High-Pressure Synthesis and Crystal Structure of CaFeTi₂O₆, a New Perovskite Structure Type

Kurt Leinenweber[1] and John Parise

Center for High Pressure Research, Department of Earth and Space Sciences, University at Stony Brook, Stony Brook, New York, 11794-2100

Single-crystal and powder samples of a new calcium iron (II) titanate, $CaFeTi_2O_6$, have been synthesized at 12–15 GPa and 1200–1400°C, and studied by X-ray diffraction. This compound is a variant of the perovskite structure and crystallizes in the tetragonal space group $P4_2/nmc$, $a = 7.5157(2)$ Å, $c = 7.5548(2)$ Å, and $Z = 4$. Calcium and two iron atoms are ordered on three different A sites, with calcium in approximately 10-fold coordination, with one iron atom in tetrahedral coordination (Fe–O = 2.084(2) Å), and the other iron atom in square-planar coordination (Fe–O = 2.097(2) Å). The system of octahedral tilts which this compound adopts has not been observed previously in a perovskite. The tilt system was described in a theoretical treatment of perovskites ($a^+a^+c^-$ in the notation of A. M. Glazer (*Acta Crystallogr. Sect. B* 28, 3384, 1972) and was (incorrectly) assigned to space group Pmmn. © 1995 Academic Press, Inc.

INTRODUCTION

The perovskite structure is of fundamental importance in solid state science. The holosymmetric structure (1) possesses cubic ($Pm\bar{3}m$) symmetry ($Z = 1$, $a \approx 3.8$ Å for oxides). This structure is based on an ordered cubic closed-packed array AX_3. The relatively small B cations occupy $\frac{1}{4}$ of the octahedral sites, namely those formed exclusively by X atoms. The A cations are surrounded by 12 X atoms arranged as a cubo-octahedron. The X_6 octahedra form a corner-sharing three-dimensional network.

Modification of the $Pm\bar{3}m$ symmetry occurs through tilting of the octahedra about the flexible B–X–B linkages. Glazer (2) demonstrated that 23 tilt system are possible for the doubled holosymmetric unit cell (some corrections to the original table were made by Burns and Glazer (3)). The predictive capabilities of this technique were demonstrated by the later discovery of some of the anticipated structures. For example, a series of compounds with the tilt system $a^+a^+a^+$ was found, an example being $NaMn_7O_{12}$ (4). A number of other interesting structures derived by Glazer are still unknown.

A useful method for finding new perovskite compounds is by high-pressure treatment of promising starting compositions. Perovskites are often stabilized by pressure, due to their relatively high density. The perovskite-related superconducting oxides (5) and the geologically important $MgSiO_3$ perovskite (6, 7) are among the many examples.

In the present investigation of the join $CaTiO_3$–$FeTiO_3$, we have recovered two novel compounds, $CaFe_3Ti_4O_{12}$ and $CaFeTi_2O_6$, from high pressure and temperature. $CaFe_3Ti_4O_{12}$ is a new member of the $NaMn_7O_{12}$ series and is discussed separately (8). $CaFeTi_2O_6$ is the first example of a perovskite structure which follows the Glazer tilt system $a^+a^+c^-$. The structural details of this compound are presented here.

EXPERIMENTAL

Initial high pressure experiments were carried out at 14–15 GPa and 1150–1200°C in a uniaxial split-sphere apparatus (USSA-2000), using powdered mixtures of $CaTiO_3$ and $FeTiO_3$. The experimental cell assembly is illustrated in Fig. 1. Each sample was contained in an iron capsule, which was then placed in a solid-medium high-pressure cell with a graphite resistance furnace. The pressure medium was an MgO octahedron with a 14-mm edge length. Force was applied by eight tungsten carbide cubes with corners truncated to triangular faces of 8-mm edge length. The cell was designed for exploratory work on large volumes (20 mm³) in the pressure and temperature ranges 5–15 GPa and 25–2000°C. Additional features of the high-pressure system are described in Liebermann and Wang (9).

