

Three tridymite structural modifications and cristobalite intergrown in one crystal

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ABSTRACT

The coherent intergrowth in single crystals of several structural modifications of tridymite with or without cristobalite was found by the X-ray precession method. With three structural modifications plus cristobalite, there are eleven possible combinations of intergrowths. Nine of these combinations have been observed in synthetic and natural crystals. As an extreme case, the intergrowth of all four (MC, PO, and MX tridymites and low cristobalite) is described. This is the first description of intergrowth patterns involving so many of these SiO₂ structural modifications.

INTRODUCTION

Tridymite has many structural modifications at ambient conditions. The relationships among them have been discussed by Nukui and Nakazawa (1980). This study gives further interpretation of these complicated relations.

Description of the numerous structural modifications is made possible by analysis of the coexistence of the three structural modifications of tridymite MC (Cc, $a = 17.216$, $b = 4.991$, $c = 25.832$ Å, and $\beta = 117.75^\circ$), PO-10(5) [F1, $a = 17.216$, $b = 9.932$, and $c = 81.864(40.91)$ Å] and MX ($a = 5.008$, $b = 8.60$, $c = 8.21$ Å, and $\beta = 91.512^\circ$, incommensurate with a fundamental cell) with low cristobalite ($P4_12_1$, $a = 4.97$ and $c = 6.94$ Å) in one crystal. Previously, Flörke (1955) had mentioned the coexistence of cristobalite with tridymite in a single crystal, as deduced from extra reflections on oscillation photographs.

The coexistence phenomena described indicate complicated relationships among the different structural modifications of tridymite and between tridymite and cristobalite.

EXPERIMENTAL METHODS

Conditions of synthesis or of occurrence of crystals that include the different configurations are given in Table 1. Single crystals in which the three different structural modifications of tridymite coexist with cristobalite were synthesized by the flux method (quartz fragments in a Li₂WO₄ melt at 1000°C for 3 d). The resultant crystals were colorless and transparent. After the Soxhlet treatment (Flörke and Langer, 1972), the crystals contained less than 0.01 wt% Li and 0.001 wt% Na. Many crystals from these syntheses form well-shaped hexagonal platelets; however, in polarized light, the crystals display an intricate intergrowth pattern of sectors with curved boundaries. It should be mentioned that the crystals initially formed at a temperature

where the hexagonal high-temperature form of tridymite (HP) is stable, that they transformed displacively during cooling to ambient temperature, and that the rate of quenching affects the transformation of the MC modification into the MX phase (Hoffmann et al., 1983). These crystals were examined by the X-ray precession method.

RESULTS AND DISCUSSION

Many single-crystal X-ray diffraction patterns of tridymite crystals cannot be explained either by diffraction of a single structural modification or by twinned crystals but only by combinations of the three structural modifications of tridymite—MC, PO, and MX—with or without cristobalite. With intergrowth of these four crystal structures and structural modifications, in principle, eleven configurations of coexistence are possible. To date, we have observed nine of them (Table 1). A precession photograph that indicates the coexistence of MC, PO, and MX tridymite structural modifications with low cristobalite in a single crystal is reproduced in Figure 1. The detailed crystallographic relations among these structural modifications plus cristobalite are given below.

Crystallographic relations of four structures and structural modifications in a single crystal

The reciprocal net of this crystal is schematically shown in Figure 2 in order to understand the crystallographic relations among the structures and structural modifications. The pattern of MC and PO tridymites can be described as superstructures of the same fundamental cell (Kato and Nukui, 1976; Konnerth and Appleman, 1978) derived from high tridymite (HP). Although the MX structural modification is an incommensurate structure (Hoffmann et al., 1983), it can also be derived from high tridymite. Since all of these three modifications are derived from the high tridymite structure, all of the main

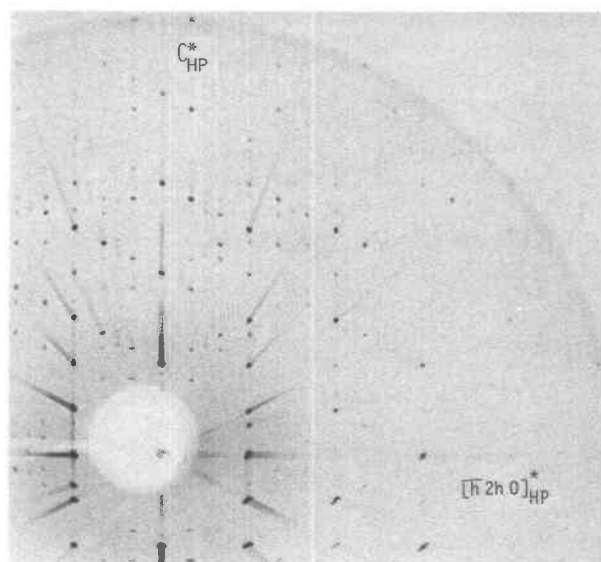


Fig. 1. Precession photograph of the plane normal to $(h0l)_{HP}$ of a flux-grown single crystal of tridymite, representing the intergrowth of three tridymite structural modifications and of cristobalite.

