

Pressure-induced phase transitions in tridymite

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Abstract

Phase transitions in tridymite were examined at pressures up to about 30 kbar by X-ray single-crystal and optical methods, using a hydrothermally synthesized monoclinic crystal of MC type tridymite and a natural crystal (from Kumamoto, Japan) of orthorhombic symmetry tentatively named PO-5 type. In MC type tridymite, a reversible pressure-induced phase transition has been observed at about 5 kbar without destroying the crystal. The unit-cell dimensions of the high-pressure phase were $a = 17.07$, $b = 9.81$ and $c = 81.26\text{\AA}$ in an orthorhombic lattice. The SiO_4 tetrahedron displacement on this phase transition is discussed. PO-5 type tridymite did not change to any other phase.

Introduction

Tridymite (SiO_2) is known to have many modifications at ambient conditions. The fact that the several modifications exist at the same pressure-temperature conditions for the same composition is an interesting problem from the viewpoint of crystal chemistry. It is important to study the phase transitions and the relations between the modifications at various conditions.

Thermal changes in some types of tridymite have already been studied in detail along these lines (e.g. Nukui *et al.*, 1978; Sato, 1964).¹ In these studies, various types of tridymites have been shown to transform reversibly to other modifications at high temperature. However, the transition between the modifications found at ambient conditions have not been observed in these studies. The phase relations between them have remained unexplored. We have applied high pressure to this interesting material in expectation of a new transition between the modifications found at ambient conditions.

Experimental

As starting samples, two kinds of tridymite crystals were used. One was hydrothermally synthesized MC type tridymite (Nukui *et al.*, 1978). MC type tridymite is monoclinic with space group Cc ; $a = 18.49$, $b = 4.991$, $c = 25.83\text{\AA}$, $\beta = 117.75^\circ$. The other is a

natural crystal collected at Kumamoto, Japan and is orthorhombic with space group $C22_2$; $a = 17.21$, $b = 9.93$, $c = 40.91\text{\AA}$. Because the c period is 5 times longer than that of the high-temperature hexagonal tridymite (Gibbs, 1927), it is named here PO-5 type tridymite.

The crystals were examined under hydrostatic pressure by a single-crystal X-ray diffraction method using a precession camera. A sample and a small amount of ruby powder were inserted with an alcohol pressure medium into a miniature diamond anvil type high-pressure apparatus which can be attached to a standard goniometer head (Yamaoka *et al.*, 1979). The experiments were done at room temperature, and pressure was measured by the ruby fluorescence technique with accuracy of ± 1.5 kbar. In order to see clearly the superstructure reflections and the profile of diffuse streaks, the film-to-crystal distance was chosen to be 100 mm. A polarizing microscope was also used to examine optically the crystal under high pressure.

Results

Before the X-ray experiments, crystals in the diamond anvil cell were observed by the polarizing microscope. Figure 1a shows an MC type crystal which has two domains twinned by 60° rotation about $[301]_{\text{MC}}$, which corresponds to the c axis of high-temperature hexagonal tridymite. When pressure was increased, the domain boundary disappeared rapidly and the crystal seemed to be a single domain at about

¹ The thermal changes in PO-5 type tridymite will be given elsewhere (Nukui *et al.*, in preparation).