The compound $CaFeTi_2O_6$ was recovered from a high-pressure and -temperature run on an equimolar mixture of $CaTiO_3$ and $FeTiO_3$. Electron probe microanalysis (eight points) indicated the presence of a homogeneous phase, with an analyzed composition of $1.02 \pm .02$ FeO, $1.01 \pm$

■ Zirconia insulation

▦ TZM ring

■ Graphite furnace

▨ Iron capsule

▨ Sample

☐ MgO
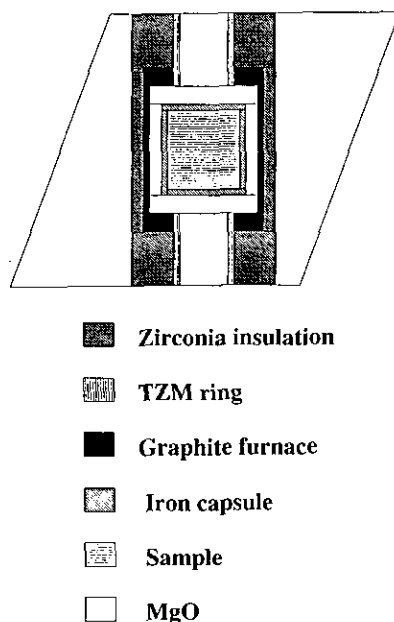
FIG. 1. Diagram of the high-pressure cell assembly used for synthesis of $CaFeTi_2O_6$.

which is a subgroup of $Pm\overline{3}m$. The structure may be described using two independent tilts of each octahedron. The first is a rotation about a twofold axis, leading to space group $I4/mmm$. This operation is described by O'Keeffe and Hyde (10). It leads to a differentiation into three distinct A sites. We follow the notation of O'Keeffe and Hyde in labeling these sites: two smaller sites are labeled A' and A'' (Wyckoff sites $2a$ and $2b$), and one relatively large site is labeled A''' (Wyckoff site $4c$). The general structural formula is $A_2'''A'A''B_4O_{12}$.

The second rotation is about the already tilted apical axes of the octahedra which are subparallel to the c-axis of the unit cell. This leads to distortion of the A''' sites from mmm to $2mm$ synmmetry and, more interestingly, a tetrahedral distortion of the A' and A'' sites from $4/mmm$ to $m2$ symmetry. This rotation has a notable effect on the coordination of the A' and A'' cations, leading to square-planar and tetrahedral nearest-neighbor configurations, respectively. In $CaFeTi_2O_6$, the A''' site is occupied by Ca, and the A' and A'' sites are occupied by Fe(2) and Fe(1). The magnitude of the first rotation is close to $16.5°$, and that of the second is close to $11.3°$.

The Ca^{2+} and Fe^{2+} ions each occupy half of the total

.02 CaO, and 1.99 ± 0.1 TiO_2, referred to six oxygens. The total was 99.6 ± 0.7%, indicating no ferric iron within the limit of the resolution of the instrument. Preliminary powder X-ray diffraction showed this compound to be perovskite-like.

Following the initial characterization of the compound, a single-crystal sample was synthesized from a mixture of $Ca(OH)_2$ + $2TiO_2$ + Fe + Fe_2O_3 in a welded gold capsule. Water was introduced, via the hydroxide, to act as a mineralizer and aid in the growth of crystals. This material was treated in the cell assembly described above at 12 GPa and 1400°C for 2 hr. The recovered sample consisted of shiny, black, equally sized prisms of about 40 × 40 × 80 μm.

The data collection parameters are summarized in Tables 1a and 1b. Both the photographic and the diffractometer data were consistent with the extinction symbol $Pn-c$ which unambiguously implicated space group $P4_2/nmc$ (No. 137). Although surprised not to find this group in the compilations offered by Burns and Glazer (3), we nonetheless were able to derive a reasonable model consistent with the perovskite structure and the stoichiometry observed for the new compound, $CaFeTi_2O_6$. This model was refined to convergence (Table 1) and the resulting atomic parameters are summarized in Table 2.

DISCUSSION

The structure of $CaFeTi_2O_6$ is based on a perovskite linkage of TiO_6 octahedra in the space group $P4_2/nmc$,

