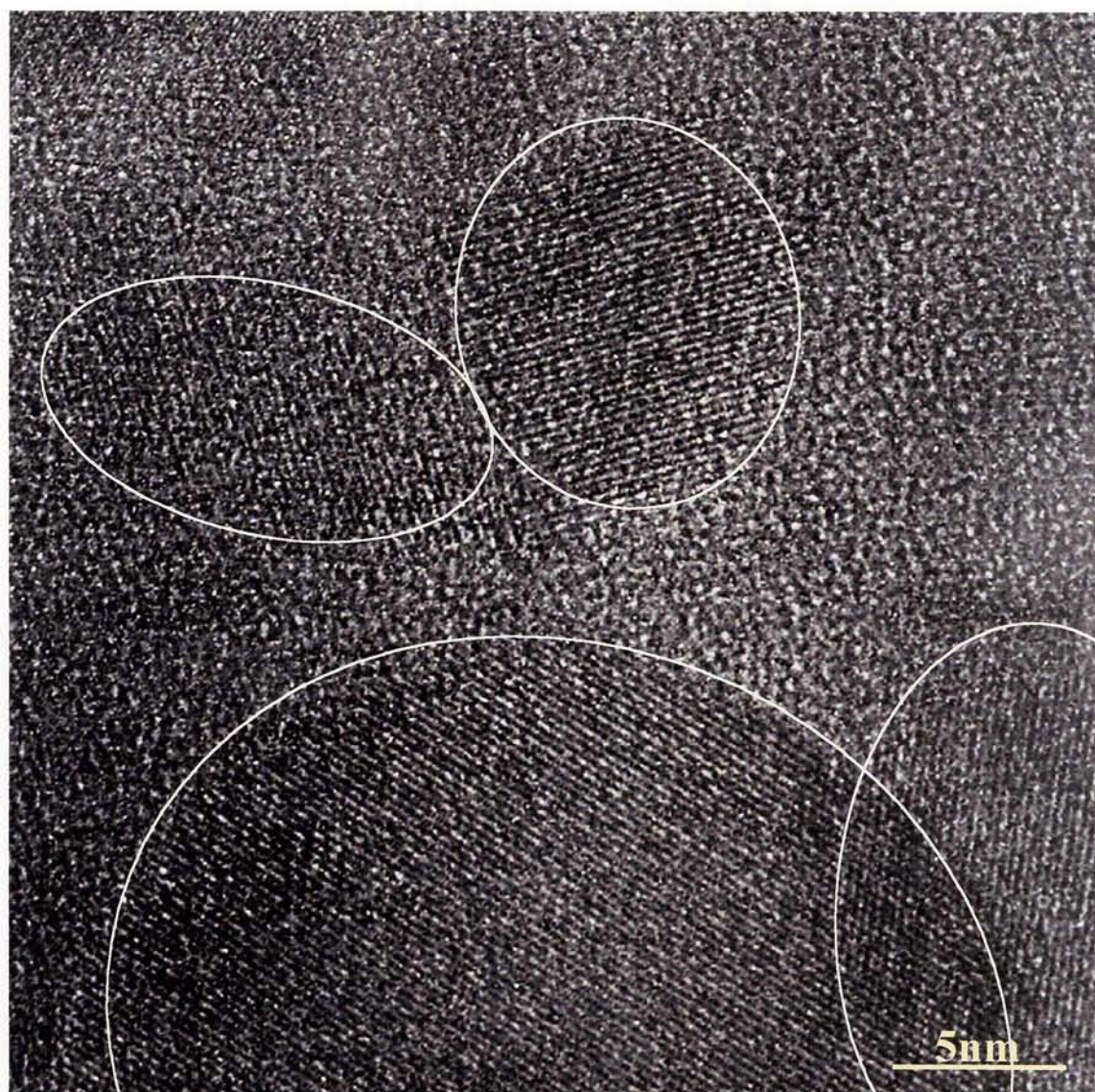
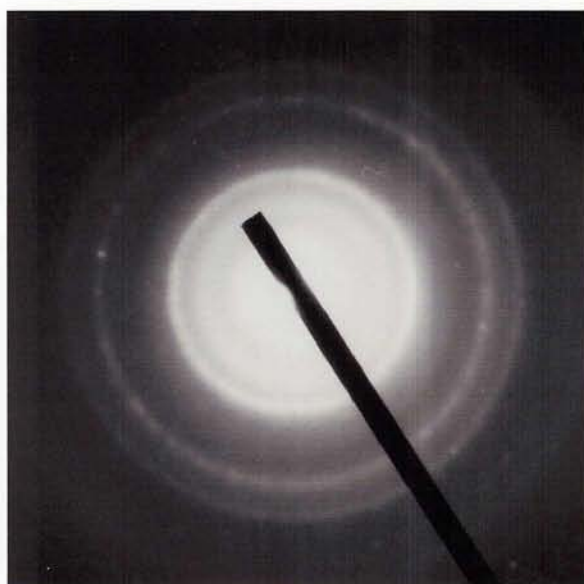


Fig. 4-3 (b) Electron microimage of the SiO specimen annealed at 1300°C for 1 hour.

(a)



(b)



(c)

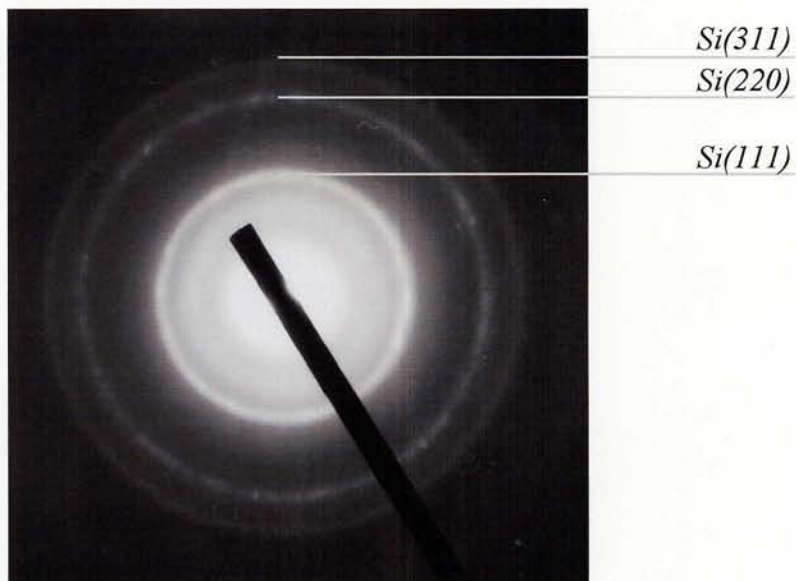


Fig. 4-4 Time-dependance in electron diffraction pattern at 900°C.
(a) 1 hour (b) 4 hours (c) 10 hours

