Orientational ordering of three SiO₄ tetrahedra in α'_L -Ca_{1.5}Sr_{0.5}SiO₄ that satisfies bond-valence requirements and avoids O-O repulsion

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The crystal structure of α'_L -Ca_{1.55(4)}Sr_{0.45(4)}SiO₄ was analyzed by single-crystal X-ray diffraction. Refinement with isotropic temperature factors yielded $R = 5.4\%$. The occupancies of the M(11), M(12), M(13), M(21), M(22), and M(23) sites by Sr are 0.40(3), 0.37(3), 0.42(3), 0.11(3), 0.04(2), and 0, respectively. The structure contains SiO₄ tetrahedra in three different orientations. The orientational ordering of the Si(n)O₄ ($n = 1-3$) tetrahedra accommodates the M(1 n)-O ($n = 1-3$) bond-valence unbalances caused by the ionic radii mismatch and also avoids increasing the O-O electric repulsions between adjacent Si(n)O₄ tetrahedra.

Keywords: α'_L -Ca_{1.5}Sr_{0.5}SiO₄, Orientational ordering, Ionic radii mismatch, Bond-valence, O-O repulsion

INTRODUCTION

Trömel (1949) was the first to discover α' -Ca₂SiO₄—a polymorph that is stable between 850 °C and 1400 °C. Later, Niesel and Thormann (1967) first discovered the existence of two varieties of α' -Ca₂SiO₄: the α'_L phase (stable between 690 °C and 1160 °C) and the α'_H phase (stable between 1160 °C and 1420 °C). Saalfeld (1975) determined the lattice parameters of α'_L -Ca₂SiO₄ from single-crystal X-ray oscillation photographs taken at high temperatures. He observed the superstructure reflections of the α'_L phase, which triplicate the length of the a -axis ($Pnam$) at 800 °C and 1000 °C.

The incorporation of Sr atoms into Ca₂SiO₄ makes the α'_L phase quenchable to room temperature. Udagawa et al. (1979) studied synthetic single-crystal α'_L -Ca_{1.65(4)}Sr_{0.35(4)}SiO₄ by X-ray diffraction and first determined its crystal structure by the Patterson method ($R = 6.8\%$). α'_L -Ca_{1.65(4)}Sr_{0.35(4)}SiO₄ has a superstructure attributable to the orientational ordering of the SiO₄ tetrahedra. The structure has SiO₄ tetrahedra in three different orientations periodically arranged along the a -axis ($Pna2_1$), making the a -axis three times as long as that of a subcell. Furthermore, Il'inets et al. (1982) determined the structure of

synthetic single-crystal α'_L -Ca(Ca,Sr)SiO₄ by the Patterson method and X-ray diffraction data ($R = 7\%$) that independently confirmed the structure reported by Udagawa et al. (1979).

The crystal structures determined by Udagawa et al. (1979) and Il'inets et al. (1982) are consistent and their structural determinations are considered to be satisfactory. But the mechanism that allows the α'_L phase to become quenchable to room temperature after the incorporation of Sr atoms is unclear. The orientational ordering of the SiO₄ tetrahedra in the structure is considered to be related to this mechanism, but the mechanism of the orientational ordering itself is also unclear. To identify the factors that control the orientational ordering of the SiO₄ tetrahedra in the α'_L structure, we performed structural analysis on α'_L -Ca_{1.55(4)}Sr_{0.45(4)}SiO₄.

EXPERIMENTAL METHOD

To synthesize single-crystals ($60 \times 60 \times 30 \mu\text{m}^3$), a mixture of CaCl₂, SrCl₂, and SiO₂ in the molar ratio 1.5 : 0.5 : 1 was heated at 1300 °C for 5 h, cooled to 500 °C in 20 h, and then quenched in air to room temperature. The chemical composition of the crystal was confirmed by crystal structure refinement as being Ca_{1.55(4)}Sr_{0.45(4)}SiO₄. Since the crystal was heated at a temperature where α'_H -Ca₂SiO₄ is stable [between 1160 °C and 1420

Figure 1. Distribution of $|F_o|$ against h indices. The reflections with $h \neq 3n$ were systematically weaker than those with $h = 3n$.

°C (Niesel and Thormann, 1967)], the α'_L phase was thought to have been obtained through the $\alpha'_H \rightarrow \alpha'_L$ phase transition during cooling.