TABLE 1a
Summary of X-Ray Diffraction Data for $CaFeTi_2O_6$

Color	Black
Size (mm)	0.07 × 0.05 × 0.04
Crystal system	Tetragonal
Space group	$P4_2/nmc$ (No. 137)
a (Å)	7.5157(2)
c (Å)	7.5548(2)
Temperature (°C)	20
Volume (Å³)	426.7
Z	4
Formula weight	287.724
Calculated density (g/cm³)	4.478
μ(Mo) (cm⁻¹)	81.1
Diffractometer	Picker
Radiation (graphite monochromator)	Mo$K\alpha$
Data collected	1849
Max 2θ (°)	65.0
Max h,k,l	11, 11, 11
Data octants	$-+++, +-+$
Scan method	$\omega/2\Theta$
Absorption correction	Analytical
No. unique data ($I > 3.0\theta(I)$)	437
R_{Merge}	0.022
Refinement method	Full-matrix least-squares on F
Anomalous dispersion	Ca, Fe, Ti
Weighting scheme	$[\sigma^2(I) + 0.0008I^2]^{-1/2}$
Atoms refined	All anisotropic
Parameters varied	33
Data/parameter ratio	13.24
R	0.038
R_w	0.022
Error of fit	1.45

TABLE 1b
Anisotropic Thermal Parameters ($\text{Å} \times 1000$)

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Fe(1)	11.9(3)	11.9(0)	8.4(4)	0.0(0)	0.0(0)	0.0(0)
Fe(2)	8.6(3)	8.6(0)	60.9(8)	0.0(0)	0.0(0)	0.0(0)
Ti(1)	6.1(3)	6.3(3)	7.7(2)	−0.9(2)	−0.2(2)	−0.1(2)
Ca(1)	7.5(4)	14.6(4)	6.4(3)	0.0(0)	0.0(0)	0.0(0)
O(1)	11.3(10)	4.6(9)	11.1(8)	0.0(0)	−1.0(8)	0.0(0)
O(2)	4.4(9)	11.0(10)	12.6(8)	0.0(0)	0.0(0)	−0.1(8)
O(3)	10.5(6)	10.5(0)	5.8(7)	0.6(8)	0.2(5)	−0.2(0)

Note. $\exp[-19.739(U_{11}hha^*a^* \cdots + 2(U_{12}hka^*b^* \cdots))]$

available A sites within the TiO$_6$ octahedral framework (Figs. 2A and 2B). They are ordered into Fe- and Ca-containing columns parallel to the c-axis. The coordination geometry adopted by Ca^{2+} (Fig. 3) is not unusual, with the 10 Ca–O distances close to those expected from the sum of the ionic radii (11). The Ca cations lie on and are related by the 4$_2$ axis in this space group.

The two Fe^{2+} sites alternate along the Fe column. The local geometry of each site is shown in Fig. 4. Fe(1) has four nearest oxygen neigbors in a distorted tetrahedron at 2.084(2) Å, with four second neighbors in a larger distorted tetrahedron rotated 90° from the first at 2.800(2) Å, and four third neighbors in an undistorted square at 3.218(2) Å. Fe(2) has the inverse sequence, with four nearest neighbors in an undistorted square at 2.097(2) Å, four second neighbors in a distorted tetrahedron at 2.844(2) Å, and four third neighbors in a larger distorted tetrahedron, rotated 90° from the first, at 3.147(2) Å. The distributions of Fe–O distances are similar about the two sites, despite the obvious differences in local geometry (Table 3 and Fig. 4). The distances (but not the configurations) would be identical in the ideal case of regular TiO$_6$ octahedra.

Square-planar Fe^{2+} is very unusual. The mineral gillespite (12), BaFeSi$_4$O$_{10}$, is a rare example of its occurrence,

TABLE 2
Fractional Coordinates ($\times 10^4$) and Equivalent Isotropic Thermal Parameters (Å^2)

Atom	Site	x	y	z	B_{iso}
Fe(1)	2b	7500	2500	2500	0.85(3)[a]
Fe(2)	2a	7500	2500	7500	2.14(4)[a]
Ti(1)	8e	0	0	0	0.53(4)[a]
Ca(1)	4d	2500	2500	2246(1)	0.76(4)[a]
O(1)	8g	4457(3)	2500	4638(2)	0.72(9)[a]
O(2)	8g	2500	5437(3)	5657(3)	0.74(8)[a]
O(3)	8f	4473(2)	−527	2500	0.71(8)[a]

Calculated as the mean of the body diagonal elements for the anisotropic thermal parameters.

with an Fe–O distance of 1.98 Å. In this mineral the Fe and O are not constrained to be coplanar, yet the Fe lies only 0.03 Å ouside of the plane of the oxygens. A nearly square-planar FeO$_4$ configuration has also been found recently in CaFe$_3$Ti$_4$O$_{12}$ perovskite, with an Fe–O distance of 2.04 Å (8). In that case, the four nearest neighbors are constrained by symmetry to be coplanar with the Fe^{2+} ion, but the two angles are unconstrained, adopting values of 87° and 93°. In the present compound, Fe^{2+} and the four oxygen neighbors are fully constrained by symmetry to be square-planar.