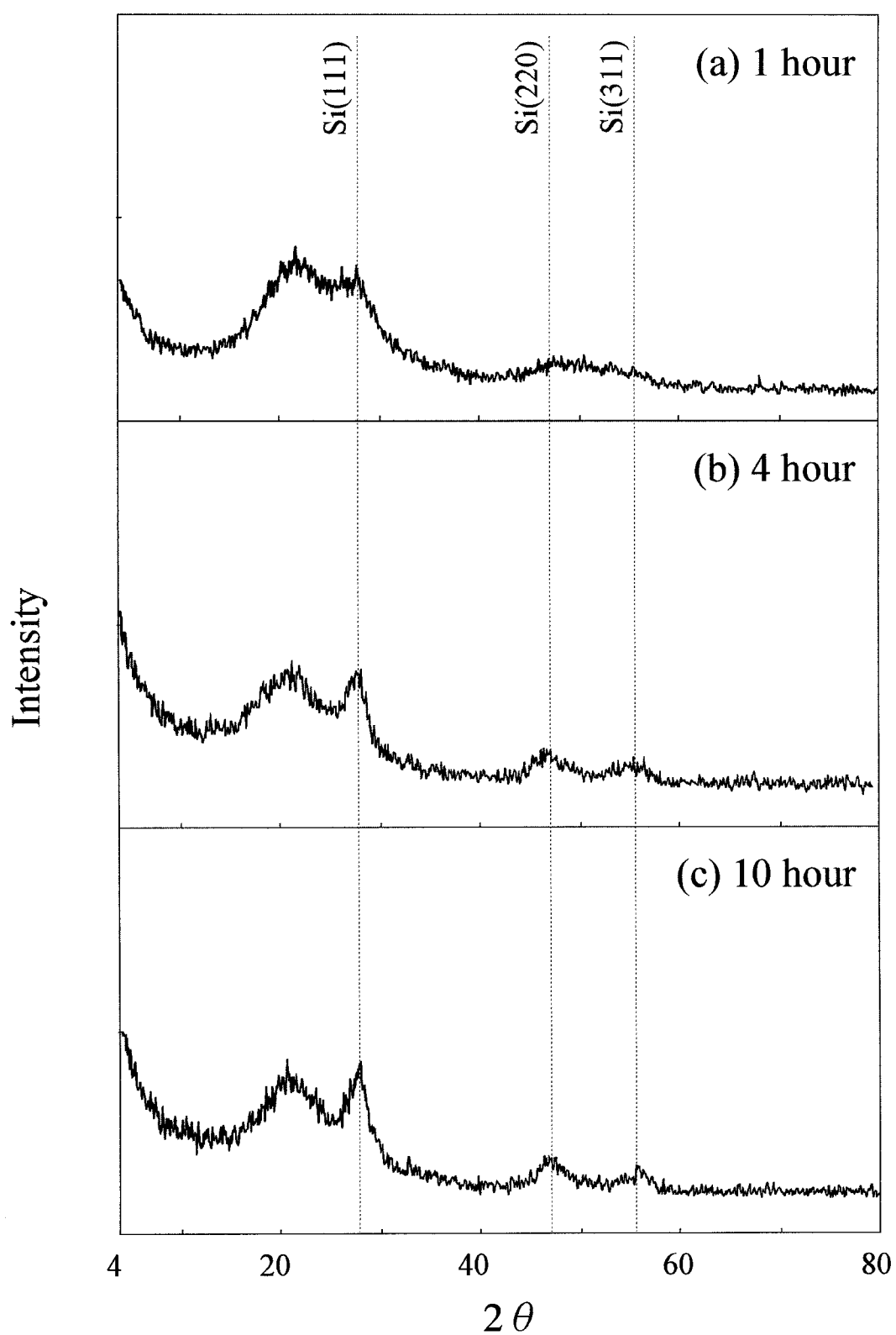
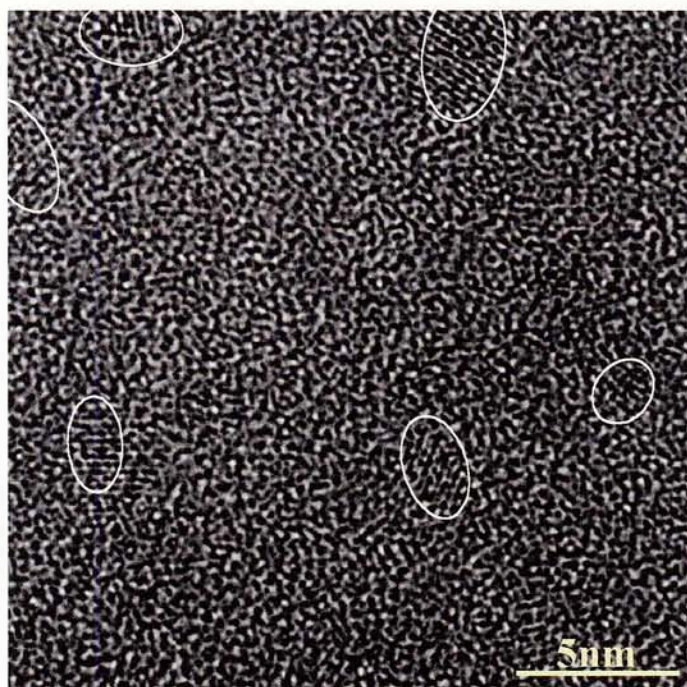


Fig. 4-5 XRD pattens of SiO on heating at 900°C for 1, 4 and 10 hours.

(a)



(b)

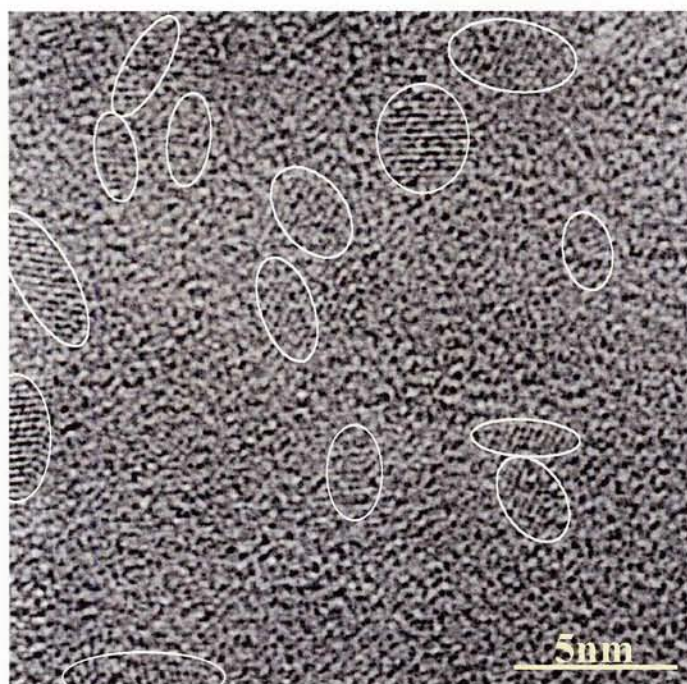


Fig. 4-6 Electron microimages on the SiO specimen annealed at 900°C.
(a) 4 hours (b) 10 hours

4.4 Changes in particle size of Si

The averaged particle size of the crystallized Si was calculated using the data of full width at half maximum (FWHM) of the XRD peaks. There are three ways to determine the FWHM values using 1) the second order differential curve in XRD peak profiles, 2) the width of XRD peaks, or 3) the area of peaks. In the present work, the third way was adopted because it was believed to be the most adequate method for analyzing the present peaks, which were apparently very broad and wide. Here, the FWHM value was estimated from the parallelogram area, which equals to the integrated peak area, as shown in Fig. 4-7.

