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Structure and Properties of $CaTiO_3$

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A new determination of the atomic structure of $CaTiO_3$ has been made. It is orthorhombic, with space group *Pcmn*; atomic coordinates are given. Synthetic crystals are identical with the majority of natural perovskite specimens. Two of the modes of twinning reported by Bowman from optical analysis have been confirmed by both X-ray and optical methods.

With increasing temperature in the range −200° C. to 900° C. changes in cell dimensions are such as to approximate more closely to those characteristic of higher symmetry, but the substance is still orthorhombic at 900° C.

1. Introduction

There are now many known materials of the type ABO_3 which have the so-called perovskite structure, named after the mineral form of $CaTiO_3$. In its most symmetrical form, such as occurs in the cases of $SrTiO_3$, $KTaO_3$, $BaSnO_3$, and others, this structure is cubic and contains one formula unit per cell. Choosing *A* ions at cube corners for convenience, then *B* ions occur at body centres and O ions at face-centres. In actual fact, however, most of these materials have structures slightly distorted from cubic, the displacement of ions from the ideal position being only a few tenths of an Ångström unit at most, and the final symmetry varies considerably between different materials depending on mechanisms which at present can only be discussed in qualitative terms.

Since $CaTiO_3$ is one of the few minerals of this type found in nature it has been the subject of much study, and other materials of this or very similar structure were called perovskite-type even though the fine structure of $CaTiO_3$ was not known with certainty. This fact, together with the growing interest in the very special ferroelectric properties of some of these materials, prompted a renewed interest in this substance.

Of the many works published on mineral perovskite, those of major interest are by Bowman (1908), who made extensive optical measurements, and from investigation of the twinning concluded that the material had orthorhombic symmetry; by Zedlitz (1939), who gives a detailed account of origin morphology, chemical and optical properties from which it is concluded that the symmetry is pseudo-cubic (probably monoclinic); and by Náray-Szabó (1943), who states that X-ray photographs showed a monoclinic cell ($P2_1/m$) and whose intensity measurement, together with 'packing' considerations, gave rise to a structure which has not been superseded by any single-crystal work since that date. However, insufficient evidence was printed in the English translation of this last work to allow of independent assessment of the value of these results.

All previous measurements suffered from the difficulty that observations were made on crystals of widely differing origin, and from the impossibility of grinding twin-free sections of the natural crystals. Thus even space-group determination was hazardous, and the accurate determination of atomic positions was even more difficult owing to the lack of resolution of X-ray reflexions from twins.

2. Materials examined

Natural crystals were obtained from various sources,* such as the Urals, Zermatt, Magnet Cove (Arkansas), Hot Springs (Arkansas) and Alnö (Sweden). Their external shapes were mostly simple cubes, but some few had octahedral and occasionally dodecahedral facial development to varying degrees and were labelled perovskite, dysanslyte, hydrotitanite and knopite by the various collectors concerned.

For comparison, synthetic powdered $CaTiO_3$ was prepared by sintering stoichiometric proportions of CaO and TiO_2 at 1350° C. for several hours, during which time these proportions were maintained, as established by chemical analysis.

Although, chronologically, large naturally occurring perovskite crystals were investigated first, X-ray and optical investigation of small pieces (~ 0·2 mm. linear dimensions) ground from such crystals showed such complexity of twinning that the final elucidation of the problems had to await the production of synthetic crystals.

These were grown from solution; molten $CaCl_2$, $BaCl_2$, $Na_2CO_3+K_2CO_3$ and $CaCl_2+BaCl_2$ were tried, with greatest success in the last case with concentration 1:5 by weight. Crystals could be grown only by using $CaO+TiO_2$ as solute in preference to $CaTiO_3$,

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* We are indebted to Dr F. A. Bannister of the British Natural History Museum for providing most of these specimens.

and clearer crystals resulted with slight excess ($\sim 5\%$) of TiO_2 (contrary to the usual ceramic procedure, where excess divalent-ion oxide is used). A solute: solvent ratio of 1:5 by weight was found to be most satisfactory; the solution was held at a temperature not greater than 1150° C. for 30 hr. to ensure complete solution, then slow-cooled and finally extracted with water. The resulting crystals were orthogonal and of size up to 1 mm. linear dimensions. The very sensitive sodium rhodizanate test for barium* failed to detect this impurity in the crystals, a fact which is perhaps only to be expected in view of the low replacement solubility of Ba in $CaTiO_3$, as judged from $(BaCa)TiO_3$ ceramics (Kay, 1945).

