Kinetic studies of the \(\alpha\)-quartz-coesite transformation of \(\text{SiO}_2\)

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Abstract

Time resolved X-ray diffraction experiments have been performed in order to investigate the kinetics of the \(\alpha\)-quartz-coesite transformation of \(\text{SiO}_2\) at around 6 GPa and 700-900°C, using the “MAX80” cubic anvil type high pressure apparatus with synchrotron radiation. The correlation between a volume fraction of transformed coesite and relative intensities of reflections from \(\alpha\)-quartz and coesite was experimentally determined. On the basis of the correlation, the volume fraction transformed coesite was estimated as a function of time. The Avrami rate equation was used for the determination of the kinetics. The value of the exponent \(n\) is determined as almost 1 and this result indicates that the grain growth of coesite is dominant mechanism of the transformation. The empirical activation energy, which is derived from the temperature dependency of the determined rate constant \(k\), was estimated as 200 (±40) kJ/mol at the pressure overstep of ca. 3.5 GPa from the \(\alpha\)-quartz-coesite equilibrium conditions. This value is similar to a reported activation energy of oxygen diffusion in the quartz structure. This consistency suggests that the oxygen diffusion is able to control the growth rate of the coesite phase at the present experimental conditions.

Introduction

It is well known that \(\text{SiO}_2\) occurs in several different forms at different pressure and temperature conditions. The \(\alpha\)-quartz form is stable at ambient conditions and is one of the most abundant minerals in crustal rocks of the earth. The \(\alpha\)-quartz form is transformed into \(\beta\)-quartz, tridymite and then cristobalite with temperature. The known high pressure forms of \(\text{SiO}_2\) are coesite and stishovite. Coesite was experimentally synthesized before the discovery of natural coesite in impact-metamorphosed rocks (Coes, 1953; Chao et al., 1960). Coesite was recognized as a stable phase in the deep crust of the earth, since the natural occurrence in metamorphic rocks was reported (Gillet et al., 1984). Stishovite is stabilized under higher pressure and is thought to be stable in the earth’s mantle.

The \(\alpha\)-quartz-coesite transformation of \(\text{SiO}_2\) has been well established in literature (e.g. Boyd and England, 1960; Mirwald and Massonne., 1980; Bohlen and Boettcher, 1982; Akaogi and Navrotsky, 1984; Akaogi et al., 1995). On the other hand, there may be a few preliminary kinetic studies of the transformation, because it is technically difficult to per-
form the kinetic experiments of pressure-induced phase transformations (Zinn et al., 1995). For example, some investigations carried out the kinetic studies of the α-quartz-rutile transformation of GeO₂ by the temperature quenching method (Zeto and Roy, 1969; Brar and Schloessin, 1981). However, the quenching method requires an assumption that a rate of a back transformation during the quenching is negligibly small. A more direct approach with in-situ X-ray diffraction investigation is important. For the last decade, the application of synchrotron radiation with high brilliance to high pressure experiments allows us to measure diffraction profiles at enough short intervals to pursue transformation kinetics. Thus, the time resolved diffraction measurements using synchrotron radiation could be applied to kinetic studies of pressure-induced phase transformations (e.g. Will and Lauterjung, 1987; Rubie et al., 1990; Yamanaka et al., 1992; Zinn et al., 1995).

In this paper, time resolved X-ray diffraction studies have been conducted to obtain new experimental data on the kinetics of the α-quartz-coesite transformation, using the "MAX80" cubic anvil type high pressure apparatus with synchrotron radiation. The obtained kinetic data were analyzed on the basis of the Avrami rate equation.

**Experimental**

Kinetic experiments were performed using the MAX80 cubic-anvil apparatus installed on the accumulation ring at the National Laboratory for High Energy Physics, Japan (Shimomura et al., 1984a, 1984b). The cell assembly is schematically shown in Fig.1. Six sintered diamond anvils of 3-mm-edge square face and a cube pressure medium of 6-mm in edge, which was made of a mixture of amorphous boron and epoxy resin, were used. Carbon disks were used as heaters and an almel-chromel thermocouple monitored sample temperatures. A half of a sample chamber was filled with quartz powder and the other half contained NaCl powder, which was used as a pressure calibrant (Decker, 1971) and which was mixed with BN powder to inhibit grain growth of NaCl powder at high temperature. Judging from the standard deviation of the determined lattice parameter of NaCl, the pressure uncertainty was estimated P = ± 0.3 GPa. Because kinetics is affected by a lot of factors, for example,

![FIG. 1. Schematic drawing of the cell assembly for kinetic experiments at high pressure and high temperature. 1: zirconia cap; 2: boron epoxy pressure medium; 3: molybdenum electrode; 4: carbon disc; 5: sample; 6: almel-chromel thermocouple; 7: mixture of NaCl and BN powder.](image-url)
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...on, the pressure cells were carefully made. The reagent-grade powder sample, which is synthesized by a precipitation method, was grounded in a mortar for about 30 minutes and the average grain size of the sample was about 1-5 \( \mu \text{m} \). The sample was always kept in a desiccator until being used for one of runs, and was loaded into the sample chamber as small amount as possible, in order to inhibit thermal gradient of the sample chamber and pressure drop during the transformation.