X-ray measurements were performed using an automated four-circle X-ray diffractometer (Rigaku, AFC-7S) with graphite-monochromatized MoK α radiation operated at 50 kV and 30 mA. The orthorhombic lattice parameters were determined from 16 reflections in the 2θ range between 14° and 26°. The X-ray intensity data over the 1/8 sphere was collected up to $\sin\theta/\lambda = 0.7$ (Å⁻¹) by the ω - 2θ scan. The reflections with $h \neq 3n$ were systematically weaker than those with $h = 3n$ (Fig. 1), where n is an integer. Thus, the reflections with $h \neq 3n$ are considered to

be superstructure reflections. The 947 reflections with $I_o > 1.5\sigma(I_o)$ were used for the structural analysis. Of the 947, the number of reflections with $h \neq 3n$ was 483. The linear absorption coefficient μ of Ca_{1.5}Sr_{0.5}SiO₄ for MoK α radiation is 100 cm⁻¹. The absorption correction was applied using the ψ -scan method; the transmission coefficient ranged from 0.87 to 1.0. The observed reflection conditions were $0kl$ with $k + l = 2n$, $h0l$ with $h = 2n$, $h00$ with $h = 2n$, $0k0$ with $k = 2n$, and $00l$ with $l = 2n$, indicating either the space group $Pnam$ or $Pna2_1$. We assumed that the noncentrosymmetric space group $Pna2_1$ was the true space group, and the appropriate initial parameters were then taken from Udagawa et al. (1979). The struc-

Table 1. Structure refinement information

	Ca _{1.55(4)} Sr _{0.45(4)} SiO ₄
Crystal dimensions (mm)	0.06 × 0.06 × 0.03
Space Group	$Pna2_1$
a (Å)	20.522(3)
b (Å)	9.339(4)
c (Å)	5.558(2)
$2\theta_{\max}$ (°)	60
Collected reciprocal regions	$h-, k+, l+$
Reflections measured	1841
Reflections used ($I_o > 1.5\sigma(I_o)$)	947 (51.4% of measured)
Superstructure reflections used ($I_o > 1.5\sigma(I_o)$)	483 (51.0% of used)
Number of variables	89
R (%)	5.4
R_w (%)	6.6
Goodness of fit	1.13

$$R = \sum |F_o| - |F_c| / \sum |F_o|, R_w = \{\sum w(|F_o| - |F_c|)^2 / \sum w |F_o|^2\}^{1/2}, \text{ where } w = 1/\sigma^2(F_o).$$

Table 2. Final atomic coordinates

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> _{iso}	Occupancy	
					Ca	Sr
M(11)	0.2791 (2)	0.0733 (6)	0.2632 (10)	1.32 (11)	0.60(3)	0.40(3)
M(12)	0.6103 (2)	0.0797 (4)	0.2386 (9)	0.50 (8)	0.63(3)	0.37(3)
M(13)	0.9459 (2)	0.0714 (4)	0.2124 (10)	0.61 (9)	0.58(3)	0.42(3)
M(21)	0.9969 (2)	0.7018 (5)	0.2160 (7)	0.80 (11)	0.89(2)	0.11(2)
M(22)	0.3316 (2)	0.7039 (6)	0.2531 (8)	0.75 (12)	0.96(2)	0.04(2)
M(23)	0.6646 (2)	0.7026 (6)	0.2700	0.34 (7)	1.0	0
Si(1)	0.0952 (3)	0.0851 (8)	0.2203 (14)	0.51 (10)		1.0
Si(2)	0.4266 (3)	0.0860 (8)	0.2532 (12)	0.25 (10)		1.0
Si(3)	0.7584 (3)	0.0832 (9)	0.2651 (13)	0.49 (10)		1.0
O(11)	0.1712 (7)	0.0489 (18)	0.2012 (29)	1.08 (25)		1.0
O(12)	0.5030 (8)	0.0522 (22)	0.3236 (29)	0.95 (30)		1.0
O(13)	0.8308 (7)	0.0536 (19)	0.1849 (30)	1.04 (25)		1.0
O(21)	0.0519 (7)	0.9333 (18)	0.2114 (32)	1.70 (29)		1.0
O(22)	0.3878 (7)	0.9411 (17)	0.1926 (30)	1.14 (25)		1.0
O(23)	0.7214 (7)	0.9345 (19)	0.3361 (24)	0.70 (23)		1.0
O(31)	0.0752 (9)	0.1830 (21)	-0.0010 (31)	1.48 (32)		1.0
O(32)	0.4213 (7)	0.1987 (20)	0.0283 (26)	0.89 (27)		1.0
O(33)	0.7207 (8)	0.1368 (18)	0.0206 (26)	1.39 (28)		1.0
O(41)	0.0763 (6)	0.1639 (15)	0.4688 (25)	0.65 (20)		1.0
O(42)	0.3924 (7)	0.1585 (16)	0.4944 (23)	0.28 (19)		1.0
O(43)	0.7453 (7)	0.2041 (18)	0.4753 (28)	0.49 (23)		1.0