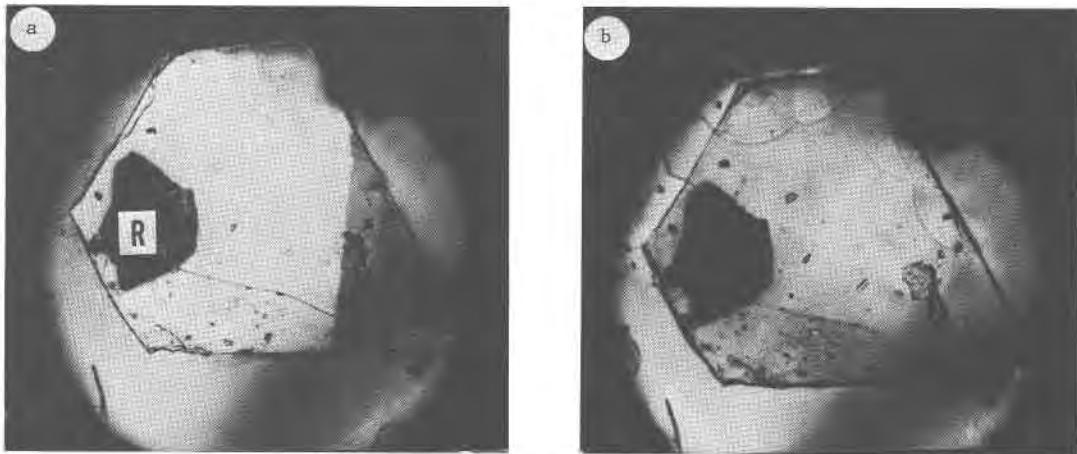


Fig. 1. Photomicrographs under polarized light of a tridymite crystal, taken at ambient condition (a), and at 5 kbar (b); R = ruby.

5 kbar, as shown in Figure 1b. This suggested that by the increase of pressure some structural change occurred without destroying the crystal.

Figures 2a and 2b are the precession photographs taken at 3 and 7 kbar respectively, where radial streaks are attributed to continuous X-ray diffraction of the diamond anvil. The diffraction pattern in Figure 2a was same as the $\bar{h}k3h$ net of the original MC phase. The X-ray diffraction pattern definitely changed at about 5 kbar: odd reflections were newly added to those of the $\bar{h}k3h_{MC}$ net. The diffraction pattern in Figure 2b indicates the $hk0$ net of the high-pressure phase. The transition pressure observed under the X-ray study was in good agreement with that observed in the polarizing microscope. When pressure decreased below 5 kbar, the diffraction pattern of the high-pressure phase returned to that of the MC phase.

To know the stacking sequence along c direction of the high-pressure phase, a precession photograph of

$h0l$ plane was taken at 7 kbar. Figure 3 shows that the main reflections were accompanied by the weak satellite reflections along the c^* direction and the c period was found to be 81.26Å. The unit-cell dimensions of the high-pressure phase at 7 kbar are $a = 17.07$, $b = 9.81$, $c = 81.26$ Å, with orthorhombic symmetry. The c period of this phase is 10 times longer than that of the high-temperature hexagonal tridymite, and this phase can be named PO-10 type. Our results show a molar volume per chemical unit (SiO_2) of PO-10 type tridymite approximately 0.4% smaller than that of MC type. It is reasonable that the high-pressure phase (PO-10) would have smaller cell volume. Some ambiguity has remained in this identification, however, because of the coexistence of the two modifications: a PO-2 form ($a = 17.07$, $b = 9.81$, $c = 16.2$ Å) and PO-5 ($a = 17.07$, $b = 9.81$, $c = 40.6$ Å) is also a possible interpretation of the diffraction pattern in Figure 3.

