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The crystal structure of high clinoferrosilite

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Abstract

The crystal structure of high clinoferrosilite ($FeSiO_3$) with $C2/c$ symmetry after the transition from orthoferrosilite at 1025°C was determined at 1050°C using a high-temperature four-circle diffractometer. The cell constants are $a = 9.928(1)$, $b = 9.179(1)$, $c = 5.338(1)$Å, $\beta = 110.20°(1)$, $V = 456.5(1)$Å^3. The Fe2 polyhedron can be considered as six coordinated because the next two oxygens are too distant (3.191Å) for effective coordination with the Fe2 ion. The mean Si–O bond length is 1.634Å and the mean Fe–O bond lengths in the $M1(6)$ and $M2(6)$ polyhedra are 2.176 and 2.300Å, respectively. The polyhedral volume calculation reveals that the six-coordinated $M1$ polyhedron (13.40Å^3) is larger than the six-coordinated $M2$ polyhedron (11.93Å^3). This is related to the large distortion of the Fe2-polyhedron in the high clinoferrosilite structure. A similar tendency has been observed for the high clinopyroxene structures reported previously.

Introduction

The existence of a $C2/c$ polymorph in Ca-poor pyroxene was predicted by Morimoto and Tokonami (1969) and Smith (1969) as a non-quenchable, high-temperature phase of $P2_1/c$ clinopyroxene. The transition between these two phases was found to be a reversible and displacive transition using the high-temperature, single-crystal X-ray technique of Smyth (1969) and Prewitt et al. (1970). The crystal structure of the $C2/c$ high-temperature phase of Ca-poor pyroxenes (hereafter high clinopyroxene) has been determined by Brown et al. (1972) for the composition $En_{65}Fs_{30}Wo_5$ and by Smyth and Burnham (1972) for the composition $En_{31}Fs_{67.5}Wo_{1.5}$.

Sueno et al. (1976) carried out high temperature crystal structure refinements of orthoferrosilite ($FeSiO_3$) at several temperatures and afterward found a rapid transition from orthoferrosilite to high clinoferrosilite that was reversible and topotactic. The details were studied by Sueno and Kimata (1979). The behavior of the ortho-clino transition in ferrosilite is quite different from that previously reported on the natural intermediate orthopyroxenes which have non-reversible, sluggish, and non-topotactic characteristics (Smyth,1969; Smyth and Burnham, 1972; Smyth,1974). To elucidate the effect of the compositional difference on the behavior of the ortho-clino transition in pyroxenes, Sueno and Kimata (1981) carried out a high-temperature *in situ* X-ray study of the ortho to clino transition using synthetic orthopyroxenes with several different chemical compositions around the ferrosilite corner of the pyroxene quadrilateral. They found systematic differences between the different compositions, but a rapid, reversible, and topotactic transition was found only in pure ferrosilite. A high-temperature crystal-structure refinement of high clinoferrosilite is, therefore, important for providing the basic data for the analysis of the ortho-clinopyroxene transition mechanism.

The main intent of this study is to compare the structure of high clinoferrosilite with those of orthoferrosilite at several high temperatures and high clinopyroxenes with different chemical compositions such as high clinohypersthene (Smyth and Burnham, 1972) and high pigeonite (Brown et al., 1972).

Experimental

X-ray intensity data collection

A single crystal of orthoferrosilite, 0.10 × 0.08 × 0.06 mm in size, was selected for high-temperature diffraction intensity measurement from those synthesized hydrothermally at 800°C and 20 kbar for 16 days by Dr. D. H. Lindsley. The crystal was mounted parallel to the **c** axis on a Suprasil quartz glass fiber with a high-temperature cement composed of high-alumina wool and liquid binder. To prevent oxidation of Fe^{2+}, the crystal was sealed in an

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evacuated silica capillary. The details of the heater and the cement were described by Brown et al. (1973). The crystal and heater were installed on a Picker diffractometer and the crystal was heated gradually while monitoring the 004 orthoferrosilite reflection peak with a chart recorder. When the crystal temperature reached approximately 1025°C, orthoferrosilite was transformed into (100)-twinned high clinoferrosilite as described by Sueno and Kimata (1979).