Systematic decreases in the FWHM values of precipitated Si were observed on annealing the specimens, as shown in Fig. 4-8. The (111) peak was used for the determination because it is the strongest one in the XRD pattern of Si. It should be noted that the changes at each temperature were almost finished before 1 hour and different heating temperatures induced different saturated values of FWHM. When the sample was kept for more than 10 hours at a target temperature above 1000°C, the peak intensity was slightly reduced from the maximum observed around 4 hours. This decrease may be explained by the oxidation of precipitated Si to SiO₂ with remaining oxygen in Ar. To avoid the problem, the analyses were performed in a short time within 4 hours.

There have been two simple models for the relationship between a crystal size and an X-ray diffraction intensity proposed by Scherrer [11] and Bragg [12], where they assumed that each specimen was made of aggregated of cubic crystals. In these theories, the FWHM values are related to the approximated differential equations in which variables are

functions of a crystal size. The difference between the Scherrer's and the Bragg's treatments are only in methods to make approximation in their differential equations. The calculated results using these equations almost agree with each other in a difference less than 5%. In this work, the Bragg's equation was adopted because it is theoretically better for fitting the Laue's diffraction function than the Scherrer's one in approximation.

The Bragg's equation is described in the following formula;

$$B = \frac{0.89\lambda}{D \cos \theta} + b,$$

where B is the FWHM value, λ is the X-ray wavelength, D is the edge length of cubic crystals, θ is the diffraction angle, and b is the apparatus constant. In this work, the X-ray CuK α radiation of $\lambda=0.154\text{nm}$ was used. It was supposed from the preliminary study that the term b was negligible in calculation. The effect of b will be explained in the later paragraph.

When a sample was kept above 1350°C , the changes were finished within a few minutes and growth of cristobalite crystals became significant, as already described precisely in Section 3-3. Consequently, the FWHM data were changed very rapidly and affected by the crystallization of cristobalite. On the other hand, the XRD peaks appearing in the specimens annealed below 900°C were so broad that it was difficult to measure the exact FWHM values. Thus, the temperature range between 1000 and 1300°C was adopted in this analysis.

To estimate the effect of the apparatus constant b , the particle sizes were compared with the results of TEM observations in Fig. 4-3, in which the sizes were determined by measuring directly the diameter of lattice images in the photographs. In the specimens annealed at 1300°C for 1 hour, for example, the average size of Si was estimated from XRD to be

13.6 nm. The observed Si sizes in TEM were about 11 nm. The specimens annealed at 1000°C for 1 hour represented the average size to be 3.67 and 4 nm in XRD and TEM, respectively. These values suggest that errors from the apparatus constant b are not so large and would possibly be neglected in rough estimation.

The size changes of Si particles with annealing temperature are shown in Fig. 4-9, where all the changes were almost finished within 1 hour, and fine crystallite sizes were dependent on the annealing temperatures. From the obtained curves, the relationships between the growth rate of the fine Si crystals and temperature were induced. Fig. 4-10 shows the maximum particle size for each annealing temperature. As the present disproportionation reaction is considered to be regarded as a simple decomposition reaction, the changes should be expressed by the first order reaction formula, which would have a capability to imply the limiting size of the particles. Details of the formula will be described in the next chapter.

The results in the figure evidently follow a simple relation between the size and temperature, though the data are thought to involve some unexpected errors. Therefore, it can be proposed from these data that the present technique provide a new simple method for synthesizing fine Si particles with desired size. Recently, fine Si particles are interested in the remarkable properties of photo- or electroluminescence at room temperature. Recent studies of this field have been done on thin film specimens synthesized by vacuum evaporation using sophisticated apparatuses and techniques. Furukawa *et al.*[1] synthesized the specimens by a planar magnetron rf sputtering technique. They succeeded to prepare small crystalline particles of hydrated Si, which showed a visible photoluminescence at room temperature. However, the particle size was

varied from 2 to 5 nm. Yoshida *et al.* [11] also tried a pulsed laser ablation (PLA) technique.

As pointed out earlier, the above-sited experiments require some special apparatus or techniques for preparation of films. In addition, it is hard to control the particle sizes of Si crystals precisely. The present technique has an ability to prepare fine particles of crystallized Si with desired size under control of the annealing temperature and time.

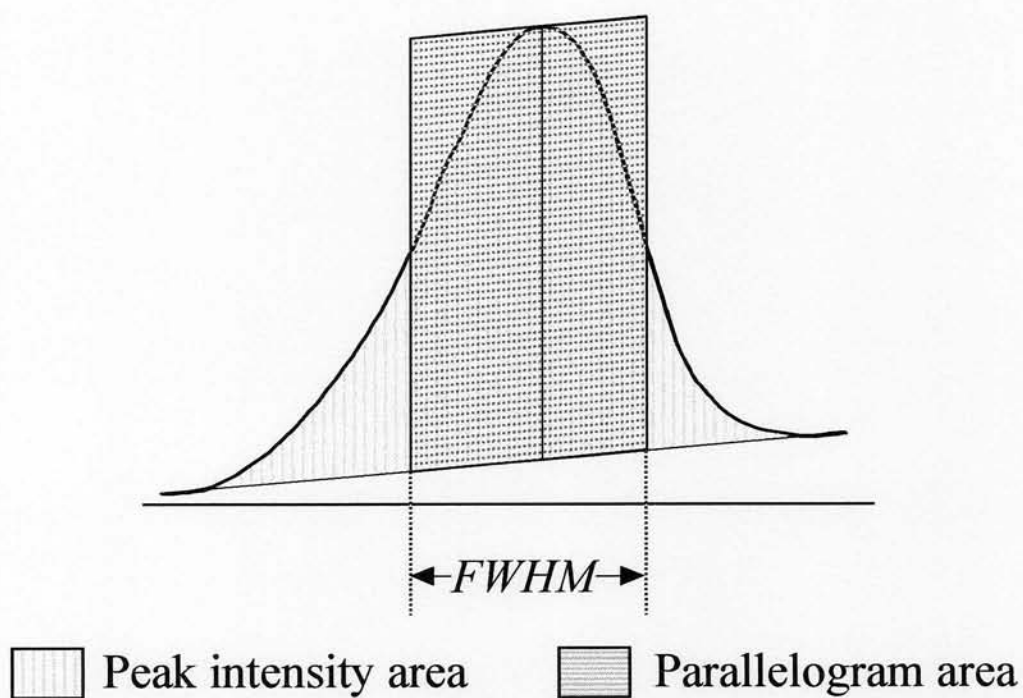


Fig. 4-7 A schematic model for the determination of FWHM, where the parallelogram area equals to the peak intensity area.

