MATHEMATICAL MODELING OF THE STRUCTURES AND BULK MODULI OF TX₃ QUARTZ AND CRISTOBALITE STRUCTURE-TYPES, T = C, Si, Ge AND X = O₅

G.V. GIBBS*, M.B. BOISEN, JR.*, R.T. DOWNS* AND A.C. LASAGA 1

*Virginia Polytechnic Institute and State University, Blacksburg, VA 24061
†Yale University, New Haven, CT 06511

ABSTRACT

Models of the oxide and sulfide structure-types of quartz and cristobalite have been made using potential energy surfaces derived from MO calculations on small molecules. The bond length and angle and the volume compressibility data calculated for quartz match those observed for pressures up to 40 kbars. An analysis of the force constants that define the potential energy surface indicates that the bulk modulus of the mineral is governed primarily by the bending force constant of the bridging angle. Similar calculations were completed for the GeO₂ form of quartz, but the agreement with the observed data is somewhat poorer. A modeling of the CO₂ form of quartz predicts that it would be significantly harder, more incompressible and show less expansibility than the SiO₂ form.

INTRODUCTION

A mathematical modeling and a minimum-energy structure determination of a silicate crystal like quartz, SiO₂, at the near-Hartree-Fock level is severely limited by computational effort. For instance, more than 30 CPU hours on a supercomputer were required to complete a comparable modeling and structure determination of a relatively tiny H₃Si₂O₇ disilicate acid molecule (C₃ point symmetry), using molecular orbital (MO) methods. As such a calculation for quartz is far too ambitious at this time [1], mathematical models based on a variety of empirical and theoretical interatomic potentials have been devised for generating structures, volume compressibilities, vibrational spectra and defect properties of silicate crystals. Also, such models have been devised to study the condensation of silicate tetrahedra, reaction energies, diffusion, crystal growth and nucleation, processes that are very difficult to probe and study at the microscopic level (cf. [2] and [3]).

In particular, Catti [4], Parker [5], Price and Parker [6], Miyamoto and Takeda [7] and Matsui and Busing [8] have derived pair-potentials from the structures and compressibility properties of the monosilicate forsterite, Mg₂SiO₄, and several other crystals. With these potentials, not only were these workers able to reproduce the structure and compressibility of forsterite, but they were also able to reproduce those of the spinel polymorph of Mg₂SiO₄. However, when the pair-potential model was applied to a framework silicate like quartz, it did not give accurate results. Not only did the calculation fail to reproduce an accurate SiOSi angle for the structure but, more importantly, it failed to reproduce accurately the variations of the angle and the unit cell volume with pressure. In an attempt to improve the model, the OSi angle bending force constant, the shell model parameters, and the parameters of the SiO short range potential were adjusted by regression methods until the calculated elastic and dielectric properties matched those observed for quartz as well as possible. With this model and with the cell dimensions clamped at values observed at a variety of pressures, Sanders et al. [9] found that the resulting SiOSi angles accurately match those observed for the mineral for pressures up to 28.2 kbars [10]. They also reported that their model reproduces the cell dimensions of the silica polymorphs cristobalite, tridymite and coesite to within 1 to 1.5% and the positional parameters of the Si and O atoms to within 0.10Å of the observed values, but they did not give the results of these calculations. Also, Price et al. [11] found that when their model for forsterite was expanded to include the OSi angle-bending force constant, a set of infrared and Raman spectra could be generated that matched that observed reasonably well.

A number of studies have also been completed using the modified electron gas (MEG)
model which employs theoretical potentials provided by Hartree-Fock wave functions [12]. In a calculation of the minimum-energy structures of the forsterite and spinel polymorphs of Mg$_2$SiO$_4$, Post and Burnham [13] found that this purely ionic model not only reproduces the crystal structures and relative stabilities of these minerals reasonably well, but it also reproduces, at least in part, the observed distortions of the edge sharing SiO$_4$ tetrahedra and MgO$_6$ octahedra.

