K. Kihara

Molecular dynamics interpretation of structural changes in quartz

Abstract Constant temperature and constant pressure molecular dynamics (MD) simulations were applied to quartz to calculate the structural details which are indeterminable in usual X-ray structure studies. The dynamics of the structural changes was analyzed by means of time-dependent atomic displacement parameters. The Si-O bonds expand with increasing temperatures through the x- and β-phases, and atoms vibrate around the \( x_1 \) (or \( x_2 \)) sites at lower temperatures in the x-phase, and over the energy barriers between the \( x_1 \) and the \( x_2 \)-sites at higher temperatures in the \( x- \) and the β-phases. The ratios of time lengths spent by atoms in the \( x_1 \) and \( x_2 \)-sites determine the apparent atomic positions as obtained in usual structure studies of x-quartz. More frequent transfer of atoms over the \( x_1 \) and the \( x_2 \)-sites contributes positively to the thermal expansions, whereas larger amplitudes of vibrations, which carry atoms more distantly and more frequently from the β-sites, contribute negatively. The well-known steep thermal expansion in the x-phase is attributed to the additive contribution from the expansions of the Si-O bond lengths, the widening of Si-O-Si angles, and the increase of the atomic transfer-frequency between the \( x_1 \) and the \( x_2 \)-sites. The nearly zero or negative expansion in the β-phase is caused by balancing the negative to the positive effects. The MD crystal transforms to the β-phase via a transitional state, where the x- and β-structures appear alternately with time, or coexist. The slight and continuous expansions observed right after the steep rise(s) of the volume or cell dimensions up to the nearly horizontal curve(s) are attributed to the continuous changes within the transitional state.

Key words Quartz · Thermal expansion · Molecular dynamics simulation

Introduction

Crystals with quartz (SiO\(_2\)) type structure with x–β transition show quite different thermal-expansion behaviors below and above the transition points (Jay 1933; Young 1962; Ackermann and Sorrell 1974; Sorrell et al. 1974; Kosten and Arnold 1980). The rapid thermal expansion in x-quartz has been discussed by many authors in relation to the x–β transition. Young (1962) attributed the expansion to the shifts of atomic equilibrium positions under the two restrictions that the Si-O distance be kept constant and that the shifts take place along the lines joining the Dauphiné twin-related positions, \( x_1 \) and \( x_2 \). Since then, this static interpretation has dominated the thermal expansion studies of x-quartz, resulting in the development of the rotational model, in which the shifts of atomic equilibrium positions are approximated by the rotational displacements of corner-linked rigid (and nearly regular) SiO\(_4\) tetrahedra around \( (100)_{\text{hex}} \), combined with translation along \( (100)_{\text{hex}} \). The rotational model has been also used to study dynamic aspects such as the soft modes in the x–β transitions. In fact, many authors since Young (1962) have taken advantage of the simplicity in the rotational model (for instance, Höchli and Scott 1971; Megaw 1973; Grimm and Dorner 1975; Liebau and Böhmi 1982, and others).

Megaw (1973) showed that the rotation of rigid SiO\(_4\) tetrahedra around \( (100)_{\text{hex}} \), from the high symmetry 222 positions produces a reduction of the lattice in both the a- and c-directions. However, she had to introduce a homogeneous reduction of tetrahedral size for improving the agreement with the observed changes of the cell dimensions at higher temperatures. Grimm and Dorner (1975) considered a similar model. Taking account of possible distortions of the tetrahedra, they further refined the model such that the mean Si-O distance within the tetrahedron decreases with increasing temperature (or rotational angles decrease), being associated with the increase of the Si-O-Si angle.
The negative expansion coefficient of the tetrahedra in the Megaw’s (1973) model appears to be consistent with those of the measured Si-O distances in the structure refinements using Bragg diffraction. Grimm and Dorner (1975) refined the model by employing the coordinates of O atoms in the harmonic structure analyses of β-quartz. However, in a more generalized structure refinement of quartz and berlinite, the T-O bond lengths expand with increasing temperature (Kihara 1990; Muraoka and Kihara 1997). The Si-O bond lengths in cristobalite also increase with increasing temperature in a correlation function analysis of neutron powder-scattering intensities (Dove et al. 1997). According to Downs et al. (1992), almost all of the Si-O bond lengths in nine silicates expand with increasing temperature when corrected for tetrahedral libration using a TLS (translational, librational, and screw modes of motion)-rigid-body thermal analysis. All these suggest that the negative expansion of the Si-O bonds in the usual structure refinements using Bragg diffractions is only apparent.