tural parameters listed by Udagawa et al. (1979), i.e., for $P2_1cn$, were converted for the different unit-cell configuration in the present study ($Pna2_1$). The z coordinate of the M(23) site was fixed at $z = 0.27$, and this site was defined as the origin of the coordinate system. The occupancies of the M(11), M(12), M(13), M(21), M(22), and M(23) sites by Ca were independently refined to verify the correlation between the occupancies of the M sites by Ca and the rotations of the $Si(n)O_4$ ($n = 1-3$) tetrahedra around them. During refinement, the occupancy of the M(23) site by Ca converged to 1.0 and was then fixed. The weight applied was $w = 1/\sigma^2(F_o)$. Refinement with isotropic temperature factors yielded $R = 5.4\%$. Refinement with anisotropic temperature factors was unsuccessful because the temperature factors of several atoms became nonpositive-definite. This is considered to be due to the insufficient number of reflections used for calculation. The ratio of the number of reflections (947) to the number of variables (194) used in the refinement procedure with anisotropic temperature factors is 4.9. Thus, refinement results with the isotropic temperature factors were taken as final. The crystal structure was refined using the teXsan crystallographic package from the Molecular Structure

Corporation (1992).

The conditions used for the structure refinements are summarized in Table 1. The final atomic coordinates are listed in Table 2. The labels for the atoms follow Udagawa et al. (1979). VESTA (Momma and Izumi, 2008) was used to draw the structural details.

RESULTS AND DISCUSSION

Description of the crystal structure

The crystal structure of $\alpha'_L\text{-Ca}_{1.55(4)}\text{Sr}_{0.45(4)}\text{SiO}_4$ consists of $Si(n)O_4$ tetrahedra, $M(1n)O_{10}$ polyhedra, and $M(2n)O_8$ polyhedra ($n = 1-3$; Fig. 2). The $Si(n)O_4$ tetrahedra are isolated and do not share oxygen atoms with each other. All the oxygen atoms of the $Si(n)O_4$ tetrahedra are shared with the $M(1n)O_{10}$ polyhedra and $M(2n)O_8$ polyhedra.

Occupancy of M sites by Sr

The occupancies of the M(11), M(12), and M(13) sites by Sr are 0.40(3), 0.37(3), and 0.42(3), respectively (Table 2). The occupancies of the M(21), M(22), and M(23) sites by

Figure 2. The crystal structure of α'_L -Ca_{1.55(4)}Sr_{0.45(4)}SiO₄ projected along the *c*-axis (left) and along the *b*-axis (right). The structure consists of Si(*n*)O₄ tetrahedra, M(1*n*)O₁₀ polyhedra, and M(2*n*)O₈ polyhedra (*n* = 1–3).

Sr are 0.11(3), 0.04(2), and 0, respectively (Table 2). Clearly, the Sr atoms preferentially occupy the M(1*n*) sites (*n* = 1–3). Further, although there were no significant differences in the site occupancies, significant differences were found in the distortions among the M(1*n*)O₁₀ polyhedra. The distortion of the M(11)O₁₀ polyhedron is larger than those of the M(12)O₁₀ and M(13)O₁₀ polyhedra (Table 3).

Orientational ordering of three SiO₄ tetrahedra

The SiO₄ tetrahedron is rigid because of the strong covalent character of the Si–O bond; possible variations in Si–O bond distances and O–Si–O angles are restricted to a narrow range of values. The displacements of the oxygen atoms in the α'_L structure are considered to be accompanied by the translation and rotation of the Si(*n*)O₄ tetrahedra, because all the oxygen atoms belong to the Si(*n*)O₄ tetrahedra.