Equally important, Wolfe and Bukowski [14] and Hemley et al. [15] have used the MEG model to calculate the correct zero pressure perovskite structure-types of MgSiO$_3$ and CaSiO$_3$. They also found that the calculated equation of state for MgSiO$_3$ is in good agreement with experiment. On the other hand, the model has proven unsuccessful in modeling the structure of diopside, CaMg$_2$Si$_2$O$_6$, where oxygen atoms link silicate tetrahedra into single chains of disiloxo SiOSi groups [13]. It has also proven unsuccessful in modeling the structures and stabilities of the quartz and cristobalite structure-types of silica each of which consist of a framework of silicate tetrahedra linked together by disiloxo groups [16]. Not only do these calculations generate structures that are much too incompressible, but they also predict that the low temperature modifications of the minerals should be absent in nature [17]. As the disiloxo groups in these minerals are believed to have appreciable covalent character, Jackson [16] has modified the model to allow for an ad hoc polarization of the bridging oxygen atom along the SiO bond. With this model, Jackson [16] and Jackson and Gibbs [17] found that the structures, volume compressibilities and stabilities of the silica polymorphs quartz, cristobalite and coesite can be modeled considerably better than with the fully ionic MEG model. However, in an unsuccessful attempt to accurately generate the structure of forsterite, Jackson [16] concluded that more complicated polarization models may be required to generate structures having oxygen atoms with coordination numbers greater than 2. Thus, for a case like diopside that has both bridging and nonbridging oxygen atoms with a range of possible coordination numbers, more complicated polarization shell models may be required, one for each nonequivalent SiO bond.

Recently, Lasaga and Gibbs [18] showed that several of the structural properties of low quartz can be reproduced for pressures up to 10 kbars using a crystal molecular mechanics model that employs a potential calculated for a disilicic acid H$_4$Si$_2$O$_7$ molecule with molecular orbital methods. Molecular orbital calculations completed at VPI&SU and in collaboration with others (cf., [19]) have shown that the bond lengths and angles, the deformation densities, and the elastic properties and the vibrational spectra of a molecule like H$_4$Si$_2$O$_7$ mimic those observed for the silica polymorphs like quartz and coesite rather closely [20], [21], [22], [23], [24] and [25]. The success of these calculations suggests that the forces that govern the properties of the disiloxo group in such a molecule are not all that different from those that govern the properties of the group in a silicate crystal like quartz. Further evidence for this assertion has been given by Dovesi et al. [1] who showed, in a periodic LCAO calculation of the electronic structure for a quartz crystal using an STO-3G basis, that the charge density in the group in the vicinity of the bridging oxygens accurately reproduces that calculated for H$_4$Si$_2$O$_7$. In addition, a calculation of the minimum-energy SiO bridging bond length and SiOSi angle for the crystal yielded values (1.605 Å; 133°) that agree with minimum-energy values calculated for the molecule (1.613, 1.624 Å; 129°), with an STO-3G basis and C$_1$ point symmetry. These results suggest that crystal field effects, disregarded in the MO calculations, play a secondary role in governing the structure of a crystal like quartz.

In the Lasaga and Gibbs [18] study of quartz, a set of global force constants used to define the force field in the crystal were found by a least-squares fit to a potential energy surface calculated for H$_4$Si$_2$O$_7$ over a relatively wide range of distortions of bond lengths and angles. We use the term “global” to describe the force constants obtained in this manner because they are designed to describe the potential energy surface over a relatively wide range of bond lengths and angles rather than to describe it at a particular set of bond lengths and angles. With the resulting global force constant (GFC) function, Lasaga and Gibbs [18] found that the structure of low quartz could be reproduced to within 1% using a modified version of the program WMIN [26]. Moreover, they calculated an SiOSi angle and a volume compressibility for the mineral that matched those observed at pressures up to 10 kbars. Using the same GFC function as was used in the quartz calculation, they
also obtained bond lengths and angles for cristobalite that agree to within 2% of those observed. It is important to note that unlike the quartz calculations completed by Sanders et al. [9], the minimum-energy structures derived by Lasaga and Gibbs [18] were obtained by varying all the cell dimensions and the positional parameters of all the non-equivalent atoms in the crystal within the constraints of the observed space group of the mineral. Lasaga and Gibbs [27] have also used GFC functions to study the condensation of silicate tetrahedra and the structures and dynamic properties of the resulting hydroxyacid silicate oligomers.

