American Mineralogist, Volume 82, pages 836–839, 1997

LETTER

Transformation of fivefold-coordinated silicon to octahedral silicon in calcium silicate, $CaSi_2O_5$

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ABSTRACT

A single-crystal high-pressure diffraction study in a diamond-anvil cell shows that under hydrostatic conditions triclinic $CaSi_2O_5$ transforms to a monoclinic structure at a pressure between 0.17(2) and 0.205(5) GPa. The transition is of the zone-boundary type and first order in character with a 2.9% volume change. The monoclinic phase can be recovered from the diamond-anvil cell. Its room pressure unit-cell parameters are a = 6.5430(6) Å, b = 8.3918(4) Å, c = 6.3416(5) Å, β = 113.175(6)°, V = 320.10(4) Å^3. The structure was refined using single-crystal X-ray intensity data and is of the titanite aristotype, space group $A2/a$. Unlike the triclinic phase, which contains SiO_5 polyhedra in addition to SiO_4 tetrahedra and SiO_6 octahedra, the monoclinic phase contains only tetrahedra ($\langle$Si-O$\rangle$ = 1.630 Å) and octahedra ($\langle$Si-O$\rangle$ = 1.796 Å). The phase transition between the monoclinic and triclinic phases of $CaSi_2O_5$ is the first example of a displacive-like transition involving a coordination change of Si to be observed directly in a crystalline oxide or silicate.

INTRODUCTION

The recent determination of the room-pressure structure of the triclinic phase of $CaSi_2O_5$ (Angel et al. 1996) showed that it contains Si in four-, five-, and sixfold coordination by O atoms, confirming previous ^{29}Si NMR peak assignments (Kanzaki et al. 1991). The structure of this phase is a derivative of the common titanite aristotype structure, which would contain, for $CaSi_2O_5$, Si in fourfold and sixfold coordination only. It has been proposed that $CaSi_2O_5$ should adopt the titanite structure at high pressures (Hazen et al. 1996), as is also suggested by the recovery of some poorly characterized ‘‘titanite’’ phase from multi-anvil syntheses (Kanzaki et al. 1991) and the presence of twinning in many crystals of the triclinic phase (Angel et al. 1996). This paper reports the results of an in-situ high-pressure, single-crystal X-ray diffraction study of $CaSi_2O_5$, which show that the triclinic polymorph does indeed undergo a non-reconstructive transition to a titanite structure at a pressure of about 0.2 GPa. This transition involves the conversion of SiO_5 polyhedra to SiO_6 octahedra and provides some possible insights into the driving forces for such coordination changes in silicate glasses and melts and during the amorphization of high-pressure silicate phases.

EXPERIMENTAL METHODS

The single-crystals of $CaSi_2O_5$ used in these experiments were synthesized at 11 GPa and 1350 °C in a multi-anvil press (Angel et al. 1996). X-ray diffraction data were collected from several single crystals loaded in turn into a BGI-design diamond-anvil cell (Allan et al. 1996) with 4:1 methanol:ethanol mixture as a hydrostatic pressure medium. Pressures were determined to a precision of typically 0.01 GPa from the unit-cell volumes of a quartz single crystal included in the cell and the equation of state of quartz (Angel et al. 1997). Details of the experimental methods used to determine unit-cell parameters of both the sample and the quartz crystal are given in Angel et al. (1997).

Initial measurements of the unit-cell parameters of a $CaSi_2O_5$ crystal initially pressurized to 4.4 GPa and then up to 5.8 GPa indicated that the crystal symmetry had become monoclinic. During pressure reduction in several steps to room pressure the crystal retained monoclinic symmetry. The crystal was then unloaded from the DAC and mounted for conventional X-ray data collection in air, during which it remained monoclinic. Room-pressure cell parameters were a = 6.5430(6) Å, b = 8.3918(4) Å, c = 6.3416(5) Å, β = 113.175(6), V = 320.10(4) Å^3. This survival of the monoclinic phase contrasts with the recovery of triclinic $CaSi_2O_5$ from the multi-anvil experiments in which the material was synthesized at high temperatures and pressures. This would suggest that the monoclinic-to-triclinic transformation is promoted by non-hydrostatic stresses in the multi-anvil press during decompression.

