American Mineralogist, Volume 80, pages 454–456, 1995

H in rutile-type compounds: II. Crystal chemistry of Al substitution in H-bearing stishovite

JOSEPH R. SMYTH, R. JEFFREY SWOPE
Department of Geological Sciences, University of Colorado, Boulder, Colorado 80309-0250, U.S.A.
ALISON R. PAWLEY
Department of Chemistry and Biochemistry, Arizona State University, Tempe, Arizona 85287, U.S.A.

ABSTRACT

The crystal structures of a synthetic H-bearing aluminous stishovite, containing approximately 1.6 wt% Al_2O_3, and a pure-silica stishovite have been refined from three-dimensional, single-crystal X-ray diffraction data. The space group of both is $P4_2/mnm$, and the unit cell parameters of the aluminous crystal are $a = 4.1839(8)$ and $c = 2.6684(6)$ Å, which are slightly larger than those of pure silica [$a = 4.1773(4)$ and $c = 2.6652(2)$ Å]. The Al-bearing octahedron is slightly larger and more regular than that of pure-silica stishovite. Unit cell and atom position refinement are consistent with 1.6% substitution of Al for Si. The observation of 1.9% Al substitution for $^{[6]}$Si, even without clear charge balance, is evidence that this substitution may be significant in many lower mantle silicate phases.

INTRODUCTION

Rossman and Smyth (1990) reported significant quantities of H in Fe-bearing rutile of mantle origin and speculated that isostructural stishovite might similarly accept H charge-balanced by minor amounts of Al. H substitution in rutile has been recently reviewed by Vlassopoulos et al. (1993). Pawley and Holloway (1992) and Pawley et al. (1993) reported the synthesis of stishovite in the presence of alumina and H_2O with up to 2.0 wt% alumina and 500 ppm OH^- at 10 GPa and 1200 °C. To observe the effects of this substitution on crystal structure and molar volume, we have compared the refined crystal structure of the aluminous material with that of the pure-silica stishovite.

EXPERIMENTAL METHODS

The grain size of the synthesized aluminous stishovite was small, with acicular crystals ranging up to 150 μm in length but typically <20 μm in cross section. A small prismatic crystal measuring 20 × 20 × 100 μm was selected for study and mounted on a glass fiber. The crystal was placed on a Siemens four-circle automated diffractometer equipped with a rotating-anode X-ray generator operating at 15 kW. The unit cell edges were refined from centering parameters of 18 reflections with 2θ ranging from −40 to 40°. The cell edges (Table 1) are significantly larger than those of pure-silica stishovite (Hill et al., 1983).

For comparison, an equant crystal of pure-silica stishovite measuring 80 × 80 × 100 μm was selected for study and mounted on a glass fiber. The crystal was centered on the Siemens four-circle automated diffractometer operating at 10 kW. The unit cell edges were refined from centering parameters of 20 reflections with 2θ ranging from 15 to 40°, plus their negative 2θ equivalents. Prior to cell measurement, the instrument goniometer and monochromator were carefully aligned, and the unit cell parameters of a standard ruby sphere were reproduced to about one part in ten thousand.

In addition, a very large equant crystal of pure-silica stishovite measuring 800 × 800 × 1000 μm was selected for study, mounted on a glass fiber, and placed on the Siemens four-circle automated diffractometer. The unit cell edges were refined from centering parameters of 22 reflections with 2θ ranging from 95 to 110°. The cell edges (Table 1) are in very good agreement with those determined for the smaller crystal of pure-silica stishovite. The ambient instrument temperature during all measurements was 24 ± 1 °C.

REFINEMENT

For the aluminous crystal, X-ray intensities were measured over one octant of reciprocal space with $2\theta < 60°$. The very small size of the crystal (approximately 0.1 μg) effectively restricted observable data to less than about 60° 2θ. This yielded 100 observations, of which 45 were unique and 37 had intensities greater than three times the standard deviation of the count rate. The data were corrected for Lorentz and polarization effects but not for absorption. Variation in absorption was calculated to be less than about 2% for this very small crystal. The O-position parameter and anisotropic displacement factors were refined by full-matrix least-squares methods using the program package SHELLXTL. The final R for all reflections was 0.035. Positional and displacement parameters are given in Table 2 and selected interatomic distances and coordination polyhedron volume and

0003–004X/95/0506–0454$02.00

TABLE 1. Unit cell parameters of aluminous and pure-silica stishovite

Sample	a (Å)	c (Å)	V (Å^3)
This work			
Aluminous stishovite	4.1839(8)	2.6684(6)	47.710(12)
Pure-silica stishovite (lg. crystal)	4.1767(11)	2.6662(10)	46.511(20)
Pure-silica stishovite (sm. crystal)	4.1773(4)	2.6652(2)	46.507(4)
Previous studies (pure-silica stishovite)			
Hill et al. (1983)	4.1773(1)	2.6655(1)	46.512(2)
Sinclair and Ringwood (1978)	4.1772(7)	2.6651(4)	46.503(10)
Ross et al. (1990)	4.1801(6)	2.6678(6)	46.615(16)
Sugiyama et al. (1987)	4.1797(2)	2.6669(1)	46.591(3)

distortion parameters in Table 3. Electrostatic site potentials were computed from a full-valence point-charge model by the method outlined by Smyth (1989).