One drawback of the GFC model is that when the geometry of a molecule of the size of H₄Si₂O₇ is optimized with a more robust basis or with fewer symmetry constraints, the computational effort required to produce enough points to construct the GFC model becomes very expensive. Another drawback is that the potential energy surface obtained by the GFC model is determined by values found for geometries relatively far from the minimum-energy geometry and so is less accurate for applications dealing with geometries close to the minimum energy geometry. To circumvent these problems, we constructed a mathematical model based on instantaneous force constants (IFC) calculated for a molecule at its minimum-energy configuration. Details on how the IFC are calculated are given in the next section. The IFC model of the potential energy surface more faithfully reflects the curvature of the actual potential energy surface near the minimum-energy geometry and requires far fewer calculations than does the GFC model. Consequently, we were able to obtain the IFC from the optimization of the geometry of H₄Si₂O₇ (C₄ point symmetry) at a more robust 3-21G* basis which yields an SiOSi angle of 141.0° in close agreement with that recorded for low quartz (142.4°) at 13 K [28]. With these force constants we undertook a mathematical modeling of the structures and volume compressibilities of quartz and cristobalite. Similar models were also constructed for the quartz and cristobalite structure-typical of CO₂, CS₂, SiS₂ and GeO₃. The results of these calculations will be compared with the available experimental data and used to predict the structures and bulk moduli for such unknown materials as CO₂ with the quartz and cristobalite structures.

THE MATHEMATICAL MODEL

Given a geometric configuration for a crystal, a potential energy function is supposed to yield the energy difference between this configuration and the minimum-energy configuration. The mathematical model used to mimic the quartz and cristobalite TX₂ crystals considered in this study assumes the potential energy function \( V(x) \), \( x = (x_1, x_2, \ldots, x_n)^T \), to be a quadratic function of the nonequivalent internal coordinates \( x_i \): the nonequivalent TX bond lengths and \( XTX \) and \( TXT \) angles each weighted so as to reflect the number of times each appears in the unit cell. Our construction of \( V(x) \) employs the methods of molecular mechanics as they apply to crystals [29]. In such an approach, it is assumed that the minimum-energy internal coordinates and the potential energy function that define the force field of a molecule are transferable and can be used to construct the force field of a chemically similar crystal (with the exception that we have taken the minimum-energy \( XTX \) angles to be 109.47°). This approach is reasonable since, as observed above, the forces that govern the geometry and charge density distribution of a molecule like H₄Si₂O₇ appear to be similar to those in a quartz or cristobalite crystal.

Since \( V(x) \) is assumed to be a quadratic function, with respect to any choice of \( x \), say \( x_0 \), it can be expressed in the form

\[
V(x) = \frac{1}{2}(x - x_0)^T H(x - x_0) + \nabla V(x_0)^T (x - x_0) + V(x_0)
\]

where the Hessian \( H \) and the gradient \( \nabla V \),

\[
H = \begin{pmatrix}
\frac{\partial^2 V}{\partial x_1^2} & \cdots & \frac{\partial^2 V}{\partial x_1 \partial x_n} \\
\vdots & \ddots & \vdots \\
\frac{\partial^2 V}{\partial x_n \partial x_1} & \cdots & \frac{\partial^2 V}{\partial x_n^2}
\end{pmatrix}
\quad \text{and} \quad
\nabla V(x_0) = \begin{pmatrix}
\frac{\partial V}{\partial x_1} \\
\vdots \\
\frac{\partial V}{\partial x_n}
\end{pmatrix},
\]

are given by

\[
\begin{align*}
\frac{\partial^2 V}{\partial x_i \partial x_j} &= \left. \frac{\partial}{\partial x_i} \right| \left. \frac{\partial V}{\partial x_j} \right|_{x_0}, \\
\frac{\partial V}{\partial x_i} &= \left. \frac{\partial V}{\partial x_i} \right|_{x_0}.
\end{align*}
\]
are both evaluated at \( x_0 \). If \( V(x) \) were actually quadratic, then \( H \) would be the same for all values of \( x_0 \). However, our assumption that \( V(x) \) is quadratic is not quite correct and so a different \( H \) should be constructed for each choice of \( x_0 \). In this study, we choose \( x_0 = x_{\text{min}} \), the value associated with the minimum-energy internal coordinate vector provided by the molecular orbital calculations. Consequently, the quadratic expression for \( V(x) \) reduces to

\[
V(x) = \frac{1}{2} (x - x_{\text{min}})^T H (x - x_{\text{min}})
\]