In the present kinetic experiments, starting materials were first pressurized to about 1.5 GPa at room temperature. The broadening of X-ray diffraction peaks of \( \alpha \)-quartz has been observed during the pressurization at room temperature. This evidence suggests that the existence of high elastic strain in crystalline quartz. It is well known that the presence of high elastic strain in the crystal lattice greatly influences transformation kinetics. In order to remove the strain, hot pressing was conducted at 1.5 GPa and 700°C, which conditions are within the \( \alpha \)-quartz stability field, and kept at these conditions for 10 minutes. X-ray diffraction peaks became sharp by the hot-press treatment and this means that the elastic strain was removed. After the hot-pressing, temperature decreases to room temperature and then the pressure was increased to the desired value at a rate of between 0.3 and 0.5 GPa/min. During this process, peak broadening was not observed. Finally, the temperature was changed to a condition required for a kinetic experiment within 1 minute. Kinetic time \((t = 0)\) was started after the required PT conditions were attained.

Time resolved X-ray diffraction patterns were collected at measurement intervals of 30 ~ 40 s with energy-dispersive measurements. A pure Ge solid state detector was placed at a fixed 20 angle of 4.00°.

**Results and discussion**

Time resolved X-ray diffraction measurements were performed at four conditions (6.3 GPa, 700°C; 6.2 GPa, 800°C; 6.6 GPa, 900°C; 6.0 GPa, 900°C). The pressure uncertainty was estimated \( P = \pm 0.3 \text{ GPa} \) as previously described and it was concluded that these conditions overstep by ca. 3.5 GPa from the \( \alpha \)-quartz-coesite equilibrium conditions (Akaogi et al., 1995). Typical sequence of diffraction patterns as a function of time is shown in Fig. 2. The reflections of \( \alpha \)-quartz lose their intensities gradually and, on the other hand, the reflections of coesite appear progressively. Two reflections indexed as 100 and 011+101 of \( \alpha \)-quartz and two reflections indexed as 111+130 and 040+200 of coesite were clearly observed.

Generally, in kinetic analyses, estimates of the volume fraction transformed are required as a function of time. In this study, the volume fraction of coesite has been estimated from the relative integrated intensities \((S)\) of the diffraction peaks as follows.

\[
X(t) = \frac{F_{040+200}}{F_{011+101} + F_{040+200}} \quad (= S)
\]

where the \( I_{hkl} \) denotes the integrated peak intensity for the \( hkl \) reflection and the superscripts C and
Fig. 2. An example of a typical sequence of diffraction patterns as a function of time (6.2 GPa and 800°C). Some diffraction peaks around 65 keV are overlapped by some quartz and coesite reflections.

Fig. 3. Calibration curve relating the ratio $S$ (see text) to the volume fraction transformed coesite.

$Q$ represent coesite and $\alpha$-quartz, respectively. The 040+200 reflection of coesite and the 011+101 reflection of $\alpha$-quartz were selected to estimate a volume fraction of coesite, because both each of those reflections is the most intense in each diffraction pattern. Calibration curve was determined experimentally using some standard mixture samples of $\alpha$-quartz and coesite as shown in Fig. 3. It is well known that preferred orientation of the sample often occurs in a pressure cell. The preferred orientation must give a wrong estimation of coesite fraction. In this study, the relative intensities, which are $I_{Q_{100}}$ and $I_{Q_{011+101}}$ and $I_{c_{111+130}}$ and $I_{c_{040+200}}$, were checked in order to monitor the preferred orientation. Their ratios were constant during the experiment, therefore, the effect of the preferred orientation was negligible in the present experiments. On the basis of the obtained calibration curve, the volume fraction transformed, $X(t)$, of
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![Graph showing transformation of coesite as a function of time](image)

**Fig. 4.** The volume fraction transformed coesite, \( X(t) \), as a function of time. Transformation-time curves obtained by least squares fits of the Avrami rate equation \( n \)-values were fixed as 1.

