

Rietveld refinement of $\text{Ca}_2\text{TiSiO}_6$ perovskite

KURT LEINENWEBER,¹ AND JOHN PARISE²

¹Department of Chemistry, Arizona State University, Tempe, Arizona 85287-1604, U.S.A.

²Center for High Pressure Research, Department of Earth and Space Sciences, State University of New York, Stony Brook, New York 11794-2100, U.S.A.

ABSTRACT

The structure of the high-pressure cubic double perovskite $\text{Ca}_2\text{TiSiO}_6$ was refined using synchrotron X-ray powder data [S.G. $Fm\bar{3}m$, $a = 7.4105(1)$ Å, $Z = 4$]. Ti and Si are fully ordered into alternating octahedra in the perovskite framework, with Ca occupying a tetrahedrally distorted cuboctahedron. The cation-anion bond lengths are Ti-O = 1.947(3) Å, Si-O = 1.758(3) Å, and Ca-O = 2.622(1) Å.

INTRODUCTION

The double perovskite $\text{Ca}_2\text{TiSiO}_6$ (Leinenweber et al. 1997), midway along the join between CaTiO_3 and CaSiO_3 , is the first double perovskite with silicon as one of the octahedral cations. Despite the large amount of research devoted to silicate perovskites, few examples are known. $\text{Ca}_2\text{TiSiO}_6$ perovskite is also interesting as a relative of CaSiO_3 perovskite, an unquenchable high-pressure phase that might be better understood through studies of $\text{Ca}_2\text{TiSiO}_6$.

Double perovskites form a large family of materials, with approximately 300 examples given in a recent review (Anderson et al. 1993). Their structures are made up of a framework of corner-linked octahedra similar to that of ABO_3 perovskites, but with the B cations ordered onto two distinct octahedral sites, leading to the stoichiometry $\text{A}_2\text{B}'\text{B}''\text{O}_6$. The B' and B'' cations form a face-centered array like that of Na and Cl in rock salt. The ordering leads to a reduction in symmetry from $Pm\bar{3}m$ with cell parameter a (ABO_3 perovskite), to an $Fm\bar{3}m$ cell with cell parameter $2a$ ($\text{A}_2\text{B}'\text{B}''\text{O}_6$ perovskite) (Steward and Rooksby 1951). The structure of the $Fm\bar{3}m$ double perovskite is specified by the unit-cell parameter and an oxygen-position parameter that defines the sizes of the two different octahedra.

In the present work, the structure of $\text{Ca}_2\text{TiSiO}_6$ is refined using powder X-ray data collected with synchrotron radiation to determine the a unit-cell parameter, oxygen position, and displacement parameters. The structure is then compared with some other silicate and titanate perovskites.

EXPERIMENTAL METHODS

The sample of $\text{Ca}_2\text{TiSiO}_6$ perovskite is the same as that described in a recent high-pressure reconnaissance study of the CaTiO_3 – CaSiO_3 join (Leinenweber et al. 1997). High-purity CaSiO_3 and CaTiO_3 (Aldrich) were combined and treated for 5 h at 14 GPa and 1200 °C in the 2000 ton uniaxial split-sphere apparatus (USSA-2000) at State

University of New York, Stony Brook. Following the heating, the sample temperature was quenched in a few seconds, and pressure was released in about 10 h. Powder X-ray patterns, Raman spectroscopy, and TEM showed majority conversion to a single phase of ordered perovskite, with minor regions (<10% of the sample) apparently having different ordering schemes in the double perovskite cell, as evidenced by reflections violating $Fm\bar{3}m$ symmetry in electron-diffraction patterns collected from these regions.

Synchrotron X-ray powder diffraction data, shown in Figure 1, were collected over the range $2\theta = 11.12^\circ$ to 74.0° at ambient pressure and 298 K, in high-resolution mode, using a Si(111)-Ge(220) channel-cut monochromator-crystal analyzer combination at the X7-A beamline of the National Synchrotron Light Source, Brookhaven National Laboratory (Cox et al. 1988; Cox 1992). The wavelength [$\lambda = 1.15032(2)$ Å] was calibrated using a Si standard ($a = 5.430825$ Å). To account for sample absorption, the technique of Hewat (1979) was used: The packing density of the material (30%) was determined by weighing the capillary before and after loading and measuring the capillary diameter (0.50 mm). The Debye-Waller factor B was corrected ($\Delta B = 0.7134$ Å²) using a calculated absorption coefficient of 241.8 cm⁻¹ for $\text{Ca}_2\text{TiSiO}_6$.