An investigation of the energetics of a crystal that has been distorted significantly from its equilibrium position may require the use of models of \( V(x) \) based on other values of \( x_0 \). As noted above, the calculated values used to construct \( V(x) \) were obtained from the MO calculations made on \( \text{H}_6 \text{T}_2 \text{X}_7 \) molecules whose geometries include representations of each of the internal coordinates used to define \( V(x) \). In each case, the minimum-energy geometry for the molecule was found assuming \( C_{2v} \) symmetry except for \( \text{H}_6 \text{Si}_2 \text{O}_7 \) and \( \text{H}_6 \text{Ge}_2 \text{O}_7 \) where \( C_1 \) symmetry was assumed. To find the entries of the Hessian, we observe that the \( i \)th column of \( H \) is the partial derivative of the gradient with respect to \( x_i \) which can be approximated by

\[
\frac{\Delta V(x_{\text{min}} + \epsilon e_i) - V(x_{\text{min}})}{\epsilon}
\]

where \( e_i \) is the vector consisting of all zeros except in the \( i \)th position in which a one appears and \( \epsilon \) is a small value. Using this finite difference method, the entries of the Hessian were found.

The theoretical structure of the mineral is determined by minimizing the model of the potential energy function. The theoretical cell dimensions and the position parameters of the \( T \) and \( X \) atoms were found in this manner (Tables 1 and 2). Using the resulting

### Table 1: Observed and Calculated Data for Quartz Structure-types

<table>
<thead>
<tr>
<th></th>
<th>SiO₂</th>
<th>GeO₂</th>
<th>CO₂</th>
<th>CS₂</th>
<th>SIS₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>( a(\AA) )</td>
<td>4.929</td>
<td>5.114</td>
<td>4.011</td>
<td>5.232</td>
<td>5.894</td>
</tr>
<tr>
<td>( c(\AA) )</td>
<td>5.319</td>
<td>5.426</td>
<td>4.214</td>
<td>5.307</td>
<td>5.944</td>
</tr>
<tr>
<td>( x(T) )</td>
<td>0.464</td>
<td>0.450</td>
<td>0.448</td>
<td>0.431</td>
<td>0.428</td>
</tr>
<tr>
<td>( x(X) )</td>
<td>0.414</td>
<td>0.406</td>
<td>0.404</td>
<td>0.390</td>
<td>0.388</td>
</tr>
<tr>
<td>( y(X) )</td>
<td>0.276</td>
<td>0.300</td>
<td>0.306</td>
<td>0.334</td>
<td>0.337</td>
</tr>
<tr>
<td>( z(X) )</td>
<td>0.109</td>
<td>0.086</td>
<td>0.081</td>
<td>0.049</td>
<td>0.044</td>
</tr>
<tr>
<td>( R(TX) )</td>
<td>1.63</td>
<td>1.74</td>
<td>1.37</td>
<td>1.88</td>
<td>2.13</td>
</tr>
<tr>
<td>( R(TX) )</td>
<td>1.61</td>
<td>1.72</td>
<td>1.37</td>
<td>1.88</td>
<td>2.13</td>
</tr>
<tr>
<td>( lTXT )</td>
<td>141.0</td>
<td>131.7</td>
<td>129.8</td>
<td>118.1</td>
<td>116.5</td>
</tr>
<tr>
<td>( K_0(Mb) )</td>
<td>0.492</td>
<td>0.506</td>
<td>0.921</td>
<td>0.382</td>
<td>0.166</td>
</tr>
</tbody>
</table>