On the other hand, similar X-ray diffraction pat-

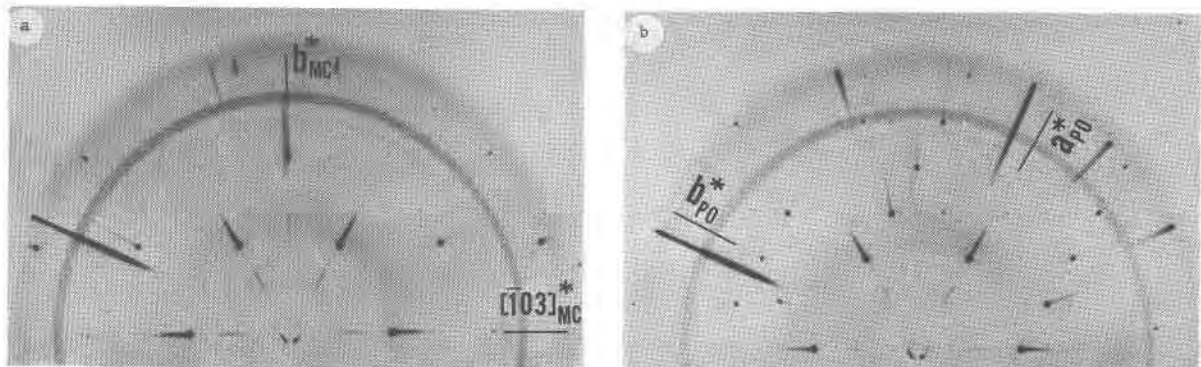


Fig. 2. Precession photograph of $\bar{h}k3h$ net (reciprocal plane normal to a_{MC}^*) of the MC phase taken at 3 kbar (a), and of the $hk0$ net of the PO-10 phase at 7 kbar (b).

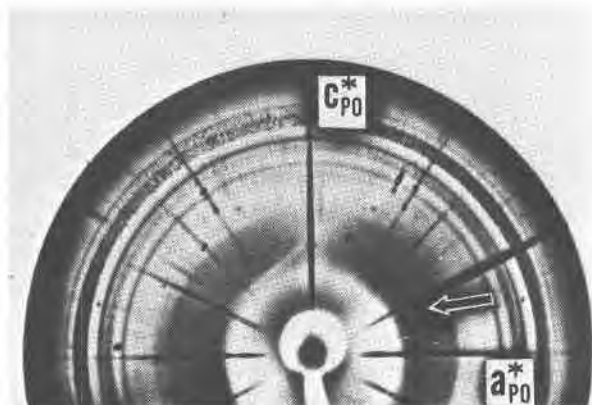


Fig. 3. Precession photograph of the $h0l$ net of the PO-10 phase at 7 kbar.

terns of PO-5 type tridymite with orthorhombic symmetry were observed at all pressures below 30 kbar, and there were no detectable changes, including the intensity distribution. No change of this crystal was observed under the polarizing microscope, either. Appleman (private communication) has, however, found tridymite with the apparent space group and cell of the PO-5 form, which has invariably proven to be submicroscopically twinned triclinic (PO-10) tridymite. If this is also true for the present case, it is reasonable that the PO-5 form did not convert to any

other phase because it has already been converted to PO-form at ambient conditions. Taking account of this assumption, high-pressure phase of tridymite is considered to be the PO-10 type.

Discussion

The modifications in tridymite found at ambient condition can be classified into two groups: a monoclinic (MC) and a pseudo-orthorhombic (PO) group, based on their respective symmetries and the unit-cell dimensions. The MC group has only one modification (the MC type tridymite: Kato and Nukui, 1976; Dollase and Baur, 1976), while the PO group has four modifications with similar periods of a ($\sim 17.2\text{\AA}$) and b ($\sim 9.9\text{\AA}$), and different periods of c ($\sim 8.2n\text{\AA}$; $n = 1, 2, 5, \text{ and } 10$).

Recently, Konnert and Appleman (1978) have determined the crystal structure of a tridymite in the PO group, which is tentatively named here the PO-10 type because of its multiplicity of the c period, *i.e.* $n = 10$. They compared it with that of MC type tridymite and pointed out that the structural difference is attributed not only to the difference of the crystallographically distinct layers but also to the arrangement of six-membered rings of SiO_4 tetrahedra. The PO-10 type structure has 10 layers and the MC type 2 layers, and the six-membered rings of tetra-