The orientation relation between ortho phase and high-clino phase ferrosilites was;

a^*(ortho)$\|a^*$(clino)
b^*(ortho)$\|b^*$(clino)
c^*(ortho)$\|c$(clino).

The crystal was then heated to 1050°C and the X-ray diffraction intensities ($\sin\theta/\lambda = 0.061 - 0.756$) were measured in the ω-2θ scan mode using Mo$K\alpha$ radiation monochromatized with a graphite crystal. All reflections were accompanied by slight diffuse streaks running parallel to the a^* axis of high clinoferrosilite; the diffuse streaks were symmetric around some Bragg reflections and asymmetric around others. All the data were converted to structure factors by applying Lorentz and polarization corrections, but no absorption corrections were made. Immediately after the intensity data collection at high temperature, 20 independent 2θ values were measured for cell parameter determinations, and the data were used to refine the cell parameters with the PODEX2 least-squares program written by A.W. Sleight (unpublished program). Final cell parameters of high clinoferrosilite are listed in Table 1 with those of two other $C2/c$ high clinopyroxenes with different compositions.

The diffraction intensities of the two components of the (100)-twinned phases were doubled on the *hk*0, *hk*4 and *hk*6 reciprocal lattice points, and these reflections were omitted from the refinement process. Full-matrix, least-squares structure refinement was carried out using MINEPAC, a version of L. Finger's RFINE program modified by Miyamoto et al. (1974), and atomic scattering factors for neutral atoms (Doyle and Turner, 1968). Starting atomic coordinates and temperature factors were taken from the high clinohypersthene structure of Smyth and Burnham (1972). All reflections that were indistinguishable from background or that had asymmetric backgrounds (mainly caused by asymmetric diffuse streaks mentioned above) were rejected from the least-squares refinements. The number of collected reflections excluding *hk*0, *hk*4, and *hk*6 reflections was 337 and the number used for the final cycle of refinement was 221. The weighted *R* factor for final anisotropic refinement was 0.050.

Table 1. Cell parameters of three high clinopyroxenes

	HCfs 1050°C	HChp 825°C	HPgt 960°C
a-axis(Å)	9.928(1)	9.870(5)	9.858(4)
b-axis(Å)	9.179(1)	9.054(5)	9.053(2)
c-axis(Å)	5.338(1)	5.328(2)	5.329(3)
β-angle(°)	110.20(1)	110.15(2)	109.42(1)
volume($Å^3$)	456.5	447.1	448 5

HCfs : Fs_{100} (this study)
HChp : $En_{31}Fs_{67}Wo_{1.5}$ (J. R. Smyth, 1974)
HPgt : $En_{39}Fs_{52}Wo_{9}$ (G. E. Brown et al., 1972).

Table 2. Final positional parameters and equivalent isotropic temperature factors ($Å^2$) for high clinoferrosilite at 1050°C

	X	Y	Z	B
Fe1	0.0	0.9014	0.25	2.03(10)
Fe2	0.0	0.2625(6)	0.25	2.84(12)
Si	0.2962(5)	0.0852(8)	0.2708(7)	1.90(10)
O1	0.1241(13)	0.0903(19)	0.1587(16)	3.28(28)
O2	0.3747(14)	0.2398(13)	0.3616(19)	2.23(25)
O3	0.3589(15)	0.0134(12)	0.0445(20)	2.40(30)

The results of high-temperature structure refinement of high clinoferrosilite are reported as follows: Positional parameters and isotropic temperature factors, Table 2; interatomic cation-oxygen distances, Table 3; interatomic angles (°) in tetrahedral chains and Fe polyhedron, Table 4; magnitude and orientation of thermal ellipsoids of atoms except for O2 and O3, because the anisotropic temperature factors for these atoms were not positive definite, Table 5; volumes of six-coordinated polyhedra in *M*1 and *M*2 sites of several high clinopyroxenes, Table 6; the list of the observed and calculated structure factors, and βij's from the final cycle of refinement, Table 7[1].

Discussion

Cell parameters

Figure 1 shows the plots of cell parameters of orthoferrosilite at several temperatures (Sueno et al., 1976) and

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[1] To receive a copy of Table 7, order Document AM-84-238 from the Business Office, Mineralogical Society of America, 2000 Florida Avenue, N.W., Washington, D.C. 20009. Please remit $1.00 in advance for the microfiche.