reflections in the precession photograph described are superimposed. Therefore, lattice analyses have to be carried out primarily by using nonsuperimposed reflections with reference to single-crystal photographs of the nonmixed polymorphs MC, PO, MX, and cristobalite (Fig. 2). All reflections of the MX structural modification in the photograph (Fig. 1) are superimposed with reflections of other tridymite structural modifications, as indicated by triangles in Figure 2. However, the coexistence of the MX structural modification can be confirmed by analyzing nonsuperimposed reflections of the other reciprocal planes [e.g., $(h0l)_{MX}$] corresponding to $(h0l)_{HP}$. As a result, the reflections in Figure 1 can be attributed to the coexistence

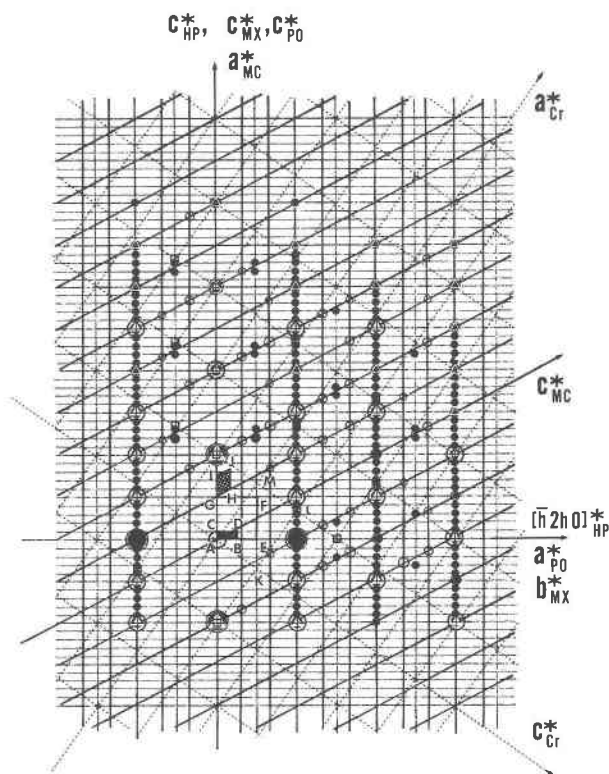


Fig. 2. Reciprocal net, schematically illustrating corresponding reflections from four coexisting structures and structural modifications; open circles, closed circles, triangles, and squares correspond to MC, PO-5, and MX tridymite and low cristobalite, respectively; The parallelogram $GHIJ$ indicates the unit cell of MC, the rectangles $ABCD$ the unit cell of PO, and $AEFG$ the fundamental cell of MX tridymite, and $AKLM$ of low cristobalite.

of three structural modifications of tridymite with cristobalite as shown in Figure 2.

From Figure 2, the mutual crystallographic orientations among these structural modifications are derived as follows:

$$\begin{aligned} c^*_{HP} \parallel c^*_{PO} \parallel c^*_{MX} \parallel a^*_{MC} \\ [h2h0]^*_{HP} \parallel a^*_{PO} \parallel b^*_{MX} \parallel [103]^*_{MC} \end{aligned}$$

The parallelogram $GHIJ$ (Fig. 2) represents the unit cell of MC tridymite, the small rectangle $ABCD$ that of PO-5 tridymite, and the large rectangle $AEFG$ represents the fundamental cell of MX tridymite.

The X-ray pattern of this crystal is further complicated by the superposition of cristobalite reflections (Fig. 1). The $[h0h]_{low} \parallel [hhh]_{high}$ reflections of low cristobalite overlap the tridymite reflections owing to similar spacing along lattice row $[h0h]_{low}$ and along c^*_{HP} of the tridymite structural modifications. However, additional reflections are apparent (indicated by squares in Fig. 2). These reflections are consistent with the low cristobalite structure if the orientation of the reciprocal lattice of cristobalite is chosen as shown by dotted lines in Figure 2. The rectangle $AKLM$ (Fig. 2) indicates the unit cell of low cristobalite.