In the α'_L structure, there seems to be a correlation between the rotations of the Si(*n*)O₄ tetrahedra and the ionic radii of the cations at the M(1*n*) sites, because all the oxygen atoms of the Si(*n*)O₄ tetrahedra are shared with the M(1*n*)O₁₀ polyhedra. This correlation can be verified by a comparison of the crystal structure of the α'_L phase with that of Ba₂SiO₄; the former includes Ca²⁺ and Sr²⁺ and the latter includes Ba²⁺. Figure 3 shows the

Si(*n*)O₄ tetrahedra in part of the α'_L -Ca_{1.55(4)}Sr_{0.45(4)}SiO₄ structure ($-0.3 < y < 0.3$) together with the SiO₄ tetrahedra in part of the Ba₂SiO₄ structure (*Pnam*; Große and Tillmanns, 1974) viewed along the *b*-axis. We describe the direction of rotation about the *b*-axis of Si(2)O₄ as right (R), that of Si(3)O₄ as left (L), and that of Si(1)O₄ as neutral (N) on the basis of the directions of the O(2*n*) → O(1*n*) vectors relative to the *a*-axis. Then, the ordering pattern of the Si(*n*)O₄ tetrahedra in the α'_L structure along the *a*-axis is NRLNRL..., using the symbols N, R, and L which represent the orientation of each tetrahedron. The orientation of the SiO₄ tetrahedra in Ba₂SiO₄ is similar to the N orientation because they are on (001) mirror planes in the Ba₂SiO₄ structure (*Pnam*). The ionic radii of Ca²⁺ and Sr²⁺ are smaller than that of Ba²⁺. The mean M(1*n*)–O bond distances in the M(1*n*)O₁₀ polyhedra are larger than the ideal value calculated from the effective ionic radii of Ca²⁺, Sr²⁺, and O²⁻ (Shannon, 1976; see Table 3). Thus, there exists ionic radii mismatch at the M(1*n*) sites in the α'_L structure. Pauling's electrostatic neutrality is considered to be maintained by the rotations of the Si(*n*)O₄ tetrahedra and the sum of the M(1*n*)–O bond-valences is insufficient without the rotations of the Si(*n*)O₄ tetrahedra. The bond-valence in Table 3 was calculated using the formula $V_i = \sum v_{ij} = \sum \exp[(R_{ij} - d_{ij})/0.37]$ (Brese and O'Keefe, 1991), where v_{ij} is an individual bond-valence, d_{ij} (Å) is an observed bond distance, and R_{ij} (Å) is the *bond-valence*

Table 3. Selected bond distances (d) and bond-valences (v)

	d (Å)	v		d (Å)	v		d (Å)	v
M(11)- O(11)	2.25 (1)	0.56	M(12)- O(12)	2.27 (2)	0.52	M(13)- O(13)	2.37 (1)	0.41
O(23)	2.37 (1)	0.40	O(22)	2.53 (2)	0.26	O(32)	2.43 (2)	0.35
O(33)	2.43 (2)	0.34	O(42)	2.61 (1)	0.21	O(21)	2.53 (2)	0.26
O(43)	2.49 (2)	0.29	O(33)	2.62 (2)	0.20	O(41)	2.62 (1)	0.21
O(22)	2.58 (1)	0.23	O(31)	2.68 (2)	0.17	O(21)	2.77 (2)	0.14
O(42)	2.77 (1)	0.14	O(23)	2.71 (2)	0.16	O(21)	2.79 (2)	0.13
O(43)	3.09 (2)	0.06	O(41)	2.80 (1)	0.12	O(31)	2.89 (2)	0.10
O(23)	3.19 (1)	0.04	O(22)	3.04 (2)	0.07	O(31)	3.09 (2)	0.06
O(33)	3.25 (2)	0.04	O(32)	3.13 (2)	0.05	O(41)	3.15 (1)	0.05
O(32)	3.40 (2)	0.02	O(43)	3.28 (2)	0.03	O(42)	3.17 (1)	0.05
Ave.	2.78 (2)	Sum 2.13	Ave.	2.77 (2)	Sum 1.80	Ave.	2.78 (2)	Sum 1.75
Ideal	2.68		Ideal	2.68		Ideal	2.68	
M(21)- O(41)	2.39 (1)	0.34	M(22)- O(31)	2.36 (2)	0.35	M(23)- O(42)	2.32 (1)	0.39
O(31)	2.41 (2)	0.32	O(33)	2.36 (2)	0.35	O(11)	2.38 (2)	0.33
O(32)	2.42 (1)	0.31	O(43)	2.37 (2)	0.34	O(32)	2.45 (2)	0.27
O(21)	2.44 (2)	0.29	O(13)	2.43 (2)	0.29	O(43)	2.47 (1)	0.26
O(12)	2.45 (2)	0.29	O(41)	2.49 (1)	0.25	O(23)	2.49 (2)	0.24
O(12)'	2.59 (2)	0.20	O(22)	2.52 (2)	0.23	O(21)	2.66 (2)	0.15
O(22)	2.61 (2)	0.19	O(23)	2.65 (2)	0.16	O(13)	2.70 (2)	0.14
O(42)	2.62 (1)	0.18	O(11)	2.88 (2)	0.09	O(33)	2.80 (2)	0.11
Ave.	2.49 (2)	Sum 2.11	Ave.	2.51 (2)	Sum 2.07	Ave.	2.53 (2)	Sum 1.88
Ideal	2.54		Ideal	2.53		Ideal	2.52	
Si(1)- O(31)	1.59 (2)	1.10	Si(2)- O(22)	1.61 (2)	1.04	Si(3)- O(13)	1.58 (2)	1.13
O(11)	1.60 (2)	1.07	O(32)	1.64 (2)	0.96	O(23)	1.63 (2)	0.98
O(41)	1.61 (2)	1.04	O(12)	1.65 (2)	0.93	O(33)	1.64 (2)	0.96
O(21)	1.67 (2)	0.88	O(42)	1.66 (1)	0.91	O(43)	1.65 (2)	0.93
Ave.	1.62 (2)	Sum 4.08	Ave.	1.64 (2)	Sum 3.84	Ave.	1.63 (2)	Sum 4.00