Table 3. Interatomic distances in high clinoferrosilite at 1050°C

Fe1 octahedron		Fe2 polyhedron		Si tetrahedron	
Fe1-O1A*	2.275(15)Å	Fe2-O1A	2.161(15)Å	Si-O1A	1.604(13)Å
-O1A'	2.104(8)	-O1B	2.161(15)	-O2A	1.611(12)
-O1B	2.275(15)	-O2A	2.016(9)	-O3A	1.647(11)
-O1B'	2.104(8)	-O2B	2.016(9)	-O3A'	1.673(13)
-O2A	2.148(13)	-O3A	2.722(13)	mean	1.634
-O2B	2.148(13)	-O3B	3.191(13)		
mean	2.176	-O3B'	2.722(13)		
		mean of 6	2.300		

* The above oxygen labels were used in order to compare the HCfs with Ofs structure (Sueno et al., 1976), although the A and B chains become equivalent in high clinoferrosilite structure. These labels are equivalent to those of Cameron et al. (1973), as follows: O1A=O1A1, O1A'=O1A2, O1B=O1B1, O1B'=O1B2, O2A=O2C1&O2C2, O2B=O2D1&O2D2, O3A=O3C1, O3A'=O3C2, O3B=O3D2, and O3B'=O3D1.

Table 4. Interatomic angles (°) in Fe and Si coordination polyhedra in high clinoferrosilite at 1050°C

Fe1 octahedron		Fe2 polyhedron		Si tetrahedron	
O1A-Fe1-O1A'	91.6(5)	O1A-Fe2-O2A	91.6(4)	O1A-Si-O2A	115.4(1.0)
O1A- -O2A	93.4(5)	O1A- -O3A	141.5(4)	O1A- -O3A	112.0(8)
O1A'- -O2A	97.2(5)	O2A- -O3A	118.2(5)	O1A- -O3A'	110.8(6)
O1A- -O1B	80.7(6)	O1A- -O1B	86.0(8)	O2A- -O3A	102.8(6)
O1A- -O1B'	85.2(5)	O1A- -O2B	87.6(4)	O2A- -O3A'	107.6(7)
O1A'- -O1B	85.2(5)	O2A- -O1B	87.6(4)	O3A- -O3A'	107.6(7)
O1A'- -O2B	85.7(5)	O2A- -O3B	63.0(4)	mean	109.4
O2A- -O1B'	85.7(5)	O3A- -O2B	63.0(4)		
O2A- -O2B	92.6(5)	O3A- -O3B	64.4(5)		
O1B- -O1B'	91.6(5)	O1B- -O2B	91.6(4)		
O1B- -O2B	93.4(5)	O1B- -O3B	141.5(4)		
O1B'- -O2B	97.2(5)	O2B- -O3B	118.2(5)		

The oxygen labels can be referred to the footnote on Table 3.

those of high clinoferrosilite at 1050°C. The unit cell lengths along the **a*** direction of the two symmetrically-different structures were compared using d_{200} and d_{100} of the orthoferrosilite and clinoferrosilite, respectively.

The cell expansions along the **a*** and **b** directions are almost linear from room temperature to 1050°C without regard to the ortho-clino transition, whereas the expansion rate along the **c** direction increases above the transition point. This may be related to the sudden extension of silica tetrahedral chains during the transition.

A comparison of cell parameters of high clinoferrosilite with those of two other high clinopyroxenes with different chemical compositions measured at high temperature (825–1050°C) reveals that the largest cell parameter difference is in *b* (larger than 0.12Å) and the next in *a* (larger than 0.06Å), but the difference in *c* (0.009Å) is much smaller than that for the others as shown in Table 1. The similarity of the *c* dimensions observed in these pyroxenes may be related to the straightened tetrahedral chains in high clinopyroxenes, which may control the **c**-length without regard to the ionic radii of atoms in the *M*1 and *M*2 sites.