Table 1. Possible and observed configurations of three tridymite structural modifications and of cristobalite

No. of coexisting phases	Combinations				Conditions of formation
	Tridymites			Cristobalite	
	MC	PO	MX		
1	X				Hydrothermal synthesis*
1		X			Terrestrial occurrence (Perlenhardt)
1			X		Quench of MC**
1				X	Hydrothermal synthesis*
2	X	X			Hydrothermal synthesis*
2	X		X		Quench of MC**
2	X			X	Hydrothermal synthesis*
2		X	X		Hydrothermal synthesis*
2		X		X	Hydrothermal synthesis*
2			X	X	(Hypothetical)
3	X	X	X		Hydrothermal synthesis*
3	X	X		X	Hydrothermal synthesis*
3	X		X	X	Flux growth (Li ₂ WO ₄ , 3d, 1000°C)
3		X	X	X	(Hypothetical)
4	X	X	X	X	Flux growth (Li ₂ WO ₄ , 3d, 1000°C)

* $P = 500$ bars; $T = 700^\circ\text{C}$.

** Observation by Hoffmann et al. (1983).

On the basis of these lattice analyses, the unit cells and symmetries corresponding to each structural modification could be deduced. It is clear that the coexisting four structures and structural modifications are intergrown with definite orientation relationships to each other (and to the high tridymite that existed during formation). It could be mentioned that during the displacive transformation from high to low tridymite, monoclinic low tridymite MC as a rule forms from high tridymite with only very low or no polytypic stacking disorder (T_0). In contrast, the pseudo-orthorhombic low tridymite PO-5(10) forms from high tridymite with a noticeable degree of polytypic stacking disorder (T_D) (Schneider and Flörke, 1982).

Varieties of coexistence

The coexistence of tridymite and cristobalite can be related by a growth process according to Flörke's (1966) nucleation-growth model. This model implies that the MC and PO tridymites are derived from regions of the high tridymite crystals with almost no polytypic stacking disorder (T_0) and with a noticeable degree of polytypic stacking disorder (T_D), respectively.

The MC and PO structural modifications change reversibly to their high-temperature phases (Nukui et al., 1978). However, a quenching process with the development of mechanical stress in the crystal regions with MC tridymite has to be taken into consideration to explain the structural change from MC tridymite into MX tridymite (Hoffmann et al., 1983). Imamura and Matsumoto (1980) suggested that the PO and MX structural modifications result from the MC structural modification by thermal quenching from above 200°C, whereas Hoffmann et al. (1983) found that the PO structural modification is formed from MX tridymite by a thermal relaxation process near 70°C. The transformation process of MC tridymite into MX tridymite by the action of mechanical stress may occur in the absence of a noticeable degree of stacking disorder in the relevant parts of the crystal. The MX structural modification is therefore converted from MC tridymite under unusual conditions (quenching or mechanical stress). In any case the coexistence of the MX structural modification and the other tridymite structural modifications (MC and PO) must be formed during not so much the growth process as the cooling process.

We did not observe the coexistence of the MX structural modification with cristobalite (Table 1). The strain associated with this intergrowth complexly affects the displacive transformation during cooling to ambient temperatures. Therefore it is difficult to achieve total conversion of the MC to the MX structural modification, if MC tridymite and cristobalite are once intergrown at high temperature. The absence of cristobalite coexisting with MX and PO tridymite may be due to the same effect.

On the basis of these models, the configuration of coexisting tridymite structural modifications with or without cristobalite not only depends on the chemical environment of growth, but also on growth temperature, time, and the cooling process.

The correlation between intergrowths of tridymite

structural modifications with cristobalite and the conditions of formation will be discussed in connection with theoretical considerations and experimental evidence of growth and stacking disorder in a subsequent paper. The knowledge of coexisting structural modifications in tridymite single crystals and our approach to the analysis of the very complex X-ray pattern, presented here, should facilitate this work.

CONCLUSIONS

Up to eleven possible combinations of coexisting tridymite structural modifications with cristobalite, coherently intergrown in single crystals, can exist: (1) six possible combinations of two structures and structural modifications, (2) four possible combinations of three structures and structural modifications, and (3) the combination of all four structures and structural modifications. Nine of the eleven possible combinations have been observed in crystals from different conditions of formation.

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