For the pure-silica crystal, X-ray intensities were measured over one octant of reciprocal space with $2\theta < 90°$. This yielded 846 observations, of which 145 were unique and 144 had intensities greater than three times the standard deviation of the count rate. The O-position parameter and anisotropic displacement factors were refined by full-matrix least-squares methods using the program package SHELLXTL. The final R for all reflections was 0.025. The isotropic extinction parameter was fairly large for this crystal and converged to a value of 0.25(3), which is not inconsistent with previous studies (Spackman et al., 1987; Hill et al., 1983). Positional and displacement parameters are given in Table 2 and selected interatomic distances and coordination polyhedron parameters in Table 3. The positional of the O atom is identical to that previously determined (Hill et al., 1983).

DISCUSSION

The cell edges of both of the pure silica samples (Table 1) are in excellent agreement with those previously determined for pure-silica stishovite by Hill et al. (1983) and Sinclair and Ringwood (1978) using single-crystal methods on samples synthesized at 9 GPa and 700 °C. Curiously, the single-crystal unit cell parameters reported by Sugiyama et al. (1987) and Ross et al. (1990) are all significantly larger than those observed here or by Sinclair and Ringwood (1978) and Hill et al. (1983). The sample studied by Ross et al. (1990) was synthesized at 15 GPa and 1650 °C in the presence of H_2O and that by Sugiyama et al. (1987) at 12 GPa and 1300 °C in the presence of a lithium tungstate flux. The methods for all these single-crystal cell determinations appear to be similar (i.e., high-angle data with Mo $K\alpha_1$ and $K\alpha_2$ resolved), and so the parameter differences are not likely to be due to X-ray instruments or methods. Also, the differences are consistent, with two samples being slightly larger in both dimensions by about one part in one thousand (six to ten times σ). One possible explanation for the discrepancy might be that the samples studied by Ross et al. (1990) and Sugiyama et al. (1987), having been synthesized at rather high temperature and in the presence of a lithium tungstate flux, respectively, might have contained more point defects than those synthesized at lower temperatures and pressures.

TABLE 3. Selected interatomic distances

	Aluminous stishovite	Pure-silica stishovite sm. crystal	Pure-silica stishovite*
O-O (Å)	2.528(6)	2.5211(8)	2.5216(4)
O-O (Å)	2.668(6)	2.6652(2)	2.6655(1)
O-O (Å)	2.306(5)	2.2933(8)	2.2912(4)
Si-O (Å) × 4	1.763(3)	1.7580(6)	1.7571(4)
Si-O (Å) × 2	1.806(4)	1.8071(6)	1.8096(4)
⟨M1-O⟩ (Å)	1.777	1.774	1.775
V (Å^3)	7.406	7.364	7.365
OAV	25.32	26.8	27.1
OQE	1.0074	1.0079	1.0080
Point-Charge Potential (V)			
Si	−49.26	−49.36	−49.36
O	28.55	28.61	28.61

* Hill et al. (1983).

The unit cell volume of the aluminous sample is substantially greater than that of pure-silica stishovite. If we assume a 2% molar substitution of $HAlO_2$ and extrapolate a linear volume increase to that of pure $HAlO_2$, we obtained a cell volume of 105 Å^3 for $HAlO_2$. This gives a molar volume of 31.6 cm^3 and a density of 1.90 g/cm^3 for this hypothetical end-member. The extrapolation, of course, results in estimates that could be in error by 50% or more. Also, the H content of this sample is much less than that required to charge balance the Al content, so there are probably some octahedral cation site vacancies, which must also contribute to the apparent increase in polyhedral volume.

Stishovite is isostructural with rutile (TiO_2) (see Swope et al., 1995), cassiterite (SnO_2), and pyrolusite (MnO_2) as well as sellaite (MgF_2). There is one octahedral cation position (Wyckoff notation 2a) located at the origin and

TABLE 2. Final positional and displacement parameters for aluminous and pure-silica stishovite

Atom	x	y	z	U_{eq}	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Aluminous stishovite										
Si	0	0	0	0.0054(7)	0.0077(12)	0.0077(12)	0.0009(13)	0	0	0.0006(12)
O	0.3052(9)	0.3052(9)	0	0.0059(11)	0.0089(19)	0.0089(19)	0.0001(19)	0	0	0.0017(20)
Pure-silica stishovite (MA-27)										
Si	0	0	0	0.0017(2)	0.0014(3)	0.0014(3)	0.0021(4)	0	0	0.0001(2)
O	0.3059(2)	0.3059(2)	0	0.0021(2)	0.0018(3)	0.0018(5)	0.0028(6)	0	0	−0.0009(4)

the body center of the tetragonal cell. There is one O at the 4*f* position, which coordinates the cation in a moderately distorted octahedron with point symmetry *mmm*. The octahedra share edges to form corner-linked, edge-sharing chains parallel to **c**. The shared octahedral edge is very short at approximately 2.29 Å, whereas the other edges range from 2.52 to 2.67 Å. Of the six cation-O distances, two are long at 1.81 and four are shorter at 1.76 Å. Calculated interatomic distances, polyhedral volumes, and distortion parameters are given in Table 3. Also given in Table 3 are electrostatic site potentials for the Si and O positions using the methods outlined by Smyth (1989).