3. Results from powder photographs

Debye–Scherrer diagrams were prepared from all specimens. That from the synthetic powder was taken as standard. Out of a total of 14 natural crystal samples, some of them containing several individuals, it was established that six samples had structures and cell size identical with the synthetic material, and that these all had cubic $\{100\}$ facial development only. Of the remainder, five samples had identical pattern as regards relative position and intensity of lines, but indicated slightly increased lattice parameters ($\not> 1{\cdot}33\%$). These latter all had octahedral face development. A sample from Sweden (Alnö) labelled knopite gave sharper diffractions than usual, but small relative intensity differences, extending even as far as the absence of some faint lines and the appearance of extra faint lines as compared with the standard pattern, indicated a more serious change of atomic parameters or chemical constitution. The remaining two samples proved to be magnetite, Fe_3O_4.

The conclusions drawn were that the larger group of mineral $CaTiO_3$ specimens have structures identical with the synthetic powder material, have smallest cell size and show only $\{100\}$ facial development of the cubic pseudomorph found in nature. Other materials have larger cell size, tending to confirm the presence of Nb, Ta and Fe so often associated with this mineral, and they tend to show octahedral $\{111\}$ facial development of the pseudomorph.

Powder photographs of the synthetic crystals showed complete identity with that of the ceramic and of the major mineral group.

Accurate parameters of the ceramic material, evaluated by the method of Cohen (1935), using the approximate values obtained from single-crystal observations of the natural material, gave refined values as follows:

$$a = 5{\cdot}3670 \pm 0{\cdot}0001, \quad c = 5{\cdot}4439 \pm 0{\cdot}0001,$$
$$b = 7{\cdot}6438 \pm 0{\cdot}0001 \text{ Å}; \quad \beta' = 90^\circ\, 48'.$$
$$(\lambda(\text{Cu } K\alpha_1) = 1{\cdot}5405 \text{ Å.})$$

Cell contents: 4 formula units.

The parameters depart slightly from the results obtained by Megaw (1946), when referred to the same cell, by about $0{\cdot}3\%$ in a but by negligible amounts in the other parameters, a fact which is not serious although the results quoted here may be more representative since the purity and conditions of preparation were not rigidly controlled in the older work.

4. Texture and twinning

In view of the X-ray identity of the synthetic ceramic and the major group of crystals, one of the latter was chosen for investigation since it was apparent that the complexity of the powder patterns made unambiguous indexing impossible.

Sections of thickness 0·2 mm. were cut and ground parallel to $(100)'$ faces* of a crystal obtained from Achmatowsk in the Urals by Dr L. Eger (Wien, August 1903). Linear dimensions of the crystals were $5{\cdot}6 \times 5{\cdot}7 \times 3{\cdot}8$ and $3{\cdot}9 \times 4{\cdot}0 \times 3{\cdot}2$ mm. as typical examples. In all cases the sections showed extremely complex crystal configuration, as judged by the rapid variation of birefringence within sections of uniform thickness.

Small regions of the crystal sections were chosen for X-ray examination but of twenty fragments of dimensions $\not> 0{\cdot}2$ mm. none gave definitely single-crystal patterns, even though at first sight a fragment might appear optically isotropic, indicating that the individual components of the twin were never greater than 0·2 mm. in all dimensions.

From simple fragments involving no more than two components it was determined that the primitive pseudo-cell of $a' = 3{\cdot}82$ Å, containing one formula unit, is distorted by a shear of 48′ to give a true orthorhombic cell of $a = 5{\cdot}37$, $b = 7{\cdot}64$, $c = 5{\cdot}44$ Å; from this the powder photograph was indexed and the accurate parameters were obtained. The orientation of the real cell is as depicted in Fig. 1(*a*) such that

$$\mathbf{a} = \mathbf{a}' + \mathbf{c}'; \quad \mathbf{b} = 2\mathbf{b}' \quad \text{and} \quad \mathbf{c} = -\mathbf{a}' + \mathbf{c}'.$$

Twinning in simple fragments is such as to keep $b = 7{\cdot}64$ Å parallel for the two components by a rotation of 180° about the normal to (101), which is the composition plane, as depicted in Fig. 1(*b*). The result is straight extinction if viewed along direction *A* or *C*, and 45° along direction *B*.

In many regions the extinction is not complete, and this results possibly from the fine-scale nature of the twinning with its resultant internal reflexion and strain rotation of the optic figure. On the other hand, the superposition of two crystal plates not having their extinction directions exactly parallel could also be the cause of incomplete extinction, and this is also possible in actual crystals, though strain must exist in this event also. However, the parameter measure-

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* Made by G. Vowles of the Inorganic Chemistry Department.