### Table 2: Observed and Calculated Data for Cristobalite Structure-types

<table>
<thead>
<tr>
<th></th>
<th>SiO₂</th>
<th>GeO₂</th>
<th>CO₂</th>
<th>CS₂</th>
<th>SIS₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>( a(\AA) )</td>
<td>4.973</td>
<td>5.146</td>
<td>4.033</td>
<td>5.232</td>
<td>5.888</td>
</tr>
<tr>
<td>( c(\AA) )</td>
<td>6.627</td>
<td>6.609</td>
<td>6.097</td>
<td>6.126</td>
<td>6.806</td>
</tr>
<tr>
<td>( x(T) )</td>
<td>0.312</td>
<td>0.329</td>
<td>0.332</td>
<td>0.354</td>
<td>0.357</td>
</tr>
<tr>
<td>( x(X) )</td>
<td>0.234</td>
<td>0.225</td>
<td>0.223</td>
<td>0.207</td>
<td>0.204</td>
</tr>
<tr>
<td>( y(X) )</td>
<td>0.123</td>
<td>0.155</td>
<td>0.163</td>
<td>0.207</td>
<td>0.214</td>
</tr>
<tr>
<td>( z(X) )</td>
<td>0.192</td>
<td>0.212</td>
<td>0.216</td>
<td>0.250</td>
<td>0.256</td>
</tr>
<tr>
<td>( R(TX) )</td>
<td>1.61</td>
<td>1.72</td>
<td>1.37</td>
<td>1.88</td>
<td>2.13</td>
</tr>
<tr>
<td>( R(TX) )</td>
<td>1.61</td>
<td>1.74</td>
<td>1.37</td>
<td>1.88</td>
<td>2.13</td>
</tr>
<tr>
<td>( lTXT )</td>
<td>141.0</td>
<td>131.7</td>
<td>129.8</td>
<td>118.1</td>
<td>116.5</td>
</tr>
<tr>
<td>( K_0(Mb) )</td>
<td>0.292</td>
<td>0.265</td>
<td>0.536</td>
<td>0.206</td>
<td>0.078</td>
</tr>
</tbody>
</table>
unit cell volume as the zero pressure volume, \( V_0 \), the energy is minimized once again with the volume constrained at a selected value, \( V \). Since the model is for \( 0 \) \( K \), the resulting increase in energy is attributed to pressure and is converted into pressure units. We use this volume-pressure function to calculate the theoretical bulk modulus employing the finite difference method. It is noteworthy that the \( V/V_0 \) vs. \( P \) (volume compressibility) data calculated with our model fit an equation of the Birch-Murnaghan form almost exactly. In addition, the resulting zero pressure bulk moduli obtain by the finite difference method are the same as those provided by fitting the Birch-Murnaghan equation to the calculated volume compressibility data. All software used to complete these calculations was written by the authors to be run on a PC.

**MATHEMATICAL MODELING OF THE STRUCTURE AND VOLUME COMPRESSIBILITY OF LOW QUARTZ**

As a test of our mathematical model for silica, we calculated the minimum energy cell dimensions and positional parameters of Si and O for low quartz, assuming the bond lengths and angles and space group \( P3_121 \) observed by Lager et al. [28]. The calculation generated a set of values that agree to within 0.0005\( \AA \) of those observed. However, this calculation does not in itself test whether our model faithfully mimics the force field in quartz. An important test of the model will be provided by the accuracy with which it reproduces the structure of the mineral as a function of pressure.

In undertaking this test, we used the model to calculate the zero pressure structure for quartz using the minimum-energy bridging SiO bond lengths and the SiOSi angle calculated for the \( \text{H}_2\text{Si}_2\text{O}_7 \) molecule. A comparison is made in Table I of the observed and calculated positional parameters of Si and O and the bond lengths and angles, where it is seen that calculated coordinates of the atoms and bond lengths agree with those observed to within 0.02\( \AA \) on average. As the accuracy of the calculated bond lengths for \( \text{H}_2\text{Si}_2\text{O}_7 \) are of the same order of magnitude, we consider the agreement between the two results to be as good as can be expected. Next we constrained the unit cell volume of the mineral to a specific value \( V \) and used the model to find the minimum-energy cell dimensions and atomic positions for that volume.