The ideal bond distances were calculated using the effective ionic radii (Shannon, 1976) on the basis of $r(\text{O}^{2-}) = 1.40$ (Å). For calculations of ideal bond distances and bond-valences, occupancies of M sites (Table 2) were used as weights.

lence parameter. The increase in the bond-valences on distortion of the coordinated polyhedron is explained by Brown (1992) via the *distortion theorem*. As is shown schematically in Figure 4, this theorem is originated from the concave shape of the bond-valence curve when plotted as a function of the bond distance. If the average bond distance remains constant, the more the difference between the shorter and the longer bonds increases, the more the average bond-valence of these bonds increases. Because the R and L orientations of $\text{Si}(n)\text{O}_4$ tetrahedra make the $\text{M}(1n)\text{O}_{10}$ polyhedra more distorted than the N orientation does, the R and L orientations of the $\text{Si}(n)\text{O}_4$ tetrahedra provide sufficient $\text{M}(1n)\text{-O}$ bond-valences.

The distortions of the $\text{M}(1n)\text{O}_{10}$ polyhedra are considered to be related to the rotations of the $\text{Si}(n)\text{O}_4$ tetrahedra around them (Fig. 2). These rotations were found to be ordered along the *a*-axis. It should be noted that this

orientational ordering of $\text{Si}(n)\text{O}_4$ tetrahedra is independent of the occupancies of individual $\text{M}(1n)$ sites, which were found to be substantially equal (Table 2).

The directions of the rotations of the $\text{Si}(n)\text{O}_4$ tetrahedra about the *b*-axis are controlled by the screw 2_1 along the *c*-axis (Fig. 3). Rotation in opposite directions by the $\text{Si}(2)\text{O}_4$ tetrahedron (R) and the adjacent $\text{Si}(3)\text{O}_4$ tetrahedron (L) prevents the shortening of O-O distances between them. These O-O distances are marked by arrows, and the adjacent tetrahedra within one unit cell that repeat along the *c*-axis are surrounded by broken circles (denoted as A, B, and B') in Figure 3. The tetrahedra in the circle A have the orientation N only and those in the circle B (B') have orientations R and L. The position of the screw 2_1 along the *c*-axis relative to the circle A is different from that relative to the circle B (B'). The tetrahedra in circles B and B' are related by the screw 2_1 along the *c*-axis,

Figure 3. Si(*n*)O₄ tetrahedra in $\alpha'_L\text{-Ca}_{1.55(4)}\text{Sr}_{0.45(4)}\text{SiO}_4$ projected along the *b*-axis (left) together with SiO₄ tetrahedra in Ba₂SiO₄ (Große and Tillmanns, 1974) (right). N, R, and L indicate orientations of Si(*n*)O₄ tetrahedra that are defined on the basis of the direction of rotation about the *b*-axis. Unit-cell is shown by solid lines and the positions of screw 2₁ along the *c*-axis are shown beside it. Orientations of tetrahedra in the α'_L structure are chosen to avoid the shortening of O–O distances between adjacent tetrahedra (shown by arrows).