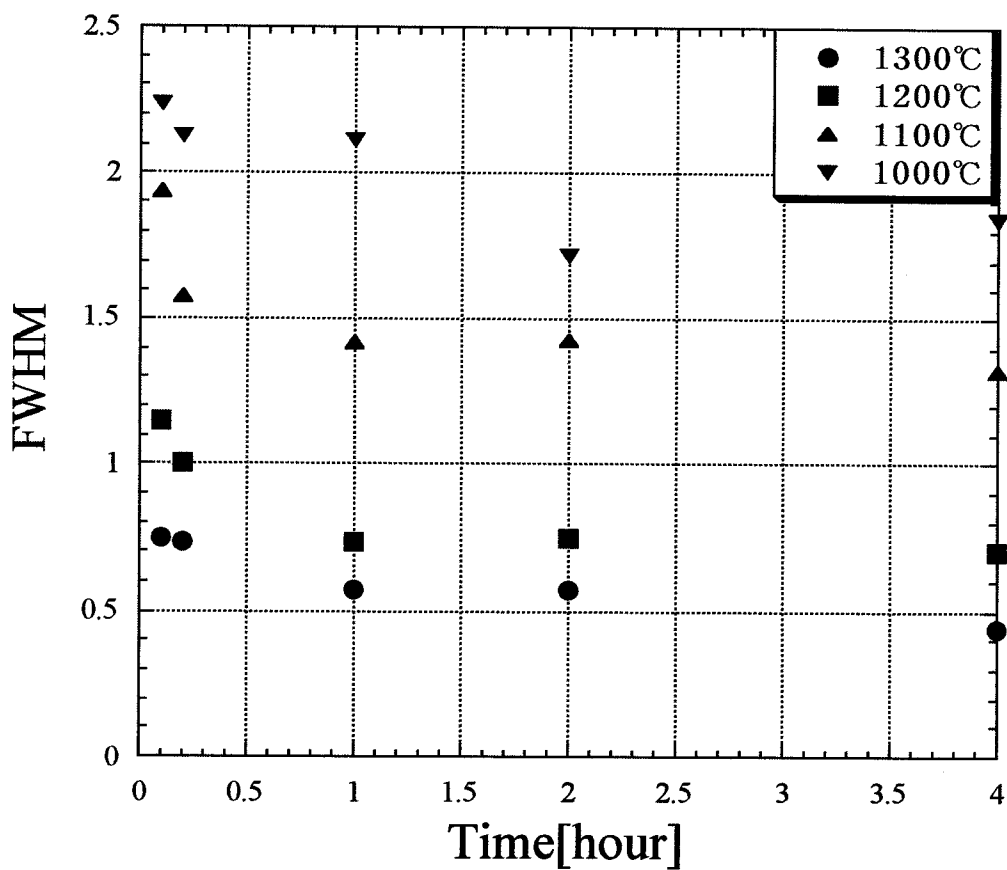


Fig. 4-8 Changing FWHM values of the Si(111) peak with time at differnt temperatures.

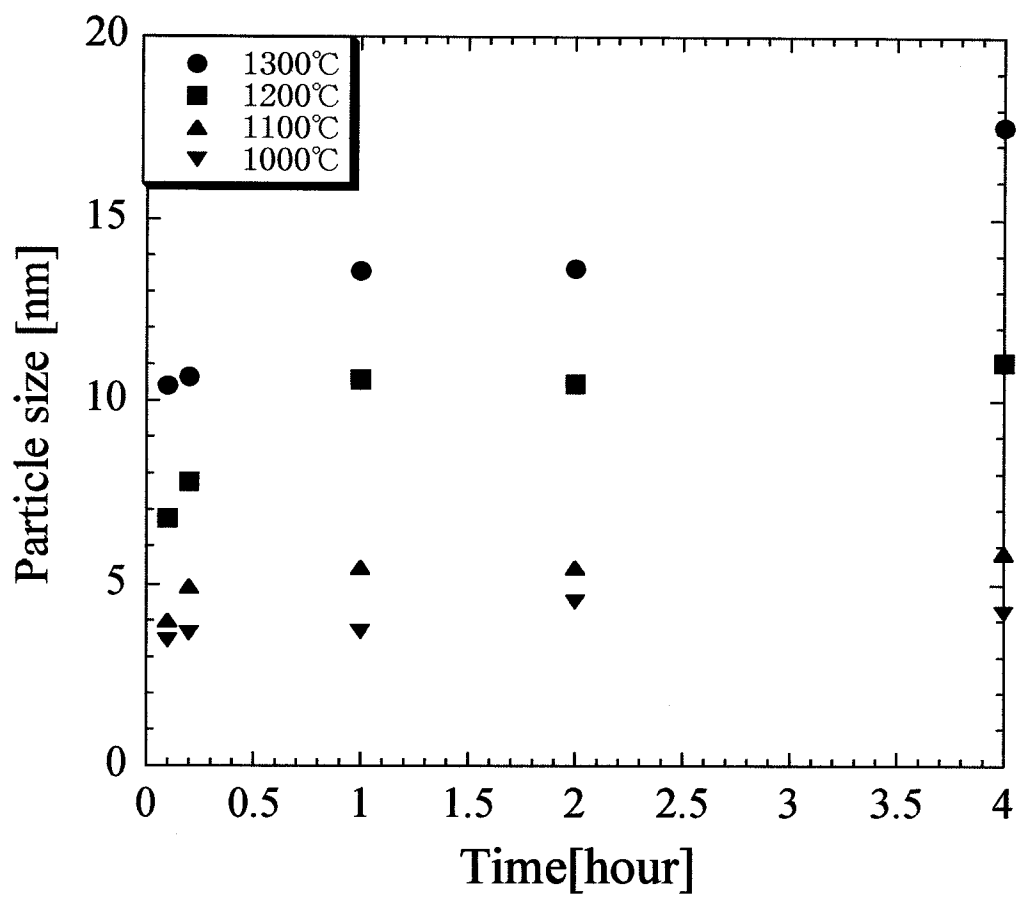


Fig. 4-9 Size changes in Si particles as a function of annealing time at different temperatures.