![Figure 1: A comparison of the volume compressibility data observed for quartz with that calculated in this study.](image-url)
The structure and the volume compressibility of low quartz have been carefully measured by a number of workers at several pressures including some in excess of 60 kbars. Figure 1 shows that the compressibility data calculated for quartz fall well within the scatter of the observed data at pressures up to 40 kbars [30]. At higher pressures the model calculations show an incipient softening of the structure in excess of that observed (see also Fig. 2(a)). The isothermal bulk modulus, \( K_0 \), of low quartz measured (at \( P \approx 0 \)) by several workers (see Table 6 in [30]) shows a range of values from 0.365 Mb to 0.445 Mb with an average value of 0.379 Mb. Using the finite difference method, our model gives a \( K_0 \) value (0.493 Mb) which is 30% larger than the average observed \( K_0 \)-value. This is not unexpected because quadratic force constants provided by MO calculations are usually larger than observed values corrected for anharmonicity and because the OSiO and SiOSi bending force constants used in our model were constrained to be independent of the magnitudes of the angles.

Figure 2: A comparison of the observed (open circles) and calculated (solid circles) variation of the unit cell volume vs. pressure for (a) quartz structure-types and (b) cristobalite structure-types.

The SiO bond lengths in quartz and other silica polymorphs are observed to shorten, on average, by 0.008 Å when subjected to a pressure of 37.5 kbars in almost exact agreement with the shortening generated by our model [31]. The model also gives an SiO bond compressibility of \( 1.37 \times 10^{-4} \) kbars\(^{-1} \) and an SiO\(_4\) polyhedra bulk modulus of 2.43 Mb for quartz. These values agree to within 3% of those \( (1.33 \times 10^{-4} \) kbars\(^{-1}; 2.51 \) Mb\) obtained in a regression analysis of bond length and angle data for the silica polymorphs.
Figure 3(a) compares the variation of the SiOSi angle in quartz measured as a function of pressure at room temperature with that provided by the model calculations. The observed angles are 2 to 3 degrees wider than those calculated. In addition, the slope of the line defining the observed data is somewhat steeper than that calculated indicating that the SiOSi bending force constant used in our model is too large. However, as the structural analyses on quartz were made at room temperature and as the model generates a 0 K structure with no thermal motion, the differences displayed in Figure 3(a) are not unexpected (see [28]).

The large change in the SiOSi angle and the small changes in the SiO bond lengths and OSiO angles with pressure suggest that the $K_0$-value observed for quartz depends in large part on the force constant of the SiOSi angle. Since, in our model, $K_0$ is a function of the force constants, we tested this assertion by determining the derivatives of $K_0$ with respect to the force constants of the SiO bond, the SiOSi angle and the OSiO angle by the finite difference method. The resulting derivatives obtained by this method are:

$$\frac{\partial K_0}{\partial f_R} = 170, \quad \frac{\partial K_0}{\partial f_s} = 1580, \quad \text{and} \quad \frac{\partial K_0}{\partial f_\theta} = 40$$

where $f_R, f_s, f_\theta$ are the force constants of the SiO bond and the SiOSi and OSiO angles, respectively. When adjusted for the magnitudes of the force constants, the relative changes in the bulk modulus with respect to the force constants are 77, 297 and 15 kbars, respectively. Thus, for our model, the force constant of the SiOSi angle is the dominant one in governing the bulk modulus of quartz. This result agrees with the assertion made by Weidner and Simmons [32] that the SiO force constant has little effect on $K_0$.

GeO$_2$ is also known to crystallize with the quartz structure. Moreover, its structure has been determined at room temperature for pressures up to 22.1 kbars [10]. Using a mathematical model defined by the bond length and angle data and the IFC's calculated for H$_2$Ge$_2$O$_7$, a zero pressure structure was calculated for the quartz modification of GeO$_2$. The cell dimensions, the bond lengths and angles, and the positional parameters of Ge and O obtained in the calculation are compared in Table 1 with those determined by
Jorgensen [10]. Despite the large number of wave functions required to define the \( \text{H}_6\text{Ge}_3\text{O}_7 \) molecule, the calculated positions of Ge and O in \( \text{GeO}_3 \) are within 0.02\( \text{Å} \), on average, of those observed. The \( V \) vs. \( P \) curve calculated for \( \text{GeO}_3 \) is approximately parallel with that observed but, for a given pressure, the calculated volume is 2 to 3\( \text{Å}^3 \) larger than observed (Figure 2(a)). A determination of the bulk modulus for the calculated \( V \) vs. \( P \) data yielded a value (0.507 Mb) that is, as noted above for quartz, 30\% larger than that observed (0.391 Mb; [10]). The observed and calculated variations of the GeOGe angle are compared in Figure 3(b) where it is seen that the calculated angle, contrary to expectation, is 2 to 3 degrees wider than that observed. As in the case of quartz, however, the calculated angle is indicated to be somewhat stiffer than that observed.