Cation polyhedron

In ferrosilite, both the *M*1 and the *M*2 sites are occupied by Fe^{2+} ions; therefore, the problem with diffusion between the metal sites encountered by Smyth (1969, 1973) for the intermediate pyroxenes in the pyroxene quadrilateral is avoided. The Fe1 cation is always coordinated by six oxygens through the entire measured temperature range (24–1050°C). However, the number of Fe2–O distances less than 3.00Å (a value arbitrarily chosen following the papers of Smyth and Burnham, 1972; Smyth, 1973; and Sueno et al., 1976) changes from six at 24°C to seven between 600°C and 800°C, and back to six at higher temperatures in orthoferrosilite as can be seen in Figure 3 (details of interatomic distance variation *vs.* temperature in orthoferrosilite are in Table 6 of Sueno et al., 1976), whereas, in the high clinoferrosilite structure, the coordination number of Fe2 is six. Therefore, the comparison of the Fe2 polyhedron between orthoferrosilite and clinoferrosilite is made on the basis of six coordination.

Figure 2 shows plots of the mean interatomic distances of the cation polyhedra. The mean Si–O distance shows a slight increase after the transition, whereas these distances in the ortho phase decrease gradually at increasing temperature. The temperature variation of the mean Fe1–O interatomic distances revealed a linear increase from 24 to 1050°C across the transition point. The mean distance in the Fe2 octahedron, considering the six shortest Fe–O distances, decreases after the transition. A similar decrease in the average *M*2–O interatomic distance was observed in the transitions from orthohypersthene to high clinohypersthene and from low to high clinohypersthene structures (Smyth, 1974). In the Fe2 cation polyhedron, the four shorter bonds that are coordinated with O1 and O2 remain relatively constant up to 1050°C (Fig. 3). However, the bonds connected with O3 atoms change their length concomitantly with the straightening of the tetrahedral chains until the temperature reaches the transition point. During the transition, the kink angles of the tetrahedral chains change drastically until the *A* and *B* chains become equivalent, as shown in Figure 4. As a result, the O3*B* oxygen moves out from the coordination sphere (from 3.01Å at 980°C to 3.19Å at 1050°C), and O3*A*

Table 5. Amplitudes and orientations of major axes of thermal ellipsoids

Ellipsoid axis (r_j)		Fe 1	Fe 2	Si	O1	O2 & O3
r_1	rms*	0.138(5)**	0.146(7)	0.116(17)	0.119(19)	
	a	74 (7)	60 (6)	44 (6)	71 (9)	
	b	90	90	50 (8)	83 (10)	
	c	36 (7)	50 (6)	91 (19)	40 (10)	
r_2	rms	0.164(9)	0.201(8)	0.116(17)	0.119(19)	non positive definite
	a	90	30 (6)	85 (15)	41 (16)	
	b	180	90	75 (13)	56 (17)	
	c	90	140 (6)	159 (7)	126 (12)	
r_3	rms	0.176(7)	0.214(9)	0.199(13)	0.260(26)	
	a	164 (7)	90	133 (6)	124 (16)	
	b	90	0	44 (6)	35 (17)	
	c	54 (7)	90	69 (6)	74 (12)	

* rms: root mean square amplitude (Å).
** Errors in parentheses are one standard deviation.
a, b, c represent angles (°) of r_i with cell edges a, b, c, respectively.

Table 6. Volumes of 6-coordinated polyhedra in M1 and M2 sites of high clinopyroxenes

minerals	measurement temperature	M1(Å^3)	M2(Å^3)	References
high clinoferrosilite	1050°C	13.405	11.932	this study
high pigeonite	960°C	12.599	11.698	Brown et al. (1972)
high clinohyperthene	760°C	12.937	11.534	Smyth (1974)
high clinohyperthene	850°C	13.068	11.616	Smyth (1974)

and O3*B*′ atoms become equivalent in the high clinoferrosilite structure. The mean value of Fe2–O3*A* and Fe2–O3*B*′ bond lengths at 980°C was 2.764Å, but it decreased to 2.722Å after the transition (Fig. 3).