* Primes will represent the pseudo-cubic axes throughout the text.

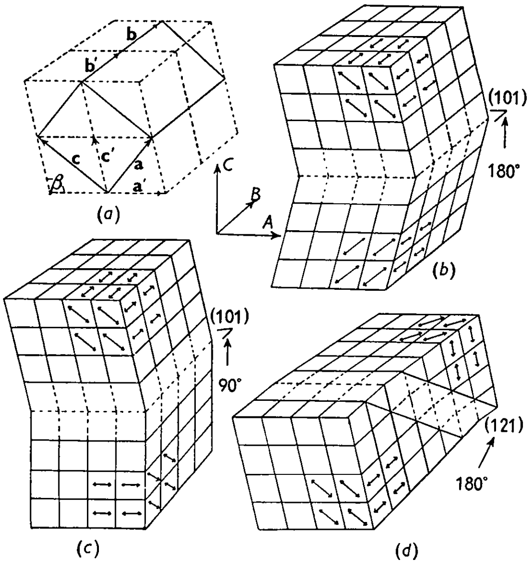

Fig. 1. (*a*) Orthorhombic unit cell of $CaTiO_3$ (full-line) in relation to sheared pseudo-cubic primitive cells (broken line). (*b*) Most common form of twinning, by rotation about normal to (101) with composition plane (101). (*c*) Twinning by rotation of 90° about normal to (101) with composition plane (101). (*d*) Twinning by rotation of 180° about normal to (121) with composition plane (121).

ments indicate that any departure of the angles from 90°, at least in the powdered material, cannot be greater than 0·2′; lower symmetry than orthorhombic is not, therefore, assumed.

Large areas of sections were composed of alternate bands, varying in width from 0·02 to 0·2 mm., of material exhibiting alternate straight and 45° extinction with boundaries roughly parallel to the cube edges. These constituted twins of the type depicted in Fig. 1(*c*) by rotation of 90° about an axis normal to plane (101); this is often the composition plane but more usually the latter departs from (101) by several degrees. This type of twinning was also checked by X-rays.

So far, the two twinning methods discussed were reported by Bowman from purely optical and etch-pit observations. He also shows a figure containing one example of twinning of the type shown in Fig. 1(*d*) formed by rotation of 180° about an axis normal to plane (121), which is the composition plane. None of our sections showed any such clear-cut boundary which would correspond to this. X-ray examination of complicated fragments have examples where it might possibly occur along with other types of twinning, but could not definitely prove its existence. Synthetic crystals, on the other hand, never showed this type of twinning.

It should be remembered that our descriptions do not conform exactly with those of Bowman, whose twinning laws related to a cell of parameters $1:1/\sqrt{2}:1$ compared with the true cell of 1:2:1.

There was found to be no close agreement in detail between the appearance of thin (100)′ sections observed by Bowman and by ourselves, which is not surprising for we have observed considerable differences between specimens of different origin. The general agreement in principle, however, is good. Summarizing the results in (100)′ sections viewed between crossed nicols, regions of the following type were observed:

(1) Areas of complete 45° extinction often lamellated parallel to (100)′, which indicates thin lamellar twinning of the type shown in Fig. 1(*b*) observed from the direction *B*.

(2) Areas composed of strips ~0·2 mm. thick of different interference colours, alternate ones extinguishing at 45° and the others showing straight but sometimes incomplete extinction. Such areas are indicative of twinning of type shown in Fig. 1(*c*) viewed from *A* or *B* directions.

(3) Areas of much greater complexity showing very poor extinction and often making up fairly regular patterns with diffuse 45° demarkations of colours; other areas showing fine-scale interpenetration of twins. These result possibly from twinning of the type shown in Fig. 1(*d*) viewed from *B* or *C*.

(4) In addition to these observations of our own, Bowman has recorded 45° boundaries in material showing straight but poor extinction. These, which indicate twinning of type shown in Fig. 1(*d*) viewed from *A*, were never seen directly in our own sections.

The complexity of optical patterns that can be obtained is not surprising when it is realized that $BaTiO_3$, with only one twin law, can produce the regular but complicated patterns which have been described (Forsbergh, 1949; Vousden, 1949).