The data confirmed the earlier observation of a powder diffraction pattern that was dominated by reflections from a primitive cubic perovskite unit cell with $a \sim 3.7$ Å. No obvious splitting of these peaks occurred to indicate a symmetry lower than isometric. The weaker superlattice reflections consistent with the doubled F -centered cubic cell with $a = 7.4105(1)$ Å were also clearly present. The peak widths of the ordering reflections were consistent with those of the primitive reflections, indicating that both sets of peaks can be assigned to a single phase.

Weaker reflections were observed at positions consistent with a doubled primitive cubic perovskite cell (i.e., violating F -centering); the strongest of these latter reflec-

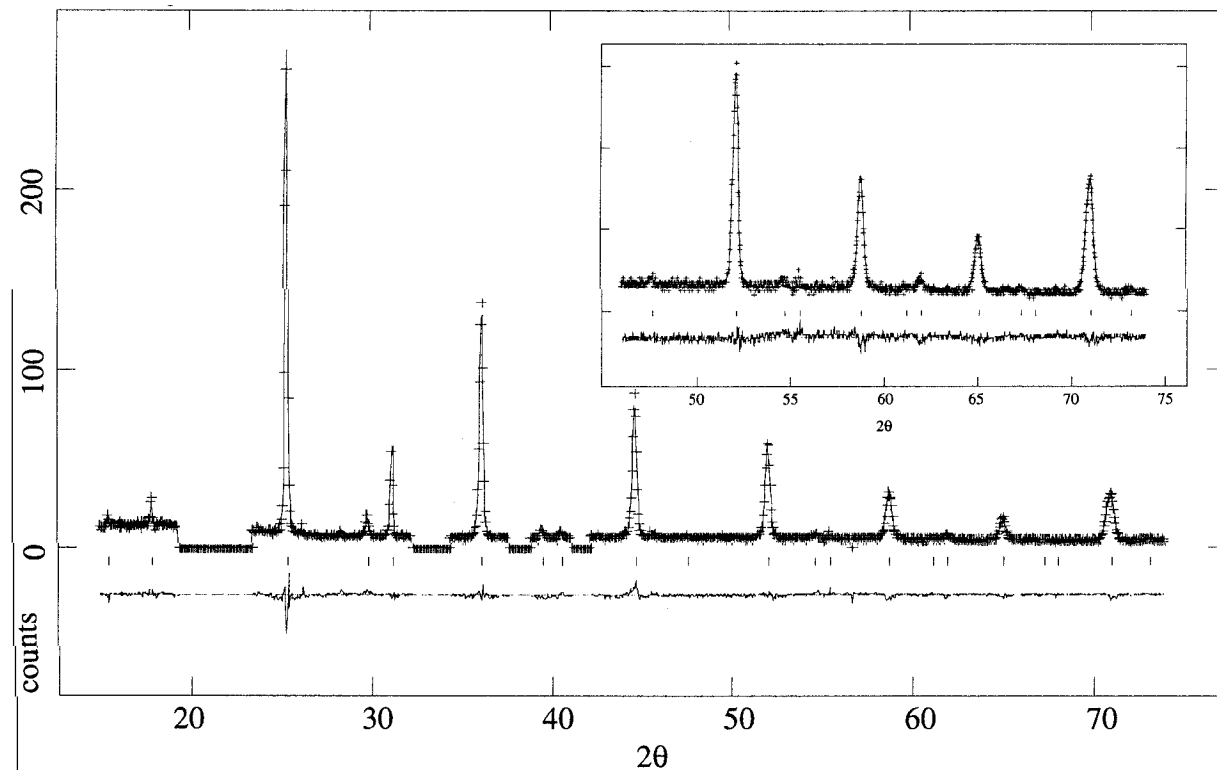


FIGURE 1. Calculated (continuous line) and observed (crosses) synchrotron X-ray diffraction profiles of $\text{Ca}_2\text{TiSiO}_6$. A difference curve ($I_{\text{obs}} - I_{\text{calc}}$) is plotted at the bottom. Allowed reflection positions are indicated by vertical lines. Inset: detail of the fit to the high-angle region.

tions (211) was approximately 15% of the strongest $Fm\bar{3}m$ ordering reflection (311), or < 1% of the strongest peak in the pattern. However, the peak widths were not consistent with those of the primary $Fm\bar{3}m$ pattern, indicating that these could represent impurity peaks or minor domains of different ordering in the perovskite sample. There was also no consistent set of superlattice reflections indicating a reduction to $P2_1/c$ or any other common subgroup of $Fm\bar{3}m$ double perovskite. In view of the TEM results, suggestive of lesser quantities of a second phase material in this sample with primitive reflections, it was decided to proceed with a model consistent with the F -centered cell.