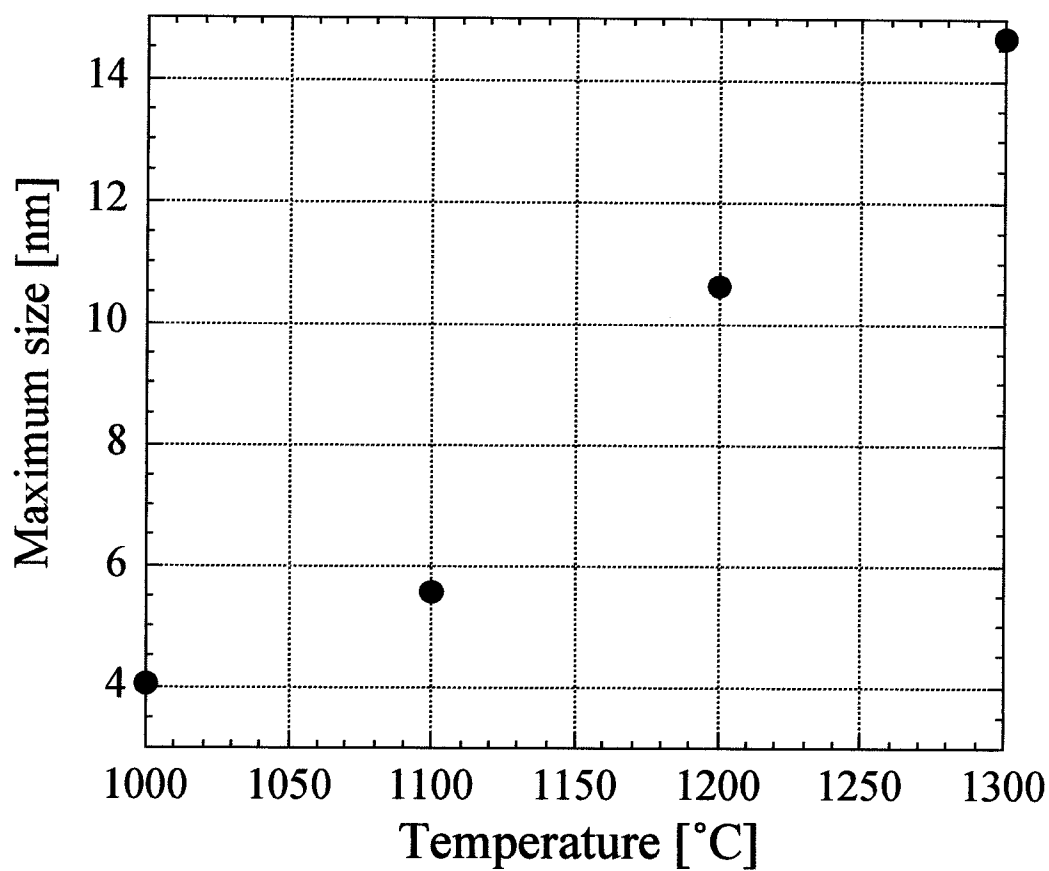


Fig. 4-10 Maximum sizes of silicon nanocrystales at each annealling temperature.

4.5 Amount of Si nanocrystals estimated from integrated intensities of XRD peaks

The whole amount of Si crystallized from SiO was estimated by measuring the integrated intensity of the XRD peak. To lower experimental errors in measuring the relative intensity values, all powdered samples were mixed with 10 wt% of NiO as an internal standard. The integrated intensities were obtained from the peak ratio of Si(111) to NiO(200).

Fig. 4-11 typically shows the data measured on the sample heated at 1100°C for 1 hour, where the horizontally striped area marked by “A” and the dotted area marked by “B” were used as the integrated intensities of Si(111) and NiO(200) peaks, respectively. After reducing the background, the net areas were determined. The result is that the net values for A and B are 33574 and 8349, respectively, and the ratio is 4.02₁. This treatment was applied for determination of the whole intensity ratios.

Fig. 4-12 is a plot of the intensity ratio to the heating time at temperature between 1300 and 900°C, showing that the changes became apparent in the specimens annealed only for 0.1 hour above 1000°C. This suggests that the disproportionation reaction started immediately after heating above 1000°C.

In the case at 900°C, the change showed a different behavior. The crystallization was thought to proceed not significantly for the peaks were very broad and weak. Consequently, it was hard to determine the peak integrated intensities in the specimen annealed even for 1 hour. Furthermore, the crystallization was not finished in annealing for 10 hours. From these reasons, the data at 900°C are omitted in the present analyses.

In all cases except 900°C, the XRD peak changes were finished within

2 hours, and the intensities converged to saturate values. They are almost identical with changing the heating temperatures, suggesting that the yield of Si is approximately the same.

By comparing Fig. 4-10 with Fig. 4-12, the Si nanocrystals are grown in different saturated sizes with the annealing temperature. It is suggested that the crystal sizes are difficult to enlarge them beyond such a limit within several hours. As the total yields of crystals are not different, almost all the starting specimens of SiO were reacted and turned into the crystallized Si and amorphous SiO₂. That is, the reaction yield is high and the products involve a good deal of the Si nanocrystals. At higher temperatures, the sizes become much larger, whereas the whole amounts of Si remain unchanged.

To grow Si crystallites in the disproportionation reaction of SiO, the growth unit of Si needs to diffuse through the remained SiO₂-rich amorphous oxide media. As the crystallization proceed under the mechanism of nucleation and growth, the diffusion unit for the growth is a Si atom, or aggregates of several Si atoms. The diffusion energy may increase with an increase of the size of growth unit. For this reason, the observed nanocrystals should be the maximum size of grown crystals at each temperature. Low heating temperatures even below 1000°C will provide enough energy to move the growth unit through the amorphous media. Detail of the energy for crystallizing Si will be described in the next section.