The twinning in the synthetic crystals was less intense and more regular than the natural material, that of Fig. 1(*b*) being the most common; it varied considerably in scale, lamellae of thickness down to 0·005 mm. or less being found, often lying parallel to the crystal faces. The twinning of Fig. 1(*c*) was also observed, but less frequently, and that of Fig. 1(*d*) was never observed in synthetic crystals. This latter, then, is a very rare type and perhaps only a result of intense pressures to which natural crystals could have been subjected.

5. Experimental method

To enable reflexions to be unambiguously indexed an untwinned crystal is necessary, but only one truly single crystal of reasonable size was ever obtained. This was plate-shaped, of dimensions 0·15 × 0·14 × 0·02 mm., which extinguished in the plate at 45° to the plate edge so that absorption anisotropy made it less suitable for accurate intensity determinations in the case of certain reflexions.

The room-temperature photographs were taken on a Unicam camera loaded with multiple films and using

Ni filtered Cu $K\alpha$ radiation. The spot intensities were estimated by eye by comparison with a series of calibrated spots of known relative exposure, and the graphical absorption correction of Albrecht (1939) was applied throughout.

Photographs were indexed in terms of the orthorhombic unit previously described; systematic absences recorded were $hk0$ for $h+k$ odd and $0kl$ for l odd, with no systematic absences of general hkl reflexions. The space group is therefore either C_{2v}^9–$Pc2_1n$ or D_{2h}^{16}–$Pcmn$, neither of which can be reconciled with the space group C_{2h}^2–$P2_1/m$ quoted by Náray-Szabó.

Of these two possible space groups, $Pcmn$ is centrosymmetrical and $Pc2_1n$ allows polar-type displacements along the orthorhombic **b** axis. Piezoelectric tests made on a sensitive Giebe & Scheibe apparatus, together with pyroelectric tests, gave negative results so that no distinction could be made directly between the two space groups.

6. Structure results

The ionic displacements in the orthorhombic unit cell can be only small fractions of the axial parameters, and this limits to three the number of ways in which the symmetry elements can be located with respect to the undisplaced ionic positions. The origin is chosen so that the undisplaced ionic parameters are:

Ca: $0, \frac14, 0;\ \frac12, \frac14, \frac12;\ 0, \frac34, 0;\ \frac12, \frac34, \frac12.$
Ti: $\frac12, \frac12, 0;\ 0, \frac12, \frac12;\ \frac12, 0, 0;\ 0, 0, \frac12.$
O: $0, \frac14, \frac12;\ \frac12, \frac14, 0;\ 0, \frac34, \frac12;\ \frac12, \frac34, 0;$
$\frac14, \frac12, \frac14;\ \frac34, \frac12, \frac14;\ \frac14, \frac12, \frac34;\ \frac34, \frac12, \frac34;$
$\frac14, 0, \frac14;\ \frac34, 0, \frac14;\ \frac14, 0, \frac34;\ \frac34, 0, \frac34.$

The parameters of the symmetry elements in the hree possible configurations are then:

(1) $Pc2_1n$

2_1: $0, y, 0;\ \frac12, y, 0;\ 0, y, \frac12;\ \frac12, y, \frac12.$
n: $x, y, \frac14;\ x, y, \frac34.$
c: $\frac14, y, z;\ \frac34, y, z.$

(2) $Pcmn$ (1)

As in $Pc2_1n$, with the addition of

2_1 in $\frac14, \frac12, z;\ \frac14, 0, z;\ \frac34, \frac12, z;\ \frac34, 0, z;$
$x, \frac14, \frac14;\ x, \frac14, \frac34;\ x, \frac34, \frac14;\ x, \frac34, \frac34.$

These introduce mirror planes at $(x, \frac12, z)$, $(x, 0, z)$, and a symmetry centre at $0, \frac14, 0$.

(3) $Pcmn$ (2)

As in $Pcmn$ (1) with all symmetry elements displaced $\frac14$ along the y axis.

The relationships between the ionic displacements, resolved along the three axial directions, which are permitted by each of these configurations are shown

Table 1. *Displacement relationships*: $Pc2_1n$

Calcium ions

${}_x\delta_{0,\frac14,0;\ \frac12,\frac34,\frac12} = -{}_x\delta_{\frac12,\frac14,\frac12;\ 0,\frac34,0}$
${}_y\delta_{0,\frac14,0} = {}_y\delta_{\frac12,\frac34,\frac12} = {}_y\delta_{\frac12,\frac14,\frac12} = {}_y\delta_{0,\frac34,0}$
${}_z\delta_{0,\frac14,0;\ \frac12,\frac14,\frac12} = -{}_z\delta_{0,\frac34,0;\ \frac12,\frac34,\frac12}$