<table>
<thead>
<tr>
<th>Pressure (GPa)</th>
<th>Temperature (°C)</th>
<th>( n )</th>
<th>( k/sec ) ((n=1\text{ fixed}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.2 (±0.3)</td>
<td>700</td>
<td>1.1 (±0.2)</td>
<td>7.8 (±2.2) \times 10^{-5}</td>
</tr>
<tr>
<td>6.2 (±0.3)</td>
<td>800</td>
<td>0.8 (±0.5)</td>
<td>9.2 (±5.1) \times 10^{-4}</td>
</tr>
<tr>
<td>6.6 (±0.3)</td>
<td>900</td>
<td>1.0 (±0.1)</td>
<td>3.5 (±2.0) \times 10^{-3}</td>
</tr>
<tr>
<td>6.0 (±0.3)</td>
<td>900</td>
<td>0.9 (±0.2)</td>
<td>8.2 (±2.1) \times 10^{-3}</td>
</tr>
</tbody>
</table>

Coesite as a function of time is shown in Fig. 4. The transformation from \( \alpha \)-quartz to coesite almost finished in the kinetic experiments at 900°C and, on the other hand, the transformation was not completed during the experiments at 700 and 800°C, in the present run durations shown in Fig.4.

Generally two processes are involved in solid-to-solid transformations, namely, nucleation and growth of the product phase within the parent phase. The isothermal kinetics of various mineral transformations can be described empirically by the Avrami rate equation as follows:

\[
X(t) = 1 - \exp(-kt)^n
\]

where \( k \) is a rate constant and \( n \) is a constant which depends on a mechanism controlling kinetics. Cahn indicated that a value of \( n \) can lie in the range from 1 to 4 (Chan, 1956). A value of \( n \) can be 1, when the reaction kinetics are dominated by growth mechanism, and an \( n \)-value can be 4, when the kinetics are dominated by grain-boundary nucleation mechanism. And intermediate values can be explained as a transition between the two extreme cases. The \( n \)-values of the \( \alpha \)-quartz-coesite transformation were calculated by a least squared fitting of \( X(t) \)-\( t \) data (Table 1). All of obtained \( n \)-values can be considered as almost 1. This suggests that the same mechanism, which can be considered as growth of coesite, possibly controls the kinetics of the \( \alpha \)-quartz-coesite transformation under present experimental conditions. Rubie et al. (1990) suggested that
$n$ -values close to 4 in the experiments performed at conditions closest to equilibrium and $n$ -values close to 1 at conditions which deviate greatly from equilibrium. The present kinetics experiments were carried out with relatively large overstepping (ca. 3.5 GPa) from the equilibrium conditions. Therefore, we can assume $n = 1$ and values of the rate constant $k$ are recalculated (Table 1).

If the same mechanism governs kinetics at various temperatures, an empirical activation energy can be estimated. In this study, it can be assumed that growth of coesite controls kinetics in all of experimental conditions, as discussed above. An activation energy can be determined from an Arrhenius plot of ln $k$ against $1/T$. Because of $k = A exp (-\Delta E_a / RT)$, where $A$ is a frequency factor, $\Delta E_a$ is an activation energy, $R$ is the gas constant, and $T$ is an absolute temperature, the Arrhenius plot should be linear with a slope of $\Delta E_a / R$. The fitted straight line yields an empirical activation energy of 200 ($\pm 40$) kJ/mol (Fig. 5).

The atomic process of grain growth is the jumping of an atom from one side of a boundary to the other and is similar to a diffusion process in the boundary. The activation energy of the volume diffusion of oxygen in the $\alpha$-quartz structure was reported as 243 kJ/mol (Farver and Yund, 1992). This value is similar to the obtained activation energy of the $\alpha$-quartz-coesite transformation. Generally, the activation energy of grain growth is intermediate between that for boundary and volume diffusion and the activation energy of boundary diffusion is much smaller than that of volume diffusion (Kingery et al., 1976). Indeed, the reported activation energy of oxygen diffusion is a little larger than that of the $\alpha$-quartz-coesite transformation. Therefore, the obtained activation energy of the $\alpha$-quartz-coesite transformation, suggests that the oxygen diffusion at grain boundary is able to control the growth rate of the coesite phase at the present experimental conditions.

The $\alpha$-quartz-coesite transformation should be reconstructive, because the two struc-
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tures differ from one another so much (e.g. The density difference is about 11\%.). The transformation requires the breaking of primary bonds and the reconstruction of some of the structural units to the new form. The structural unit may correspond to an oxygen packing in the $\alpha$-quartz structure. Although silicon in quartz diffuses much slower than oxygen such as the major silicate minerals and the high activation energy (746 kJ/mol) was reported for the silicon diffusion (Bejina and Jaoul, 1996), the $\alpha$-quartz-coesite transformation is not accompanied by the coordination change from fourfold to sixfold. Therefore, it is reasonable that the diffusion of oxygen possibly controls the kinetics of the $\alpha$-quartz-coesite transformation of SiO$_2$.

Summary

Time resolved X-ray diffraction measurements have been conducted under high pressure and high temperature with synchrotron radiation, in order to investigate the $\alpha$-quartz-coesite transformation of SiO$_2$. Obtained kinetic data were analyzed on the basis of the Avrami rate equation. Our results indicate that the transformation rate is controlled by growth of the coesite phase and that the diffusion of oxygen governs the growth rate.

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References


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