0003–004X/97/0708–0836$05.00

TABLE 1. Fractional atomic coordinates for monoclinic $CaSi_2O_5$

Site	Atom	x/a	y/b	z/c	B_{eq}(Å^2)
A	Ca	¼	0.42059(9)	¼	1.10
M	Si	½	¼	¾	0.89
T	Si	¾	0.43657(13)	¼	0.85
O1	O	¾	0.3090(4)	¾	0.98
O2	O	0.9142(3)	0.3178(2)	0.4477(3)	1.10
O3	O	0.3958(3)	0.4500(2)	0.6531(3)	0.95

Notes: Numbers in parentheses represent estimated standard deviations in the last digit. In addition to the parameters listed, anisotropic displacement parameters were refined for all atoms. Following Taylor and Brown (1976) a nonstandard setting of space group *A*2/*a* was used with symmetry operators $x,y,z;\ -x,-y,-z;\ ½ + x, ½ - y,z;\ ½ - x, ½ + y,-z$ in addition to the lattice translations.

TABLE 2. Selected bond lengths (Å) in monoclinic $CaSi_2O_5$

A-O1	2.229(3)
A-O2 × 2	2.381(2)
A-O3 × 2	2.364(2)
A-O3 × 2	2.410(2)
Average (7)	2.363
M-O1 × 2	1.709(1)
M-O2 × 2	1.862(2)
M-O3 × 2	1.824(2)
Average	1.798
T-O2 × 2	1.631(2)
T-O3 × 2	1.629(2)
Average	1.630

X-ray intensity data were then collected from the monoclinic crystal with an Enraf-Nonius CAD4 diffractometer. Procedures for data collection, data reduction, and refinement followed those recently described by Miletich et al. (1997). All reflections with indices $k + l$ = odd and those with h = odd in $h0l$ were absent, indicating space group symmetry *A*2/*a*. Refinement of a structure model based upon the titanite aristotype structure (Taylor and Brown 1976), but with Si occupying the octahedral sites in place of Ti, converged to $R_u = 0.030$, $R_w = 0.031$, and $G_{fit} = 1.25$ for 40 variables (including anisotropic displacement parameters for all atoms) with 369 reflections considered observed with $I > 3\sigma_I$. Positional parameters are reported in Table 1 and bond lengths in Table 2.

Further crystals were used in subsequent experiments to constrain further the pressure at which the transition occurred. For these experiments, only the Bragg angle of the 002 reflection of $CaSi_2O_5$ was measured as a function of pressure. The difference between $2\theta_{002} = 13.47°$ in the triclinic phase and 13.95° in the monoclinic phase at room pressure (Mo$K\alpha$ radiation) provided an unambiguous indication of which phase was present. The tightest constraint on the pressure at which the phase transition occurred on increasing pressure was provided by the observation that one crystal remained triclinic at 0.17(2) GPa but transformed to the monoclinic phase on increasing pressure to 0.205(5) GPa.

DISCUSSION

Monoclinic phase

The structure type of monoclinic $CaSi_2O_5$ is that of the titanite aristotype. This structure type is also exhibited by $CaSnSiO_5$ at room conditions (Higgins and Ross 1977) and by titanite ($CaTiSiO_5$) at high temperatures (e.g., Taylor and Brown 1976; Kek et al. 1997, and references therein) and at high pressures (Kunz et al. 1996). The structure of monoclinic $CaSi_2O_5$ consists of chains of SiO_6 octahedra that run parallel to the *a* axis of the unit cell and that are both internally bridged and cross-linked to adjacent chains by corner-sharing with SiO_4 tetrahedra (Fig. 1). The interatomic distances and angles within this polyhedral framework are within the normal range of mixed-coordination silicates quenched from high pressures and temperatures, except that the SiO_6 octahedron has an unusual range of bond lengths (Table 2), although the average Si-O bond length is normal (e.g., Finger and Hazen 1991). The reason for this distortion is the difference in the environment of the O1 atom compared to that of the O2 and O3 atoms. The O1 atom forms the link within the octahedral chains and is bonded only to one Ca atom in addition to two $^{[6]}$Si. To compensate, both the Si-O1 and the Ca-O1 bonds are very short (Table 2). The O2 and O3 atoms form the links between the octahedra and the tetrahedra. They are each bonded to one $^{[6]}$Si, one