**MODELING OF THE STRUCTURE OF LOW CRISTOBALITE**

The same Hessian matrix and bond lengths and angles used to generate the structure and bulk modulus of quartz were used to generate the structure of low cristobalite since both are polymorphs of silica. The results of the 0 pressure calculation are compared in Table 2 with those measured for low cristobalite at 10 K and 1 atm. [33]. An examination of the bond lengths and the positional parameters of the atoms in the crystal show that the two data sets agree to within 0.03\( \text{Å} \). However, because the optimized SiOSi angle assumed in the model is about 4 degrees narrower than observed, the c-cell edge calculated for the crystal is 0.26\( \text{Å} \) shorter than observed. As the structure of cristobalite has not, to our knowledge, been determined as a function of pressure, this provides us with an opportunity to undertake such structural analyses. A plot of the calculated \( V \) vs. \( P \) data indicates that the bulk modulus of cristobalite should be significantly smaller than that of quartz (Figure 2b). On the other hand, for a given volume compressibility, the calculations indicate that the SiOSi angle in cristobalite changes less than it does in quartz (see [34] and [18]).

**MODELING OF QUARTZ AND CRISTOBALITE STRUCTURE-TYPES WITH CO\(_2\), CS\(_2\), SiS\(_2\) AND GeO\(_2\) COMPOSITIONS**

One question that we might ask at this point is “Why should we want to develop a mathematical model for a framework crystal like quartz when its structure and volume compressibility have been accurately determined a number of times by diffraction methods?”. One answer to this question has to do with the prediction of the structures and properties of new materials. For example, a mathematical model like the one that yields an accurate structure for quartz at high pressures may also yield an accurate prediction of the structure and elastic properties of a new modification of CO\(_2\) with the quartz structure. The calculations should also provide insight into whether the material will be of lower expansibility and harder than quartz. Besides, it is interesting to speculate on the basis of these calculations whether a CO\(_2\) glass would be more incompressible, of lower expansibility and harder than silica glass.

To our knowledge, CO\(_2\), CS\(_2\) and SiS\(_2\) have never been synthesized with the quartz and cristobalite structures nor has GeO\(_2\) been synthesized with the cristobalite structure. In light of our success in reproducing (1) the zero pressure quartz structures of SiO\(_2\) and GeO\(_2\), (2) the zero pressure cristobalite structure of SiO\(_2\) and (3) the volume compressibilities of the quartz modifications of SiO\(_2\) and GeO\(_2\), we have undertaken structural analyses of quartz modifications of CO\(_2\), CS\(_2\), and SiS\(_2\) and cristobalite modifications of GeO\(_2\), CO\(_2\), CS\(_2\) and SiS\(_2\) as a function of pressure (Tables 1 and 2; Figure 2). It is anticipated that the systematics provided by these calculations and the ones described above will improve our understanding of the role played by the structure in determining the bulk moduli of such framework structures.

**DISCUSSION**

In a study of the bulk modulus-volume relationships for close-packed isostructural
oxide crystals, Anderson and Nafe [35] showed that $K_0$ correlates with the specific volume, $V_S$ (= volume per ion pair), the argument being, the smaller the specific volume for a given bond-type, the greater the density of bonds and the greater the bulk modulus of the crystal. If the bulk moduli and structures generated in this study are realistic, we may expect that the data provided by our calculations will show a similar relationship. Thus, for a given type of $TX$ bond and $TXT$ and $XTX$ angles like those in quartz and cristobalite, we may expect that the bulk modulus of quartz will be greater than that of cristobalite because quartz is denser of the two. The bulk moduli calculated for the quartz and cristobalite $TX_2$ structures conform with this expectation with the $K_0$-values calculated for the cristobalite structure-types being about half those calculated for the quartz structure-types. Also, a plot of log($K_0$) vs. $V_S$ for the $TX_2$ crystals described in Table 1 shows two trends, the upper one for the quartz structure-types and the lower one for the cristobalite structure-types, with $K_0$ decreasing exponentially with increasing $V_S$ (Figure 4a). Anderson and Nafe [35] have observed for a number of close-packed oxide crystals that $K_0V_S = constant$. However this relationship does not hold for the more open framework structures calculated in our study.