The shortest Fe–O distances in these perovskites are close to those expected from published ionic radii, which give Fe–O distances of 2.03 and 2.04 Å for tetrahedral and square-planar iron, respectively (11). The distances for both coordinations are not demonstrably affected by the presence of four second neighbors at $\approx$2.8 Å, so in the present treatment we consider these to be tetrahedral and square-planar sites, although they could also be considered highly distorted eightfold sites (4 + 4).

The thermal parameters for all metal sites, except for square-planar Fe(2), are approximately isotropic (Figs. 3 and 4). The thermal ellipsoid for Fe(2) is elongated perpendicular to the square plane, parallel to the c-axis; the ratio of rms displacement along the c-axis compared to the a-axis is 3. Trial refinements using two half-occupied sites located at equal distances above and below the 2a site (Table 2) did not lead to an improvement in the fit to the data. However, the large thermal parameter may indicate statistical disorder of Fe perpendicular to the square, which would make the local Fe environment square-pyramidal, like that in gillespite. The rms displacement perpendicular to the coordination plane is 0.25 Å.

A complete description of the octahedral rotations in CaFeTi$_2$O$_6$ requires the identification of a Glazer tilt symbol, which includes information on the magnitude and phase of tilts in all three principal directions. The table in Burns and Glazer (3) includes all 23 possible tilt systems which have a doubling of the original $Pm\overline{3}m$ unit cell, although the space group $P4_2/nmc$ is not listed. We have
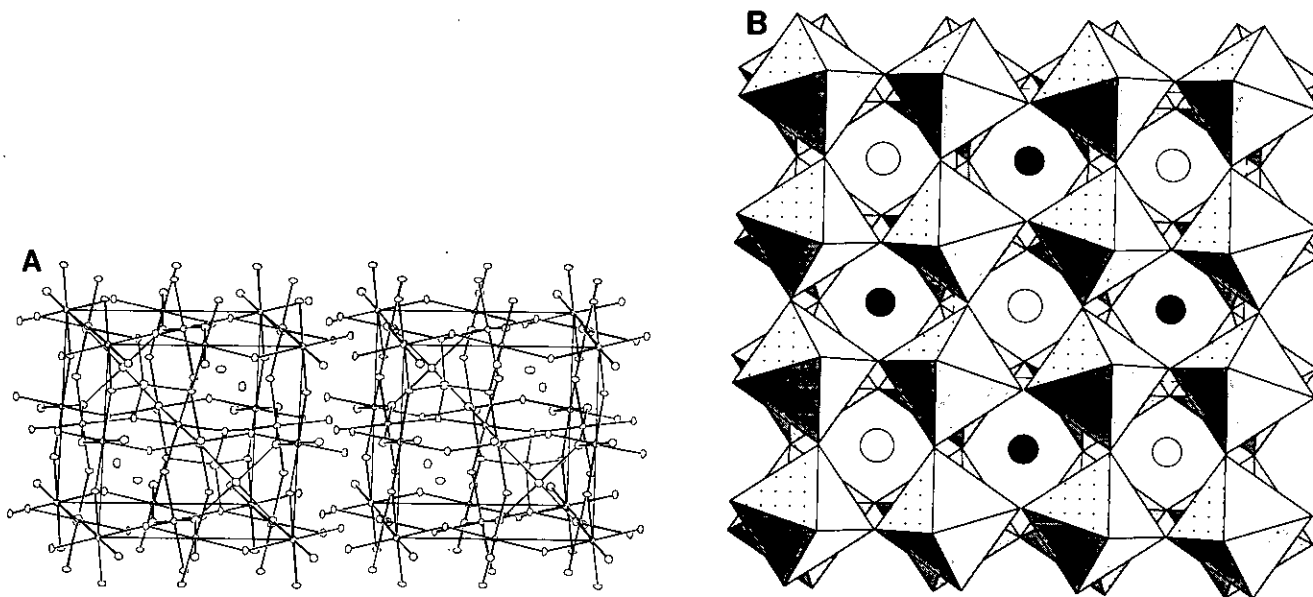
FIG. 2. (A) ORTEP [14] stereoplot of the $CaFeTi_2O_6$ structure. The Ca–O bonds have been left out for the sake of clarity. (B) A c-axis projection of the $CaFeTi_2O_6$ structure. Columns of Ca atoms (white) alternate with columns of Fe atoms (black). In the layer shown, Fe(1) sites are on the left and right, and Fe(2) sites are on the top and bottom of the figure.

