Packing systematics of the silica polymorphs: The role played by O-O nonbonded interactions in the compression of quartz

RICHARD M. THOMPSON* AND ROBERT T. DOWNS

Department of Geosciences, University of Arizona, Tucson, Arizona 85721-0077, U.S.A.

ABSTRACT

The anion skeleton of quartz is a distorted body-centered cubic (BCC) arrangement. A hypothetical ideal BCC crystal structure for quartz has been derived and used to locate and describe the unoccupied tetrahedral sites, quantify the distortion of the quartz anion arrangement from ideal BCC, and characterize the role of tetrahedral distortion and O-O interactions in the compression of quartz. Quartz has eight crystallographically nonequivalent tetrahedra, one occupied by silicon and seven unoccupied. These tetrahedra completely fill space, something that cannot be done using only regular tetrahedra. In ideal BCC quartz, the nonequivalent tetrahedra are identical in size and shape with a unique geometry and are referred to as Sommerville tetrahedra. In reality, the unoccupied tetrahedra of quartz are very distorted from both regular and Sommerville tetrahedra. Changes in the unoccupied tetrahedra are responsible for most of the compression in quartz with pressure, as the volume of the Si tetrahedron decreases by <1% over 10.2 GPa, but the volume of the bulk structure decreases by almost 16%. The ideal BCC quartz has been used to quantify the distortion from ideal BCC of the O arrangement in quartz at several pressures up to 10.2 GPa. Distortion decreases by over 60% across this domain. Other parameters have been derived to quantify the distortion of the unoccupied and occupied tetrahedra in quartz from Sommerville tetrahedra, the characteristic tetrahedra of BCC. By all measures, the anion packing in quartz approaches ideal BCC as pressure increases. The compression mechanisms of quartz are compared to those of cristobalite and coesite. Si-O-Si angle-bending controls compression in each of these minerals. The bulk moduli of these minerals are shown to correlate with average nearest inter-tetrahedral anion distances, consistent with the hypothesis that anion-anion interactions stiffen the Si-O-Si angle as inter-tetrahedral anion distances decrease. The tetrahedral distortion in quartz with pressure is attributed to anion-anion interaction, and is not considered a compression mechanism.

Keywords: Quartz, high pressure, body-centered cubic, packing

INTRODUCTION

Quartz is an important Earth material that may constitute approximately 20% of the upper continental crust (Taylor and McLennan 1985). The simple chemistry and well-characterized structure of this mineral make it an excellent material to experiment on and theorize about, and the results can provide valuable insight into more complex materials. Quartz is composed solely of corner-sharing SiO4 tetrahedra, a primary building block of many of the Earth’s crustal and mantle minerals, lunar and martian minerals, and meteoritic minerals (Deer et al. 1978). Quartz is therefore an outstanding model material for investigating the response of this fundamental structural unit to changes in P, T, and x. These facts have spawned a vast literature of experimental and theoretical studies of quartz at ambient and non-ambient conditions. Investigations into the behavior of quartz at high pressure have revealed an anomalous distortion in the silica tetrahedra with pressure not typically seen in other silicates. The present study is motivated by the desire to understand the unusual changes in the silicate tetrahedra of quartz with pressure.

Jorgensen (1978) conducted the first high-pressure structure refinements on quartz using data collected by powder neutron diffraction to 2.8 GPa. He listed three possible compression mechanisms: Si-O-Si angle-bending, tetrahedral distortion, and Si-O bond compression, concluding that Si-O-Si angle-bending makes the greatest contribution to the compression of quartz, tetrahedral distortion is also important, but the effect of bond compression is minimal. d’Amour et al. (1979) reported the first structure refinements from single-crystal X-ray diffraction. Reaching pressures of 6.8 GPa, they concluded that the observed compression could be accounted for by Si-O-Si angle-bending alone. Levien et al. (1980) compressed quartz to 6.1 GPa, collecting much more precise data than the earlier studies. In addition to angle-bending, they determined that there was a small component of bond compression, the magnitude of which lay within the error of the less precise earlier studies, and they verified the tetrahedral distortion mechanism of Jorgensen (1978). They further noted that the rate of change of distortion increased with pressure, making this mechanism more important at higher pressures. Ogata et al. (1987) saw similar trends at simultaneous high pressure and temperature. Hazen et al. (1989) compressed quartz to 15.3 GPa, interpreting irreversible crystal degradation as evidence of amorphization at the highest pressure. Discounting the role of bond compression in quartz, they attributed all volume decrease to angle-bending. They observed extreme distortion of the tetrahedra, but did not consider...