![Figure 4: Variation of log($K_0$) vs. (a) the calculated specific volume, $V_S$, and (b) the average $TX$ bond length, $<TX>$ for quartz (upper curves) and cristobalite (lower curves) structure-types. The units of $K_0$ are kbars.](image)

Newnham [36] has observed for isostructural materials that bulk modulus increases with increasing valence and decreasing bond length. As the valence is constant in the $TX_2$ crystals studied, we may expect that the bulk moduli for both the quartz and cristobalite structure types will increase as their mean $TX$ bond lengths, $<TX>$, decrease. A plot of log($K_0$) vs. $<TX>$ for the two structure-types conforms with this generalization (Figure 4b). For example, the CO$_2$ modifications of quartz and cristobalite have the shortest bond lengths and are predicted to be the least compressible of two structure-types. In fact, the SiO$_2$ form of quartz is predicted to be twice as compressible as the CO$_2$ form. Also, as is typical of sulfides, the SiS$_2$ forms of quartz and cristobalite, both of which have a relatively long (SiS) bond length, are predicted to be considerably more compressible than the SiO$_2$ forms.

The results of these calculations suggest that the CO$_2$ form of quartz will be more incompressible than the SiO$_2$ form. Thus, we may expect that the CO$_2$ form will have lower expansibility and be harder than that of the SiO$_2$ form [36]. The synthesis of the CO$_2$ form of quartz using starting materials containing the carbonate CO$_3^{2-}$ anion have in the past resulted in failure. It may be possible, however, to synthesize such a crystal from a starting material that contains the CO$_3^{2-}$ anion. The presence of this anion as well as the presence of COC groups in tetramethoxymethane [37] shows that the building blocks of the CO$_2$ form of quartz can be formed. Efforts are currently underway to form such a starting material that may be used to synthesize a new class of carbonates with 4-coordinate C analogous to silicates with 4-coordinate Si.

Finally, in the modeling of the framework structures described in this review, an extremely simple model was used. For example, we assumed that these structures possess
regular $T_X^4$ tetrahedra at $P = 0$, and that the off-diagonal entries in the Hessian matrix corresponding to the $XTX$ angles are zero. We also assumed that the force fields in these crystals can be described by a single Hessian matrix whose elements were evaluated at the optimized geometry of an $H_6T_2X_7$ molecule. Despite these assumptions, the calculations completed for quartz yield a volume compressibility curve for the mineral that matches that observed well within the accuracy of the molecular orbital calculation on $H_4Si_2O_7$.

Our next goal is to apply the model to the generation of the structures of coesite, keatite and the silica analogs of the zeolites. Also we plan to improve the potential energy function by combining a family of models centered at points in the neighborhood of the minimum-energy geometry using Equation 1. It is anticipated that such a model will reproduce the structures of a variety of framework silicates and their elastic and dynamic properties at a number of pressures and temperatures and will provide new insights into the relative stabilities of these materials in terms of their secondary building units [38], [39].

ACKNOWLEDGEMENTS

We are pleased to thank the National Science Foundation for supporting this work with Grant EAR 82-18743 for studying bonding in minerals. We also wish to thank C. G. Lindsay for his careful reading of the manuscript and his helpful comments, Sharon Chang for drafting the figures and Dr. C. Jeffrey Brinker for inviting us to present this paper at the Material Research Society Symposium: Better Ceramics Through Chemistry.

REFERENCES

26. W. R. Busing, WMIN, a computer program to model molecules and crystals in terms of potential energy functions. ORNL-5747, Oak Ridge National Laboratory, Oak Ridge, TN (1972).
32. Weidner and Simmons, J. Geophys. Res. 77, 826 (1972).