Titanium ions

${}_x\delta_{0,\frac12,\frac12;\ \frac12,0,0} = -{}_x\delta_{\frac12,\frac12,0;\ 0,0,\frac12}$
${}_y\delta_{0,\frac12,\frac12} = {}_y\delta_{\frac12,0,0} = {}_y\delta_{\frac12,\frac12,0} = {}_y\delta_{0,0,\frac12}$
${}_z\delta_{0,\frac12,\frac12;\ \frac12,0,0} = {}_z\delta_{\frac12,\frac12,0;\ 0,\frac12,\frac12}$

Oxygen ions (group 1)

${}_x\delta_{0,\frac14,\frac12;\ \frac12,\frac34,0} = -{}_x\delta_{\frac12,\frac14,0;\ 0,\frac34,\frac12}$
${}_y\delta_{0,\frac14,\frac12} = {}_y\delta_{\frac12,\frac34,0} = {}_y\delta_{\frac12,\frac14,0} = {}_y\delta_{0,\frac34,\frac12}$
${}_z\delta_{0,\frac14,\frac12;\ \frac12,\frac14,0} = -{}_z\delta_{0,\frac34,\frac12;\ \frac12,\frac34,0}$

Oxygen ions (group 2*a*)

${}_x\delta_{\frac34,\frac12,\frac14;\ \frac14,0,\frac14} = -{}_x\delta_{\frac14,0,\frac34;\ \frac34,\frac12,\frac34}$
${}_y\delta_{\frac34,\frac12,\frac14} = {}_y\delta_{\frac14,0,\frac14} = {}_y\delta_{\frac14,0,\frac34} = {}_y\delta_{\frac34,\frac12,\frac34}$
${}_z\delta_{\frac34,\frac12,\frac14;\ \frac34,\frac12,\frac34} = -{}_z\delta_{\frac14,0,\frac14;\ \frac14,0,\frac34}$

Oxygen ions (group 2*b*)

${}_x\delta_{\frac14,\frac12,\frac14;\ \frac34,0,\frac14} = -{}_x\delta_{\frac14,\frac12,\frac34;\ \frac34,0,\frac34}$
${}_y\delta_{\frac14,\frac12,\frac14} = {}_y\delta_{\frac34,0,\frac14} = {}_y\delta_{\frac14,\frac12,\frac34} = {}_y\delta_{\frac34,0,\frac34}$
${}_z\delta_{\frac14,\frac12,\frac14;\ \frac14,\frac12,\frac34} = -{}_z\delta_{\frac34,0,\frac14;\ \frac34,0,\frac34}$

Table 2. *Displacement relationships*: $Pcmn$ (1)

Calcium ions

${}_{x,y,z}\delta_{0,\frac14,0;\ \frac12,\frac34,\frac12;\ \frac12,\frac14,\frac12;\ 0,\frac34,0} = 0$

Titanium ions

${}_x\delta_{0,\frac12,\frac12;\ \frac12,0,0} = -{}_x\delta_{\frac12,\frac12,0;\ 0,0,\frac12}$
${}_y\delta_{0,\frac12,\frac12;\ \frac12,0,0;\ \frac12,\frac12,0;\ 0,0,\frac12} = 0$
${}_z\delta_{0,\frac12,\frac12;\ \frac12,\frac12,0} = -{}_z\delta_{\frac12,0,0;\ 0,0,\frac12}$

Oxygen ions (group 1)

${}_{x,y,z}\delta_{0,\frac14,\frac12;\ \frac12,\frac14,0;\ 0,\frac34,\frac12;\ \frac12,\frac34,0} = 0$

Oxygen ions (group 2)

${}_x\delta_{\frac14,\frac12,\frac14;\ \frac34,\frac12,\frac14;\ \frac14,0,\frac14;\ \frac34,0,\frac14} = {}_x\delta_{\frac14,\frac12,\frac34;\ \frac34,\frac12,\frac34;\ \frac14,0,\frac34;\ \frac34,0,\frac34}$
${}_y\delta_{\frac14,\frac12,\frac14;\ \frac34,0,\frac14;\ \frac14,0,\frac14;\ \frac34,0,\frac14;\ \frac34,\frac12,\frac34;\ \frac14,0,\frac34;\ \frac34,0,\frac34;\ \frac14,\frac12,\frac34} = 0$
${}_z\delta_{\frac14,\frac12,\frac14;\ \frac14,\frac12,\frac34;\ \frac34,\frac12,\frac14;\ \frac34,\frac12,\frac34} = -{}_z\delta_{\frac14,0,\frac14;\ \frac14,0,\frac34;\ \frac34,0,\frac14;\ \frac34,0,\frac34}$