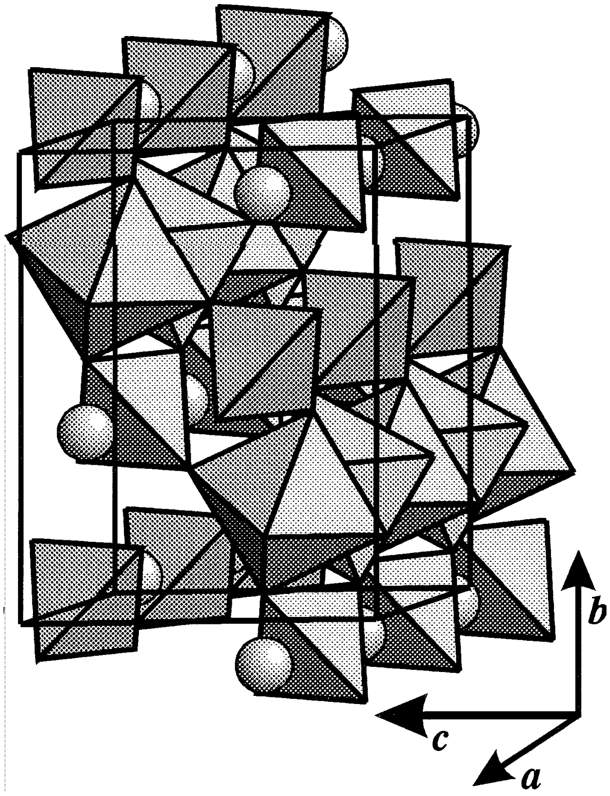

FIGURE 1. A polyhedral representation of the crystal structure of monoclinic $CaSi_2O_5$ at room pressure. The chains of corner-sharing SiO_6 octahedra are seen almost end-on, running parallel to the *a* axis. The spheres represent Ca atoms.

TABLE 3. Bond-valence sums (v.u.) for O atoms in $CaSi_2O_5$

Monoclinic phase	Triclinic phase*
O1 1.77	O1o 1.97
	O1x 1.96
O2 1.83	O2oo 2.04
	O2ox 1.83
	O2ao 1.84
	O2ax 1.88
O3 2.21	O3oo 2.26
	O3ox 1.97
	O3ao 2.15
	O3ax 1.99

Notes: Bond-valence sums were calculated from the bond lengths and the bond-valence parameters of Brese and O'Keefe (1991).

* Bond lengths for the triclinic phase were taken from Angel et al. (1996).

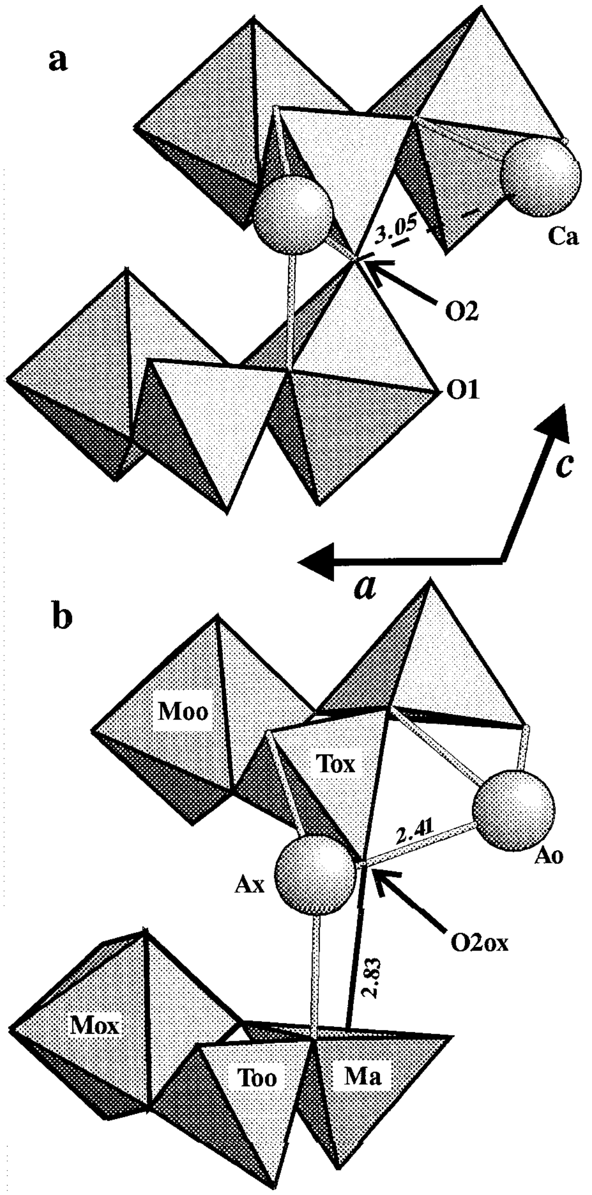

FIGURE 2. (**a**) The local environment of an O2 atom in the monoclinic phase, in which it forms the bridge between an SiO_4 tetrahedron and an SiO_6 octahedron. It is also bonded to the left-hand Ca (spheres) and has a nonbonded contact (dashed line) to the right-hand Ca atom. (**b**) In the triclinic phase, the equivalent O2ox is removed to a distance 2.83 Å away (thin line) from the Si atom on the Ma position. Other displacements create an additional bond between O2ox and the right-hand Ca on the Ao site.