Rietveld refinement was performed using the GSAS package (Larson and Von Dreele 1994). A starting model with Ca, Ti, Si, and O ordered into positions 8c, 4b, 4a, and 24e of $Fm\bar{3}m$ was used. The displacement parameters of the metal atoms were constrained to be equal because the data did not cover a 2-theta range sufficient to treat the metal atoms separately. The oxygen-displacement parameter was refined independently. Final R_p , wR_p , and $R(F^2)$ were, respectively, 8.33, 6.44, and 8.43% with $\chi^2 = 1.02$.

The peak shapes were well fit with a pseudo-Voigt (Cox et al. 1988) and with negligible particle contribution to the broadening. On the other hand, the estimated strain contribution (Larson and Von Dreele 1986) was 0.3%,

leading to peaks about three times as broad as would be expected from strain-free samples studied using the same diffractometer. The possibility that this was caused by X-ray beam damage to the sample was eliminated by separating the pattern into low- and high-angle segments and by showing that the peak widths are consistent in the two regions. Thus the high lattice strain seems to be intrinsic to the sample.

To check for cation disorder, the site occupancies of Ti and Si were refined. These converged to 0.980(3) and 0.950(5) for Ti and Si, compared with theoretical values of 1.0 for complete ordering. From this test we conclude that the Ti and Si are close to fully ordered in the structure.

RESULTS AND DISCUSSION

The structure model derived from the powder study is summarized in Table 1. The structure consists of alternating larger TiO_6 octahedra [$\text{Ti-O} = 1.947(3) \text{ \AA}$] and smaller SiO_6 octahedra [$\text{Si-O} = 1.758(3) \text{ \AA}$], corner-linked in a three-dimensional array characteristic of the double-perovskite structure (Fig. 2). The Ca atom occupies a tetrahedrally distorted cuboctahedron with $\text{Ca-O} = 2.622(1) \text{ \AA}$ (Fig. 3). There are two nearest O-O distances, corresponding to the edges of the smaller SiO_6 and larger TiO_6 octahedra: $\text{O-O} = 2.486(4) \text{ \AA}$ and $\text{O-O} = 2.754(4) \text{ \AA}$.

The Si-O bond length of $1.758(3) \text{ \AA}$ may be compared

TABLE 1. Fractional coordinates ($\times 10^4$) and isotropic displacement parameters for $\text{Ca}_2\text{TiSiO}_6$

Atom	mult.-position	x	y	z	$U_{\text{iso}} \times 10^2 \text{ \AA}^2$
Ca	8c	¼	¼	¼	0.56(2)*
Ti	4b	½	½	½	*
Si	4a	0	0	0	*
O	24e	0.2372(4)	0	0	2.54(4)

* Displacement parameters for metal atoms constrained to be equal; corrected for absorption effects using the technique of Hewat (1979).

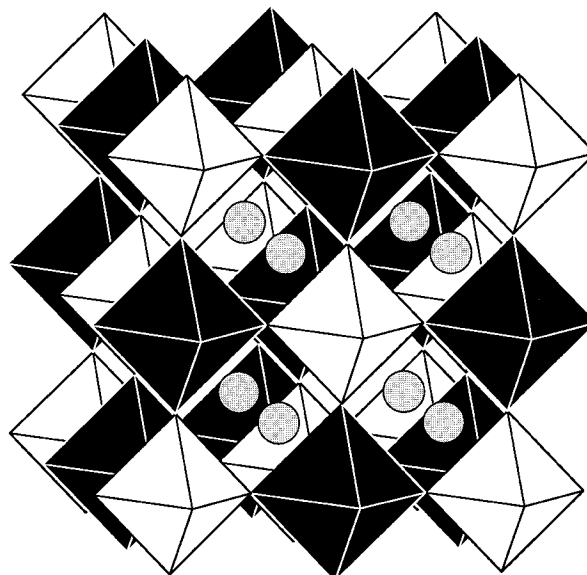
with other silicate perovskite values: 1.783–1.801 Å for MgSiO_3 perovskite (Horiuchi et al. 1987) and about 1.78 Å for recovered CaSiO_3 perovskite (Kudoh and Kanzaki 1993). The Ti-O bond is almost the same as or slightly shorter than in CaTiO_3 and SrTiO_3 perovskites [1.947(3) Å for $\text{Ca}_2\text{TiSiO}_6$ as compared with 1.950–1.959 Å for CaTiO_3 and 1.952 Å for SrTiO_3].