As shown in Figure 2, the mean Fe1–O distance in ferrosilite is smaller than the mean Fe2–O distance throughout the measured temperature range. The polyhedral volume calculation, however, reveals that the volume of the six-coordinated Fe2 polyhedron (11.93Å^3) is smaller than that of the six-coordinated Fe1 polyhedron (13.4Å^3) in the high clinoferrosilite structure at 1050°C, as shown in Table 6. If we consider the eight-coordinated Fe2 polyhedron, although the two longest Fe2–O bond lengths in this polyhedron are too distance (3.19Å) to be considered as coordinating the Fe2 ion, the polyhedral volume (25.25Å^3) is comparable with those of the *M*2 polyhedra in the Ca and Na pyroxenes (Cameron et al., 1973). Spodumene ($LiAlSiO_3$) has a six-coordinated *M*2 site (Li) in spite of having the same symmetry as those of Ca and Na clinopyroxenes. The volume of the Li polyhedron is smaller than that of Fe2 in high clinoferrosilite (11.02Å^3 at 750°C), while the volume of the *M*1 site (Al) in spodumene is 9.45Å^3, which is much smaller than that of

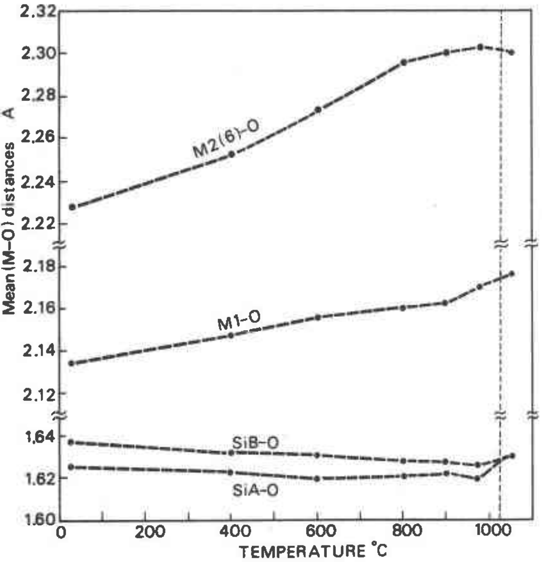

Fig. 2. Variation of mean interatomic distances of cation polyhedra in orthoferrosilite and high clinoferrosilite with increasing temperature across the transition point (vertical fine dotted line).

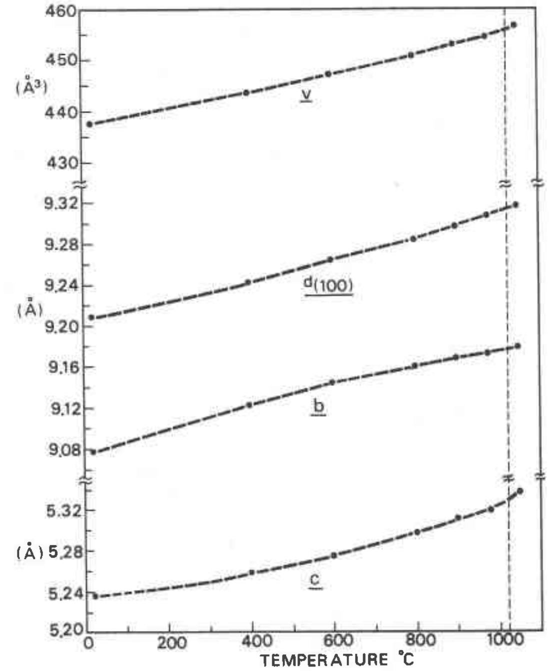

Fig. 1. Variation of crystallographic dimensions of orthoferrosilite and high clinoferrosilite with temperature across the transition point (fine dotted line).

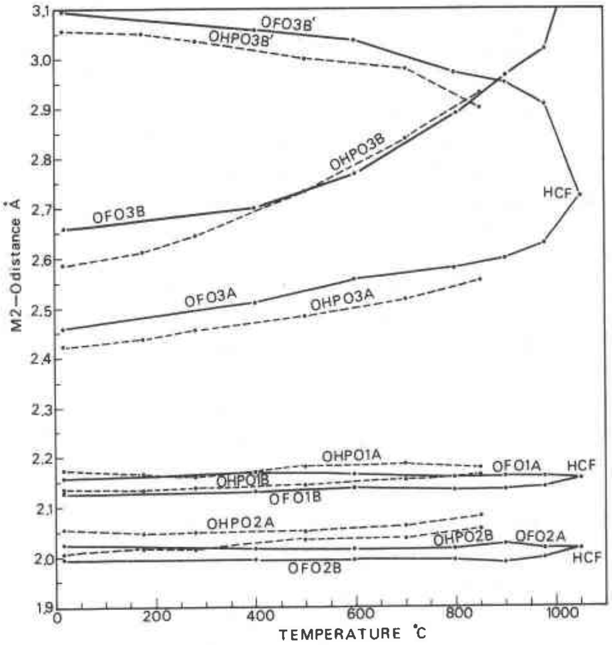

Fig. 3. Variation of individual Fe2–O distances in orthoferrosilite and high clinoferrosilite (solid lines) with temperature across the transition point. Dotted lines show those in orthohyperthene (Smyth, 1973).