$^{[4]}$Si, and the Ca atoms that occupy the cavities in the framework. Whereas O2, being bonded to just one Ca atom, is slightly underbonded the O3 atom is bonded to a second Ca and is therefore significantly overbonded (Table 3).

Phase transition

Although only the transition from the low-pressure triclinic phase to the high-pressure monoclinic phase was observed directly, all further discussion is presented in terms of the reverse monoclinic-to-triclinic transition. And because only precise room-pressure structural data exist the structural changes at the transition are approximated by the differences between the structures determined at room pressure.

The transition from the monoclinic phase to the triclinic phase involves an approximate doubling of the *a* axis of the unit cell, so that the unit-cell volume of the triclinic phase is approximately twice that of the monoclinic phase. The specific volume change at the transition, $\frac{1}{2}V_{\text{triclinic}} - V_{\text{monoclinic}}$ is 9.4(6) Å^3 per monoclinic unit cell or 1.41(9) cm^3/mol, a relative change of 2.9%. The failure of the monoclinic phase to transform back to the triclinic phase at room temperature indicates that there is at least a 0.2 GPa hysteresis associated with the phase transition under hydrostatic conditions, which, together with the volume change, demonstrates that the transition is thermodynamically first order in character.

The phase transition maintains the overall topology and connectivity of the polyhedral framework, with one major exception: One O2 atom from every second SiO_6 polyhedra in the octahedral chains of the monoclinic phase is displaced to give a nonbonded distance of 2.831(3) Å (Angel et al. 1996), thereby breaking one-eighth of the octahedral-tetrahedral bridges in the structure. To maintain local charge balance at the displaced O atom (denoted O2ox) the entire framework distorts and the Ca atoms are displaced significantly so as to bring a second Ca atom into bonded contact with O2ox (Fig. 2). In addition, the SiO_4 tetrahedron involving this O atom distorts so as to shorten the Si-O2ox bond to 1.588(3)Å from 1.631(2)Å in the monoclinic structure. The net result of these adjustments of the structure is that there is no change in the overall bond-valence sum at this displaced O2ox (Table 3). Within the Si-O polyhedron that loses its sixth O atom at the transition, the Si atom is displaced away from O2ox so that the coordination polyhedron becomes a square-based pyramid (Fig. 2). All five remaining Si-O bond distances become shorter. Not only do these displacements result in local charge balance at the central Si, but they also make the bond-valence sums at the O1 atoms ideal, whereas they are significantly underbonded in the monoclinic structure (Table 3). In fact, fully one-half of the O atoms in the triclinic phase have better local charge balance than the equivalent sites in the monoclinic phase (Table 3). With this information on both structures one can now propose that this equalization of local charge balance is the driving force for the transition. Underbonding of the O1 atoms in the monoclinic phase leads to $^{[6]}$Si-O1 bond shortening; the resulting overbonding of the $^{[6]}$Si atom results in the expulsion of one O2 atom from every alternate SiO_6 octahedra, followed by structural distortions to improve the charge balance at the expelled O2ox atom.

The interconversion of SiO_5 and SiO_6 groups occurs in glasses and melts at high pressures and temperatures (e.g., Stebbins et al. 1995) and during diffusion in silicate perovskites (Wall and Price 1988). The transformation of SiO_6 octahedra to SiO_5 pyramids has also been proposed as the first step in amorphization of calcium silicate perovskite (Hemmati et al. 1990). It is tempting to speculate that, as in $CaSi_2O_5$, the driving force for these coordination changes is the improvement of the local charge balance at the O atoms within the structure.

ACKNOWLEDGMENTS

N.L. Ross (University College, London) synthesized the calcium silicate crystals at the Bayerisches Geoinstitut with the support of the EC ''Human Capital and Mobility—Access to Large Scale Facilities'' program (Contract no. ERBCHGECT940053 to D. Rubie). R. Knoche, F. Seifert, and T. Fliervoet (Bayerisches Geoinstitut) are thanked for discussions and for collaboration on related research projects.

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