Figure 4. Variation of bond-valence with bond distance (Brese and O'Keeffe, 1991). The average bond-valence of the shorter and longer bonds (1' and 2') is always larger than that of two equal bonds (1 and 2) if the average distance remains constant.

while the tetrahedra in circle A are related with each other by the screw 2₁ along the *c*-axis. The Si(1)O₄ tetrahedra in circle A have orientation N and there is no shortening of the O–O distances between them. Thus, the orientations of the Si(*n*)O₄ tetrahedra are controlled to avoid an increase in the O–O electric repulsion between adjacent Si(*n*)O₄ tetrahedra.

Role of Sr atoms in the α'_L phase at room temperature

The average effective ionic radii of cations at the M(1*n*) sites increase with an increase in the Sr content. The greater is the number of Sr atoms at the M(1*n*) sites, the lesser is the deviation (rotation toward R and L) from the N orientation needed to satisfy the M(1*n*)–O bond-valences. The O–O electric repulsions in the α'_L structure are

considered to decrease with an increase in the Sr content because the O(11)–O(13) distance (Fig. 3) is increased by the lesser degree of rotation of the $\text{Si}(n)\text{O}_4$ tetrahedra. However, the O–O electric repulsions in the α'_L structure are considered to increase with a decrease in temperature because the effective ionic radii of cations at the M(1n) sites decrease with their thermal vibrations. Thus, Sr atoms mitigate the increase in O–O electric repulsion during cooling and make the α'_L phase quenchable to room temperature.

Possibility of antiphase domains in the α'_L phase

The antiphase domains of the α'_L phase will be formed through the $\alpha'_H \rightarrow \alpha'_L$ phase transition because the transition accompanies the loss of the inversion center ($Pnam \rightarrow Pna2_1$). The orientational ordering patterns of the $\text{Si}(n)\text{O}_4$ tetrahedra along the a -axis for each domain are described as NRLNRL... and NLRNLR.... If the antiphase domains in the crystal are small, then the possibility for the formation of antiphase domain boundaries is high; the superstructure reflections of the α'_L phase will be diffused because the orientations of the $\text{Si}(n)\text{O}_4$ tetrahedra must be disordered near the antiphase domain boundaries. For our sample, a trend of diffuse scattering was not observed for the superstructure reflections ($h \neq 3n$); the intensities of the reflections were measurable to within the same ω - 2θ scan width as that for the fundamental reflections ($h = 3n$). It is concluded that the antiphase domains in our sample are not sufficiently small to diffuse the superstructure reflections. The X-ray intensities of different antiphase domains are equal by Friedel's law if we neglect the effect of the anomalous dispersion.

Catti et al. (1984) synthesized single crystals of $\text{Ca}_{0.5}\text{Sr}_{1.5}\text{SiO}_4$, CaSrSiO_4 , $\text{Ca}_{1.5}\text{Sr}_{0.5}\text{SiO}_4$, and $\text{Ca}_{1.8}\text{Sr}_{0.2}\text{SiO}_4$ from SrCO_3 , CaCO_3 , and SiO_2 using SrF_2 and CaF_2 as flux. They heated the mixture to 1500 °C and then cooled it very slowly to room temperature. They analyzed the crystal structure of the four compounds at room temperature by X-ray diffraction and reported disordered structures ($R = 5.0, 5.2, 4.9$, and 3.0% , respectively), calling them the α' phase. The a -axis length of the α' phase ($Pnam$) corresponds to one-third of that of the α'_L phase ($Pna2_1$). The disordered structure of the α' phase is a statistical average of two $P2_1/n$ configurations related by the (001) mirror, conforming to $Pnam$ symmetry. The two mirror-related SiO_4 tetrahedra with 50% probability are disordered in this structure. We believe that Catti et al. (1984)'s samples are the α'_L phase and the disordered

structure modeled is the average structure of the α'_L phase. Catti et al. (1984) did not observe superstructure reflections for their samples. It can be concluded that the superstructure reflections from their samples were diffused and could not be measured by the diffractometer due to the presence of small antiphase domains in their samples. The differently sized antiphase domains in our study and in their study can be attributed to the different cooling histories of the samples.

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