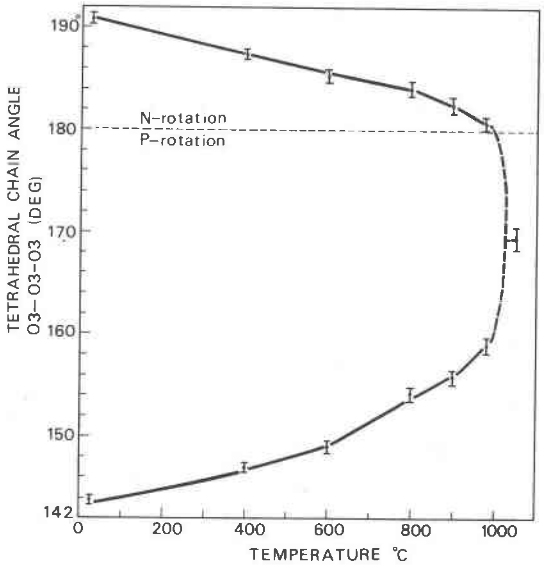

Fig. 4. Variation of the O3–O3–O3 angles of orthoferrosilite and high clinoferrosilite with increasing temperature across the transition point.

the Fe1 in high clinoferrosilite. Therefore, the spodumene structure satisfies the tendency observed on the other Ca- and Na–*C*2/*c* clinopyroxenes, namely that the volume of *M*2 is larger than that of *M*1.

For all of the high clinopyroxenes, *M*2 is coordinated by six oxygens, assuming that those less than 3.00Å distant have effective bonding. The volumes of these *M*2 polyhedra are smaller than those of the six-coordinated *M*1 sites although their mean *M*2–O distances are larger than those of *M*1. This is the result of the large distortion of the *M*2 polyhedra and is characteristic of high clinopyroxene structures. In the orthoferrosilite structure, the six-coordinated Fe2 polyhedron switches one of the O3 bonds (from Fe2–O3*B* to Fe2–O3*B*′) around 900°C as shown in Figure 3, and this switching decreases the Fe2(6) volume from 14.45Å^3 at 800°C to 11.73Å^3 at 900°C although it increases again to 11.76Å^3 at 980°C. This apparent decrease of the *M*2(6) volume is caused by the arbitrary choice of 3.00Å as the distance beyond which the given oxygen no longer forms part of the first coordination polyhedron. However, both in ferrosilite and in hypersthene, the ortho-clino transition was observed at a temperature about 140°C higher than the switching of the O3 bonds, although the transition temperatures of each pyroxene were different from each other. It is probable that the thermal behavior of the *M*2 atom, especially in bonding with O3 atoms, is most important for the pyroxene transition. The switching of the O3 atoms may bring about a spatial imbalance in the distribution of bonds around the *M*2 atom in the orthopyroxene structure and this imbalance may become one of the motive forces for the ortho-clino transition. In addition to the switching of the O3 bonds, which is caused by the straightening of the *B* chain, the *A* chain is almost completely extended at 980°C and the skew of the *A* chain would be changed from N rotation to P rotation (Sueno et al., 1976) at higher temperature if the transition did not occur. The *B* chain is P rotated at all temperatures studied. In all of the previously reported orthopyroxene structures, the *A* chains are N rotated and the *B* chains are P rotated. If the *A* chain changes to P rotation at high temperature it may bring on an energetic instability in the orthopyroxene structure because the tetrahedral chain configuration around the *M*2 site becomes N/N, which has never been observed in orthopyroxene. However, N/N, P/P and P/N configurations are permitted in the clinopyroxene structure. This may also be a reason why the ortho-clino transition occurs at this temperature. In the analysis of the mechanism of the pyroxene transition, the study of the bonding distribution around the *M*2 site including the electrical charge and the interatomic angles may be important in addition to the details of the bond lengths of the *M*2 polyhedron.

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