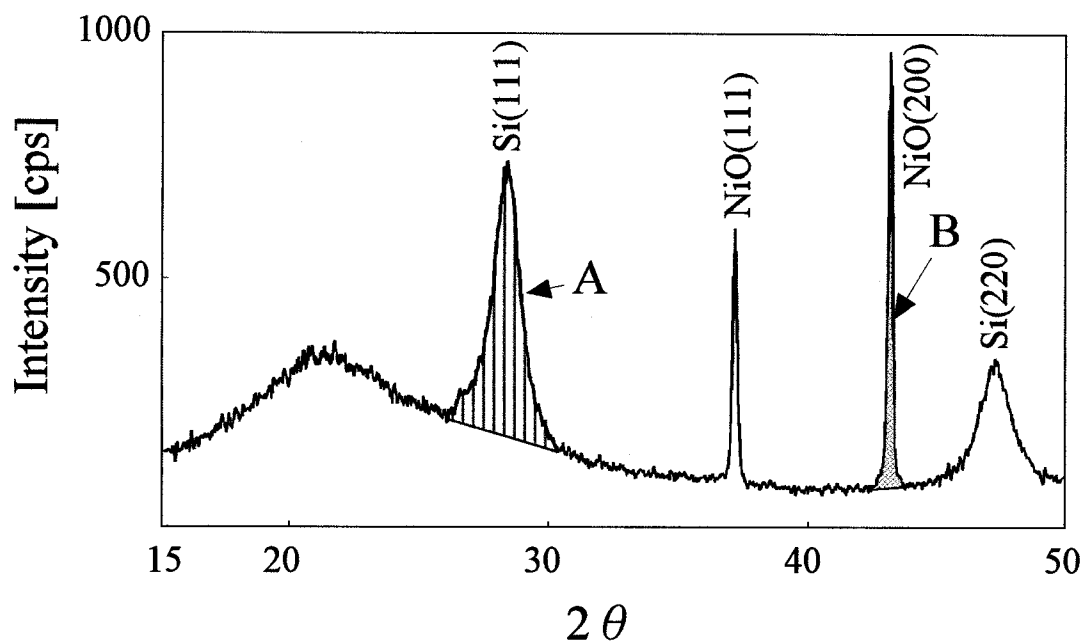


Fig. 4-11 XRD pattern of SiO annealed at 1100°C for 1 hour with an addition of NiO as an internal standard.

Areas "A" and "B" correspond to the intensities of produced Si(111) and NiO(200), respectively.

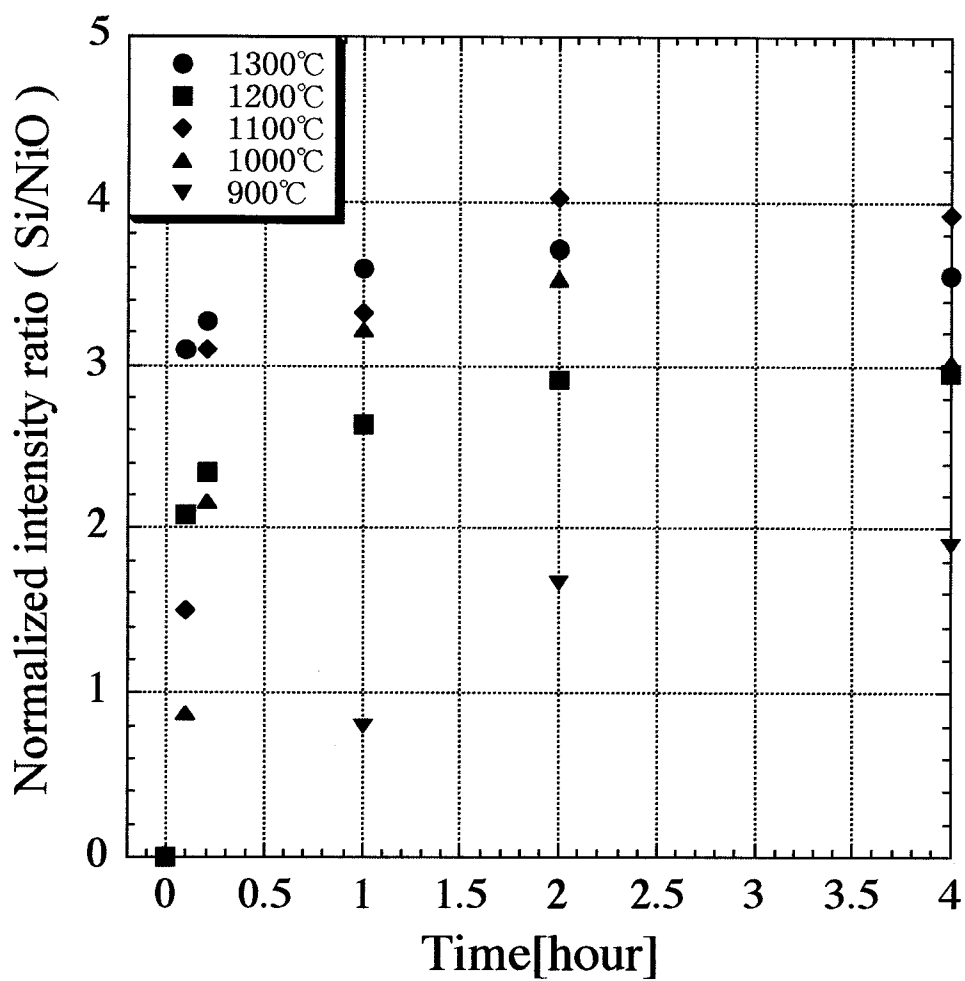
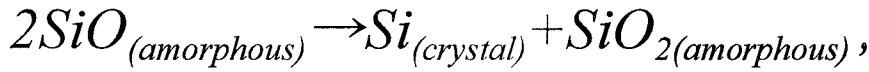


Fig. 4-12 Normalized area intensities as a function of annealing time at each temperature.

4.6 Arrhenius plot on the Si crystallization

The time dependence of the amounts of crystallized Si with various annealing temperature has been described in Section 4-5. Using these data, the Si crystallization can be analyzed more precisely. From the results of the reaction process analysis in Chapter 3, the disproportionation reaction proceeded under the following chemical formula between 900 and 1300°C;



which regards as the first order decomposition reaction of SiO to Si and SiO₂. The relationship between the reaction velocity and the peak area of the XRD profile is expressed as the formula:

$$\left(I/I_{max} \right) = 1 - \exp(-kt),$$

where I is the XRD intensity, I_{max} is the maximum value of I , k is the velocity constant and t is the reaction time.

Fig. 4-13 shows the velocity curves using the data presented in Fig. 4-12, where the parabolic curves between I/I_{max} and t having maximum values are drawn. Such a limiting behavior in I/I_{max} indicates that the reaction is finished in this period. The curve of the specimen annealed at 900°C is quite different from others in the figure, suggesting an insufficient thermal energy for the progress of the disproportionation reaction.

It should be noted that the curves have the different maximum values of I/I_{max} . If the reaction finishes completely by heating, the maximum values are considered to be identical with each other. In the present experiments, however, the data may contain some unexpected errors from such as unavoidable oxidation by intermigrated oxygen in the flowing gas

and consequently, the maximum values may be scattered.

The logarithms of k were plotted against inverse temperature T^{-1} , as shown in Fig.4-14. To determine the degree of accuracy, the systematic errors in the calculated values of k , represented by the vertical bars in the figure, were estimated from the standard deviation. The activation energy was obtained by the Arrhenius formula,

$$k = A \exp(-E^*/RT),$$

that is,

$$\log k = \log A - \frac{E^*}{R} \cdot \frac{1}{T},$$

where A is the proportional constant, E^* is the activity energy and R is the gas constant.