The probability density function (pdf) of an atom in a harmonic crystal may be unimodal with the mode at the minimum of the harmonic potential well. The mode of pdf for an atom is thus located at the position of its mean in harmonic crystals. On the other hand, if atoms undergo anharmonic thermal vibrations, the means are not necessarily at the modes of pdfs. The thermal vibrations of T-O-T bonds in silicates or silicas are typical examples showing librational motions. In the usual harmonic structure refinements of diffraction data, the mean positions of O atoms in these structures may possibly be determined to be those shifted toward the libration axes, T-T (Willis and Pryor 1975), resulting in smaller T-O bond distances than the real ones. Such shifts are expected to become larger with increasing amplitudes of the librational motions at higher temperatures. Indeed, the atomic coordinates obtained in the harmonic structure analyses of quartz (Kihara 1990) showed the Si-O bond lengths becoming smaller with increasing temperatures: the two symmetrically independent Si-O bond lengths of 1.605(2) and 1.614(2) Å at 298 K are reduced to one symmetrically equivalent bond of 1.588(3) Å in β-quartz. Essentially the same feature has also been observed for berlinite (Muraoka and Kihara 1997). On the other hand, the generalized structure analysis, which employs structure factors expanded in higher order terms, is able to locate the modes of pdf more closely to the real positions, from which we can calculate real bond lengths (Johnson 1970). In the anharmonic refinements of quartz and berlinite involving terms up to the fourth order, the separations between the modes of the pdf for bonded Si and O showed values larger than the corresponding distances in the harmonic refinements at high temperatures: 1.620 Å at 848 K and 1.624 Å at 891 K for quartz (Kihara 1990). However, we have experienced in our previous X-ray studies that the determination of anharmonic pdf is easily subjected to deterioration in the quality or reduction in the number of measured intensity data at high temperatures. The above values referring to the separations for the modes are yet to be established.

There have been a number of reported MD studies of the quartz structure. In the extended system (constant temperature and constant pressure) MD study using nonempirical potential parameters, Tsuneyuki et al. (1990) ascribed the dynamical character of β-quartz to cluster dynamics. Tautz et al. (1991) analyzed quantitatively the origin of the incommensurate phase in the MD calculations with 4096 hexagonal unit cells of quartz at different temperatures in the α- and β-phases. Miyake et al. (1998) conducted controlled temperature and pressure MD and discussed details of the change in crystallographic symmetry during the phase transition, using static structure factors calculated based on atom trajectory data.

In addition to these successful studies, we note that real bond lengths and angles are sometimes inaccessible in the usual structure refinements of real crystals, but accessible in MD simulations. It is, of course, possible to calculate the distances and angles for the mean positions of given atoms in the MD system, which are quantities comparable with atomic distances or bond lengths given in the usual structure refinements.

In the present study, constant-temperature and constant-pressure MD simulations were performed on the quartz structure with the three different MD cells of 150, 810, and 1200 hexagonal cells in the α- and β-phases. The cases for 810 and 1200 cells provided almost the same results for the static quantities examined. The mean positions and the distances between those, and the mean-squares displacements of atoms were first calculated from the trajectory data, and then compared with the corresponding X-ray values in the harmonic refinements of Kihara (1990). Next, the distances for Si-O and O-O pairs and the angles of any two given pairs, which may represent real bond lengths and angles, were calculated from the trajectory data. The trajectories of atoms were also used to calculate time-dependent atomic displacement parameters, defined for the displacements measured from the mid-points of x1–x2 lines of the atoms. The characteristic thermal expansion behavior was explained through a combination of dynamical effects represented by the atomic displacement parameters and static effects arising from bond-length expansions. Finally, the structures and their changes are discussed by means of the time series of molar volume or atomic displacement parameters. The structural data appearing in this paper are all from the case for 1200 cells. Since our MD crystal sizes are not large enough even for the largest, we have not considered the incommensurate phase.

**Computer simulation**

The present MD calculations were conducted using the semi-empirical values of the ionic charges and the energy parameters in a two-body potential energy function of the form