Bond-valence sums (O'Keeffe 1990) for the cations and anions in the structure are 2.04 for Ca, 4.19 for Ti, 4.18 for Si, and 2.08 for O. These numbers may be compared with the ideal values of 2.0 for Ca and O, and 4.0 for Ti and Si, to test the present structure against oxide systematics. The values for Ti and Si are slightly high, which may reflect the slightly shortened bond lengths, although values such as these are sometimes encountered in oxides.

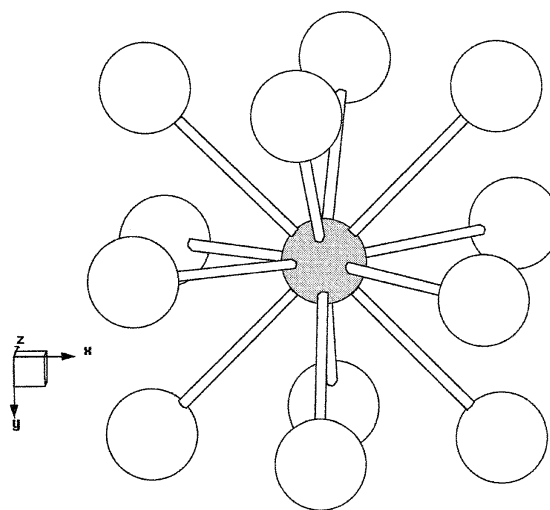
The refined displacement parameters for O are large compared with those of Si and Ti in the structure, and two to three times those obtained by us for the O atoms in high-pressure oxides (Leinenweber and Parise 1995). They are reminiscent of the large displacement parameters for F in cubic NaMgF_3 perovskite at temperatures just above the orthorhombic to cubic transition (Zhao et al. 1993). This may indicate the presence of some static or dynamic disorder of O in $\text{Ca}_2\text{TiSiO}_6$. This would also provide an explanation for the short Ti-O and Si-O bond lengths, because O positional disorder would give rise to individual Ti-O and Si-O distances, which are longer than those of the average structure reported here.

Another observation that should be noted is a splitting in the T_{2g} Raman band observed in the same sample (Leinenweber et al. 1997). This band is expected to be a single peak for an $Fm\bar{3}m$ cubic double perovskite. This could indicate a lowering of the symmetry that is not manifested in the powder X-ray diffraction pattern. There could be a relation between the Raman splitting and the large O displacements described above, if those displacements are caused by departures from an average $Fm\bar{3}m$ symmetry that are probed by Raman spectroscopy but not by X-ray diffraction.

A final note concerns the high lattice strain in this material. This strain may have been induced during decompression, and the material may be near an instability at ambient pressure. This would not be surprising considering that the closely related CaSiO_3 perovskite undergoes amorphization at 1 GPa during decompression. In the

**FIGURE 2.** Octahedral framework of $\text{Ca}_2\text{TiSiO}_6$. The alternation of larger TiO_6 octahedra (shaded) with smaller SiO_6 octahedra (unshaded) is emphasized.

case of $\text{Ca}_2\text{TiSiO}_6$, the presence of Ti in half the octahedral sites stabilizes the perovskite structure enough to allow it to be recovered to ambient pressure, even if the stability is only marginal. These two calcium silicate perovskites can be contrasted to the case of MgSiO_3 perovskite, which is also metastably recovered from high pressure, but does not show significant lattice strain or undergo amorphization at room temperature (although it is known to amorphize during heating).

**FIGURE 3.** Calcium coordination polyhedron in $\text{Ca}_2\text{TiSiO}_6$. The tetrahedrally distorted cuboctahedron is characteristic of the A site in $Fm\bar{3}m$ double perovskites.

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