The value of E^* was calculated between 1000 and 1300°C by the following empirical formula,

$$\log k = 9.190 - 9884.7 \times \frac{1}{T}.$$

By fitting the present results by the least squares method, E^* was estimated to be 82.2 kJ·mol⁻¹. This value corresponds to the crystallization energy of Si in the present oxide media.

It is apparent in the figure that the value of k at 900°C is much lower in the $\log k-T^{-1}$ line obtained between 1000 and 1300°C. This should be explained by insufficient thermal energy for crystallization of Si at 900°C, and fine Si particles having several unit cell dimensions may stably be dispersed in the amorphous oxide media. Such a situation becomes unstable above 1000°C.

The obtained E^* value is compared with the diffusion energies of Si and

O in α -quartz or forsterite, which are listed in Table 4-1 [14-18]. The listed values are considerably smaller than those in common metals, whereas the present result shows much smaller value. The low crystallization energy has been reported in a case of the amorphous-to-crystalline change of Si to be $22.2 \text{ kJ}\cdot\text{mol}^{-1}$ [10], where only a rearrangement of irregular Si-Si bondings to the regular ones of Si crystals takes place, and no migration of Si atoms occurs. Thus, such a low value would correspond only to the rearrangement energy of the Si-Si bonding and the strain energy from the irregular bondings in the amorphous state should be reduced by the crystallization. The obtained E^* value implies that this reaction proceeds through an intermediate process between the diffusion and rearrangement of Si atoms.

Because the density of Si particles is not enough in the present specimens, the properties of photo- or electroluminescence, which have been observed on fine Si particles by many investigators, have not been determined yet.

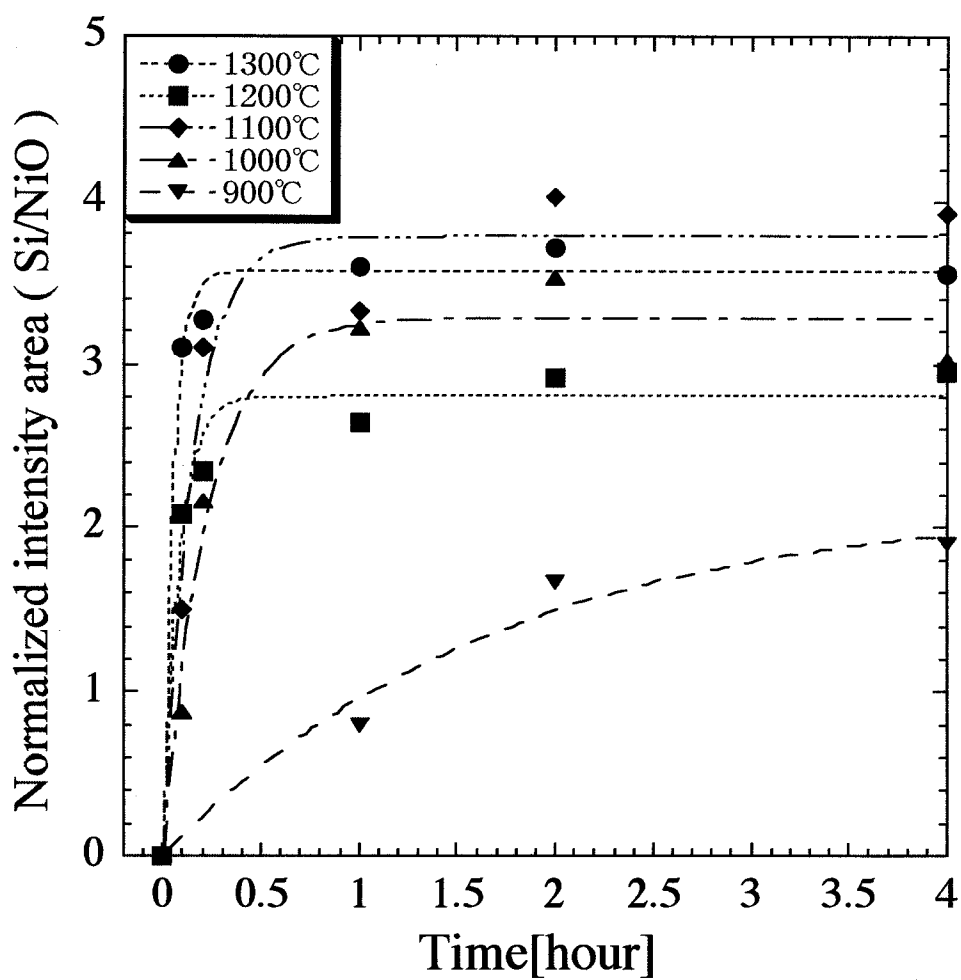


Fig. 4-13 XRD intensities of Si(111) as a function of annealing time at different temperatures.