identified two of the entries, $a^+a^+c^-$ and $a^+a^+a^-$, as belonging to the space group $P4_2/nmc$, rather than $Pmmm$ as originally listed. Because it has two independent magnitudes (a and c), the second tilt system, $a^+a^+c^-$ ($P4_2nmc$), fully describes the $CaFeTi_2O_6$ structure. In this case, the a^+a^+ part of the symbol represents the 16.5° in-phase rotations about single twofold axes of the octahedra, while the c^- part represents the 11.3° out-of-phase rotations about the apical axes of the octahedra.
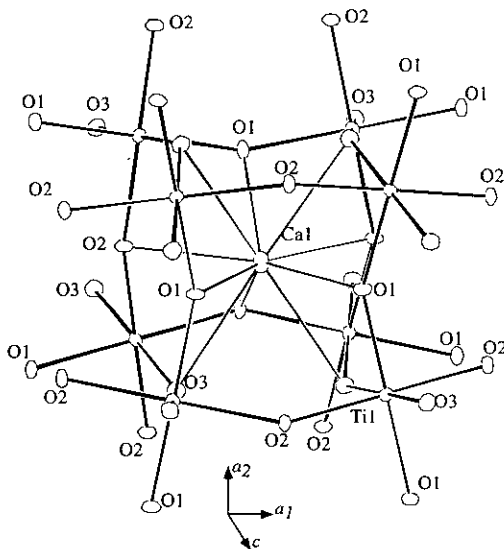
The tilt system of $CaFeTi_2O_6$, modified by octahedral cation ordering, occurs in the mineral stottite, $FeGe(OH)_6$ (13), and its analogues. The octahedra in these compounds form an ReO_3-type linkage, which is the perovskite structure without A cations. The hydrogen atoms
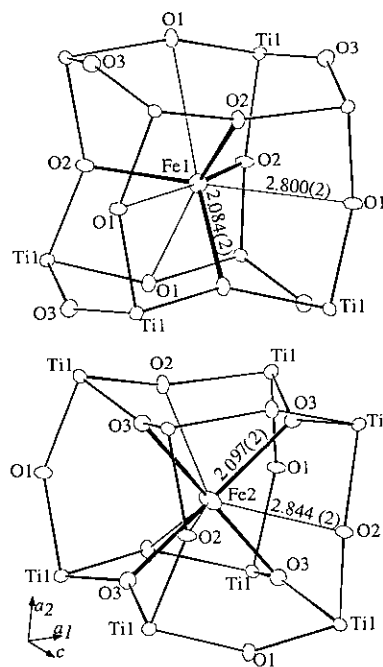

FIG. 3. Configuration of oxygen atoms around calcium in Ca $FeTi_2O_6$, showing selected bond lengths.

FIG. 4. Configurations of oxygen atoms around Fe(1) and Fe(2) in $CaFeTi_2O_6$, showing selected bond lengths.