The observed mean cation-O distance for the Al-bearing stishovite (1.763 Å) is slightly larger than that of pure-silica stishovite. If the average Al-O distance in the pure Al octahedra in the aluminosilicate minerals reviewed by Smyth and Bish (1988) is taken as 1.905 Å, then the observed increase in the cation-O distance of the aluminous stishovite over that of pure silica is consistent with 1.5% occupancy by Al. If the average polyhedral volume of Al octahedra is taken as the average volume of the Al octahedra in the aluminosilicate minerals, 9.091 $Å^3$ (Smyth and Bish, 1988), then the observed increase in polyhedral volume in the aluminous stishovite is consistent with 2.3% Al occupancy. From the refinement, it is clear that the Al is substituting for Si in the octahedral site, which results in a slight increase in the bond distances and volume of the site.

Further, it is interesting that Al substitution increases the regularity of the octahedral site. Relative to pure-silica stishovite, the very short O-O distance is longer, the short Si-O distance is longer, and the long Si-O distance is shorter. Although we cannot locate the H position directly from these data, the observed changes in interatomic distances and the observed polarization of the O-H stretching vibration are consistent with its being at a position similar to that found in rutile (Swope et al., 1992, 1995), near the very short shared edge of the octahedron.

The anisotropic and calculated isotropic displacement factors of both atoms in the aluminous structure are larger than those of pure-silica sample by about a factor of three. This might be due to a larger number of point defects (cation vacancies), increased positional disorder in the atoms owing to Al substitution, or the smaller $2\theta_{max}$ of the aluminous sample relative to that of the pure-silica sample.

These results indicate that Al can substitute for Si in significant quantities in octahedral sites under mantle conditions, and that $MgSiO_3$ perovskite is likely to contain at least minor amounts of substituted $^{[6]}Al$ in a pyrolite-composition lower mantle.

Acknowledgments

This work was supported by the U.S. Department of Energy Office of Basic Energy Sciences grant DE-FG02-92ER14233 to J.R.S. X-ray facilities at the University of Colorado were supported by the National Science Foundation grant EAR-9105340.

References cited

Hill, R.J., Newton, M.D., and Gibbs, G.V. (1983) A crystal-chemical study of stishovite. Journal of Solid State Chemistry, 47, 185–200.

Pawley, A.R., and Holloway, J.R. (1992) Stishovite in water in stishovite: A solubility study. Eos, 73, 521.

Pawley, A.R., McMillan, P.F., and Holloway, J.R. (1993) Hydrogen in stishovite with implication for mantle water contents. Science, 261, 1024–1026.

Ross, N.L., Shu, J.-F., Hazen, R.M., and Gasparik, T. (1990) High-pressure crystal chemistry of stishovite. American Mineralogist, 75, 739–747.

Rossman, G.R., and Smyth, J.R. (1990) Hydroxyl contents of accessory minerals in mantle eclogites and related rocks. American Mineralogist, 75, 775–780.

Sinclair, W., and Ringwood, A.E. (1978) Single crystal analysis of the structure of stishovite. Nature, 272, 714–715.

Smyth, J.R. (1989) Electrostatic characterization of oxygen sites in minerals. Geochimica et Cosmochimica Acta, 53, 1101–1110.

Smyth, J.R., and Bish, D. L. (1988) Crystal structures and cation sites of the rock-forming minerals, 332 p. Allen and Unwin, London.

Spackman, M.A., Hill, R.J., and Gibbs, G.V. (1987) Exploration of structure bonding in stishovite with Fourier and pseudoatom refinement methods using single crystal and powder X-ray diffraction data. Physics and Chemistry of Minerals, 14, 139–150.

Sugiyama, M., Soichi, E., and Koto, K. (1987) The crystal structure of stishovite under pressure up to 6 GPa. Mineralogical Journal, 13, 455–466.

Swope, R.J., Smyth, J.R., and Larson, A.C. (1992) Crystal chemistry of hydrogen in rutile of mantle origin. Eos, 73, 651.

——— (1995) H in rutile-type compounds: I. Single-crystal neutron and X-ray diffraction study of H in rutile. American Mineralogist, 80, 448–453.

Vlassopoulos, D., Rossman, G.R., and Haggerty, S.E. (1993) Coupled substitution of H and minor elements in rutile and the implications of high OH contents in Nb- and Cr-rich rutile from the upper mantle. American Mineralogist, 78, 1181–1191.

Manuscript received March 28, 1994
Manuscript accepted February 8, 1995