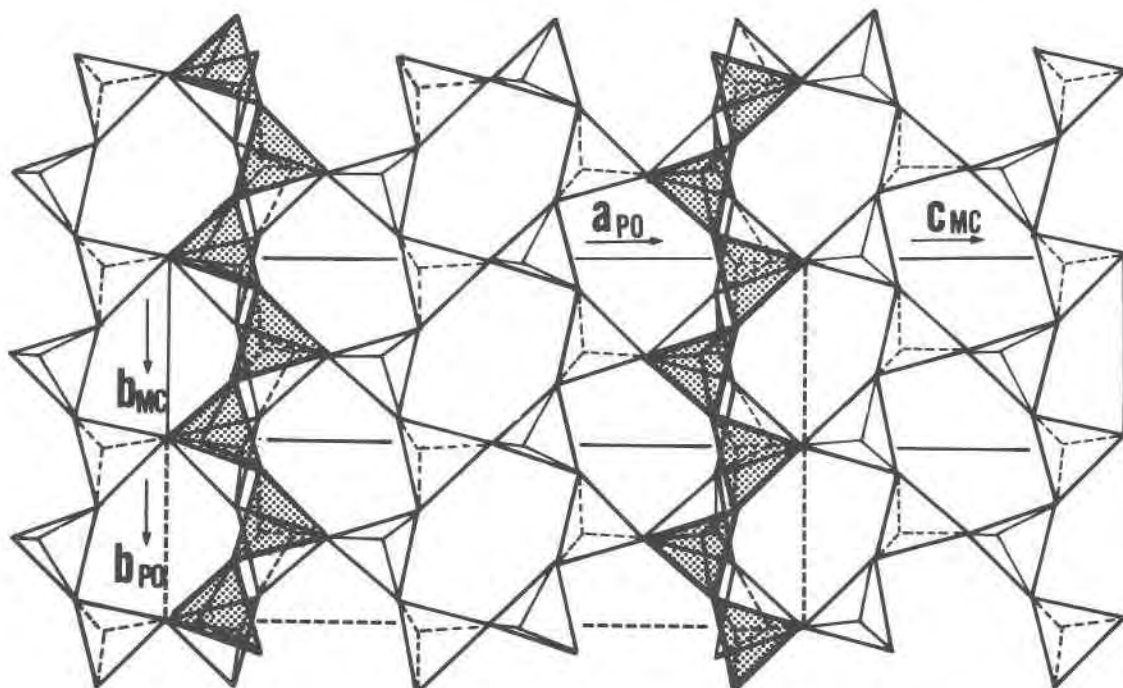


Fig. 4. Illustration of the tetrahedron displacement required by the pressure-induced transition. The configuration consisting of blank tetrahedra (Dollase and Baur, 1976) is the MC type structure projected along $[301]$, and shaded tetrahedra indicate the displaced positions.

hedra are all "oval" in the PO-10 structure while in the MC type, 1/3 of the rings are "oval" and 2/3 "ditrigoal." We calculated the volume of the openings surrounded by the oval and the ditrigoal rings in the MC type structure. The opening of the oval rings is slightly smaller in volume than that of the ditrigoal rings. Therefore, the transition from the MC to PO-10 phases at high pressure is reasonably considered to be caused by the change in the form of six-membered rings from ditrigoal to oval. Figure 4 illustrates the tetrahedron displacements required by the transition at high pressure. The configuration consisting of blank tetrahedra is the structure of the MC type tridymite projected along [301], showing the two types of six-membered rings, oval and ditrigoal. A rectangle surrounded by solid lines indicates the unit cell of the MC type tridymite. Shaded tetrahedra indicate the displaced positions at the pressure-induced transition, assuming the displacements which change the arrangement of tetrahedra from ditrigoal rings in the MC type structure to oval ones in the high-pressure phase. As can be seen in Figure 4, the structure change from the MC type structure to that of the high-pressure phase may occur without rearrangement and large displacement of tetrahedra. This configuration consisting of all oval rings is an estimated structure of the high-pressure tridymite in the PO group. A rectangle sur-

rounded by dotted lines indicates the unit cell of the high-pressure tridymite.

We have found that the MC phase reversibly transforms to a modification in the PO group at about 5 kbar. To gain more information on the phase relations in this interesting but complicated system, further study should be done under the conditions in combination with temperature and pressure.

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