TABLE 3

Selected Interatomic Distances (Å) and Angles (°) for CaFeTi$_2$O$_6$

Fe(1)–O(2)a × 4	2.084 (2)	Ti(1)–O(1)g ×2	1.9421 (5)
Fe(2)–O(3)q ×4	2.097 (2)	Ti(1)–O(2)h ×2	1.9709 (6)
O(2)a–Fe(1)–O(2)c	116.52 (6)	Ti(1)–O(3)i ×2	1.9701 (6)
O(2)a–Fe(1)–O(2)b	96.1 (1)	O(1)g–Ti(1)–O(1)j	180 (6)
O(3)q–Fe(2)–O(3)n	90.000 (2)	O(1)g–Ti(1)–O(2)k	90.2 (1)
O(3)q–Fe(2)–O(3)f	180	O(1)g–Ti(1)–O(2)h	89.8 (1)
Ca(1)–O(1) ×2	2.330 (2)	O(1)g–Ti(1)–O(3)i	89.01 (6)
Ca(1)–O(1)a ×2	2.459 (2)	O(1)g–Ti(1)–O(3)g	90.99 (6)
Ca(1)–O(2)a ×2	2.513 (2)	O(2)h–Ti(1)–O(2)k	180
Ca(1)–O(3) ×4	2.7224 (4)	O(2)h–Ti(1)–O(3)g	90.91 (7)
O(1)–Ca(1)–O(1)i	78.3 (1)	O(2)h–Ti(1)–O(3)i	89.09 (7)
O(1)a–Ca(1)–O(1)g	73.5 (1)	O(3)i–Ti(1)–O(3)g	180 (4)
O(1)–Ca(1)–O(1)a	128.42 (5)	Fe(1)d–O(2)–Ti(1)e	107.00 (6)
O(1)–Ca(1)–O(2)h	157.70 (8)	Fe(2)o–O(3)–Ti(1)i	106.53 (6)
O(1)a–Ca(1)–O(2)a	67.48 (4)	Fe(1)d–O(2)–Ca(1)d	109.52 (8)
O(1)–Ca(1)–O(2)a	79.39 (7)	Fe(2)o–O(3)–Ca(1)	101.88 (5)
O(1)–Ca(1)–O(3)	66.52 (4)	Ti(1)n–O(1)–Ti(1)f	150.7 (1)
O(1)a–Ca(1)–O(3)	123.80 (4)	Ti(1)e–O(2)–Ti(1)f	144.8 (1)
O(1)a–Ca(1)–O(3)l	63.67 (4)	Ti(1)i–O(3)–Ti(1)n	146.9 (1)
O(1)–Ca(1)–O(3)i	106.81 (4)	Ti(1)n–O(1)–Ca(1)d	90.72 (6)
O(2)a–Ca(1)–O(2)h	122.9 (1)	Ti(1)n–O(1)–Ca(1)	104.00 (5)
O(2)a–Ca(1)–O(3)	63.59 (4)	Ti(1)e–O(2)–Ca(1)d	88.50 (7)
O(2)a–Ca(1)–O(3)i	120.80 (4)	Ti(1)i–O(3)–Ca(1)p	90.51 (3)
O(3)–Ca(1)–O(3)l	113.4 (1)	Ti(1)i–O(3)–Ca(1)	82.76 (3)
O(3)–Ca(1)–O(3)i	66.0 (1)	Ca(1)–O(1)–Ca(1)d	104.11 (8)
O(3)–Ca(1)–O(3)m	171.93 (3)	Ca(1)–O(3)–Ca(1)p	156.2 (1)
Fe(1)···Fe(2)a × 2	5.314	Fe(1)···Ti(1)q ×8	3.260
Fe(1)···Fe(2) ×2	3.777	Fe(2)···Ti(1)q ×8	3.260

Symmetry operation codes: (a) $Y,X, -\frac{1}{2} + Z$; (b) $\frac{3}{2} - Y,X, -\frac{1}{2} + Z$; (c) $1 - Z, 1 - Y, 1 - Z$; (d) $Y,X, \frac{1}{2} + Z$; (e) $Y, \frac{1}{2} - X, \frac{1}{2} + Z$; (f) $\frac{1}{2} - Y, \frac{1}{2} - X, \frac{1}{2} + Z$; (g) $Y, \frac{1}{2} - X, -\frac{1}{2} Z$; (h) $\frac{1}{2} - Y,X, -\frac{1}{2} + Z$; (i) $\frac{1}{2} - X,Y,Z$; (j) $-Y, -\frac{1}{2} + X, \frac{1}{2} - Z$ (k) $-\frac{1}{2} + Y, -X, \frac{1}{2} - Z$; (l) $X, \frac{1}{2} - Y,Z$; (m) $\frac{1}{2} - X, \frac{1}{2} - Y,Z$; (n) $\frac{1}{2} - Y,X, \frac{1}{2} + Z$; (o) $Y, -1 + X, -\frac{1}{2} + Z$; (p) $1 - Y, -X, \frac{1}{2} - Z$; (q) $1 + Y,X, \frac{1}{2} + Z$.

have not been located, but presumably they project into the vacant *A* sites. The tilt system is $a^+a^+c^-$, as in the present compound, but in addition to the tilts, Fe and Ge are ordered onto adjacent octahedra. This ordering

eliminates the mirror plane and the *c*-glide plane, but maintains the *n*-glide, resulting in the space group $P4_2/n$. This was identified as an ordering of cations in the $I4/mmm$ tilt system ($a^+a^+c^0$) by O'Keeffe and Hyde (10), but is in fact an ordering within the newly identified $P4_2/nmc$ tilt system ($a^+a^+c^-$).

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