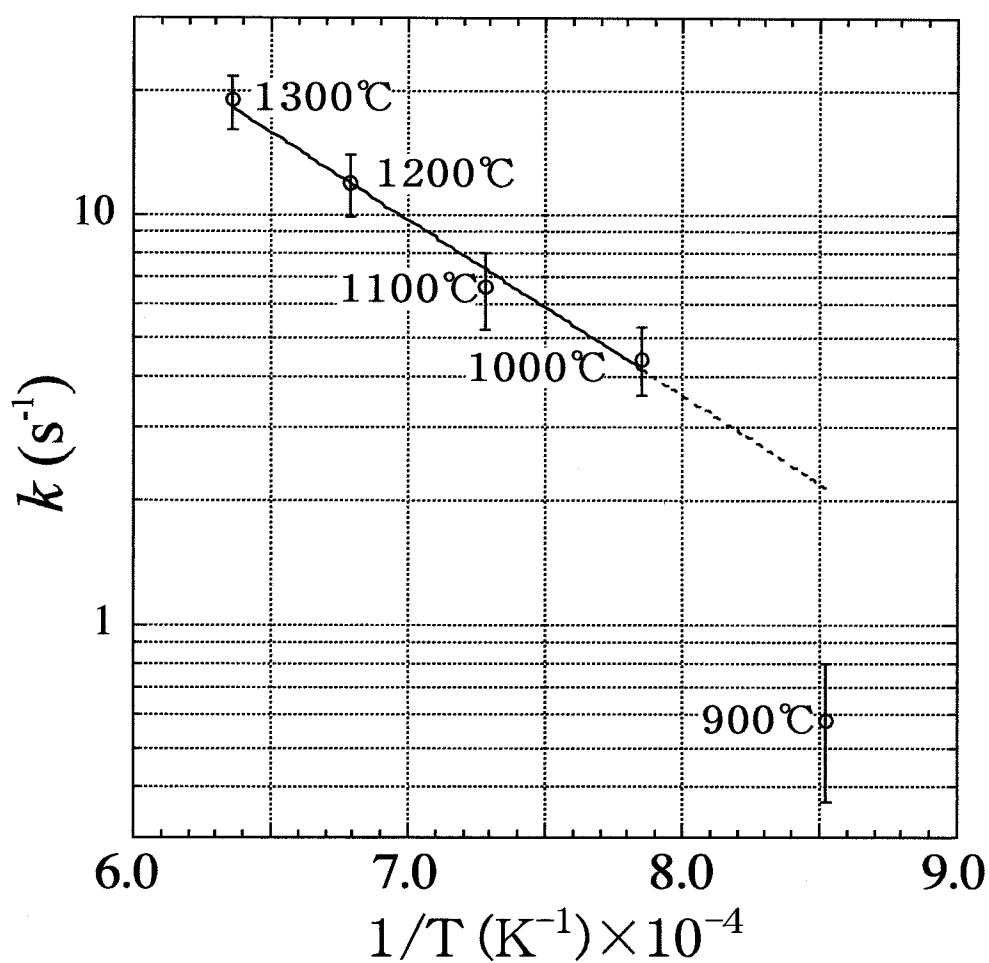


Fig. 4-14 Arrhenius plot between the velocity constant k and absolute temperature T .

Table 4-1. Volume self-diffusion coefficients in β -quartz and forsterite.

Solid	Ion	Q[kJ mol ⁻¹]	T [°C]	
β -Quartz	O	195	870-1180	[15]
β -Quartz	Si	230	910-1030	[16]
Mg ₂ SiO ₄	O	475	1000-1510	[17]
Mg ₂ SiO ₄	Si	377	1325-1725	[18]

4.7 Summary

This chapter described a new simple method for synthesis of Si nanocrystals as well as the thermochemical analysis of the crystallization. The Si nanocrystals were synthesized by the disproportionation reaction of amorphous SiO to Si and SiO₂. According to the results of the reaction process analysis, which has been also described in Chapter 3, the reaction first proceeds from the amorphous SiO to Si crystals together with deposition of amorphous SiO₂, when the annealing temperatures were below 1300°C.

The Si nanocrystals were grown into the limited sizes at each annealing temperature. From the analytical results of the FWHM values in the XRD peaks, the limited sizes increased with raising the annealing temperature; and the limited average sizes were estimated to be 4 and 15.3 nm at 1000 and 1300°C, respectively. When the annealing temperature was at 900°C, the XRD peak was so weak and broad that the crystal size was not estimated exactly.

The crystallization was directly observed by the TEM images. When the specimen was annealed at 1000°C for 1 hour, the striped areas with the diameters of about 4 or 5 nm were observed. The stripes were confirmed as lattice images for stacked layers of the Si(111) plane. The numbers of the Si(111) plane were roughly estimated for 15 and 35 layers in the specimen annealed at 1000 and 1300°C, respectively.

When the specimens were annealed at 900°C, the crystallization proceeded quite slowly, although the condition was favorable to observe the initial state of the crystallization by TEM. When the specimen was kept for 4 hours, fine Si particles with the diameters of about 2 nm were observed. The value means that the particles consisted of only the 7

stacked layers of the Si(111) plane. This size is minimum in the present TEM observations.

The thermochemical analysis of this crystallization was carried out along the “first order” reaction process. From the results, the activation energy was estimated to be $E^*=82.2\text{kJ}\cdot\text{mol}^{-1}$. This value is larger than the rearrangement energy of Si-Si bonding in an amorphous state but much smaller than normal diffusion energies. That is, this reaction is suggested to proceed on an intermediate process between diffusion and rearrangement of Si atoms.

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Chapter 5

Conclusion

Physical, structural and chemical properties of solid SiO were first investigated. The XRD patterns showed no obvious diffraction peaks and a halo pattern around $2\theta \sim 22^\circ$ in CuK α radiation. The TG results showed that the Si/O ratio was almost unity. SiO only exists as amorphous structure and never changes the structure and composition after leaving it in air at room temperature for several months. The IR results showed no clear absorption except ~ 10 and $20 \mu\text{m}$, which correspond to monomolecular motions of covalent bondings between Si and O. SiO showed a high infrared reflection around $7 \mu\text{m}$, which was attributed to a polarization of SiO molecules. The magnetic analysis showed that SiO is diamagnetic and has no magnetic species on free electrons. The molecular structure of SiO is decided to be similar to that of carbon monoxide.

By heating SiO above 800°C in an oxygen free condition, its decomposition to Si and SiO $_2$ occurs. The decomposition reaction, named the disproportionation reaction, progresses in the following 2 steps;

1. $2\text{SiO}(\text{amorphous}) \rightarrow \text{Si}(\text{crystal}) + \text{SiO}_2(\text{amorphous})$
2. $\text{SiO}_2(\text{amorphous}) \rightarrow \text{SiO}_2(\text{crystal})$.

The XRD analyses revealed that the amorphous SiO $_2$ crystallized into the cristobalite form by annealing above 1350°C . This means that the both reactions 1 and 2 proceeded simultaneously at this temperature. The difference in 1 and 2 is brought about by the difference in the crystallization rate between Si and cristobalite. The deposition of Si

proceeded in forming a good deal of nano-scale crystals and no enlargement by crystal growth was observed. A small amount of cristobalite crystallized with high crystallinity. That is, the nucleation energy of Si is small, while that of cristobalite is high.

The obtained cristobalite was the low-temperature phase, which was transformed from the high-temperature phase at about 270°C. In situ observations with a high-temperature XRD technique determined that the high-temperature phase belongs to a high symmetry space group of *Fd3m*.

Under a high-pressure condition, SiO has a tendency to decompose into Si and SiO₂ above 14 GPa without any heating.

The kinetic analyses of the disproportionation reaction were performed to clarify the deposition process of SiO to Si nanocrystals and cristobalite. The crystallization of Si was investigated by analyzing XRD peak intensities. FWHM values of the Si(111) XRD peak revealed that the Si particles were formed within 2 hours with the sizes of about 4, 5.5, 10.5 and 14.7 nm at 1000, 1100, 1200 and 1300°C, respectively. Accordingly, each temperature at fixed reaction times limited the sizes. The origination of Si nanocrystals was also directly observed by high-resolution TEM.

From the analytical data, the crystallization was regarded as a first-order decomposition. The activation energy was estimated to be 82.2 kJ·mol⁻¹, which is higher than that in the crystallization energy of Si from the amorphous state, but much lower than the normal diffusion energy of Si. Thus, Si atoms in the disproportionation reaction may behave in an intermediate manner between rearrangements and diffusion during the crystallization.

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