Table 3. *Displacement relationships*: $Pcmn$ (2)

Calcium ions

${}_x\delta_{0,\frac14,0;\ \frac12,\frac34,\frac12} = -{}_x\delta_{\frac12,\frac14,\frac12;\ 0,\frac34,0}$
${}_y\delta_{0,\frac14,0;\ \frac12,\frac34,\frac12;\ \frac12,\frac14,\frac12;\ 0,\frac34,0} = 0$
${}_z\delta_{0,\frac14,0;\ \frac12,\frac14,\frac12} = -{}_z\delta_{\frac12,\frac34,\frac12;\ 0,\frac34,0}$

Titanium ions

${}_{x,y,z}\delta_{0,\frac12,\frac12;\ \frac12,0,0;\ \frac12,\frac12,0;\ 0,0,\frac12} = 0$

Oxygen ions (group 1)

${}_x\delta_{0,\frac14,\frac12;\ \frac12,\frac34,0} = -{}_x\delta_{\frac12,\frac14,0;\ 0,\frac34,\frac12}$
${}_y\delta_{0,\frac14,\frac12;\ \frac12,\frac34,0;\ \frac12,\frac14,0;\ 0,\frac34,\frac12} = 0$
${}_z\delta_{0,\frac14,\frac12;\ \frac12,\frac14,0} = -{}_z\delta_{\frac12,\frac34,0;\ 0,\frac34,\frac12}$

Oxygen ions (group 2)

${}_x\delta_{\frac14,0,\frac14;\ \frac34,0,\frac14;\ \frac34,\frac12,\frac14;\ \frac14,\frac12,\frac14} = -{}_x\delta_{\frac34,0,\frac34;\ \frac14,0,\frac34;\ \frac34,\frac12,\frac34;\ \frac14,\frac12,\frac34}$
${}_y\delta_{\frac14,0,\frac14;\ \frac14,0,\frac34;\ \frac34,\frac12,\frac34;\ \frac34,\frac12,\frac14} = -{}_y\delta_{\frac34,0,\frac14;\ \frac34,0,\frac34;\ \frac14,\frac12,\frac14;\ \frac14,\frac12,\frac34}$
${}_z\delta_{\frac14,0,\frac34;\ \frac14,0,\frac14;\ \frac14,\frac12,\frac34;\ \frac14,\frac12,\frac14} = -{}_z\delta_{\frac34,0,\frac14;\ \frac34,\frac12,\frac14;\ \frac34,0,\frac34;\ \frac34,\frac12,\frac34}$

in Tables 1, 2 and 3. ${}_x\delta_i$, ${}_y\delta_i$ and ${}_z\delta_i$ are the vector components of the ith ion along the x, y and z directions.

7. Approximate expression for the structure amplitude for superlattice reflexions

The reflexions most sensitive to small ionic displacements are the superlattice reflections; these are produced entirely by such displacements. If x_i, y_i, z_i are the parameters of the ith ion in its undisplaced position in the unit cell, expressed as fractions of the cell repeat distances, and ${}_x\delta_i$, ${}_y\delta_i$, ${}_z\delta_i$ are the fractional vector displacements, then, putting

$$\begin{aligned} 2\pi(h_x\delta_i+k_y\delta_i+l_z\delta_i) &= \Delta_i\,, \\ 2\pi(hx_i+ky_i+lz_i) &= \theta_i\,, \end{aligned}$$

the structure amplitude for reflexion (hkl) for the unit cell is given by

$$|F|^2_{hkl} = \{\sum_i f_i^{hkl} \sin\,(\theta_i+\Delta_i)\}^2+\{\sum_i f_i^{hkl} \cos\,(\theta_i+\Delta_i)\}^2.$$

Expanding this equation, and introducing the approximations that for ${}_x\delta$, ${}_y\delta$, ${}_z\delta$ small

$$\cos\Delta_i \simeq 1, \quad \sin\Delta_i \simeq \Delta_i\,,$$

we have

$$\begin{aligned} |F|^2_{hkl} = {} & \{\sum_i f_i^{hkl} \sin\theta_i+\sum_i f_i^{hkl}\Delta_i \cos\theta_i\}^2 \\ & +\{\sum_i f_i^{hkl} \cos\theta_i-\sum_i f_i^{hkl}\Delta_i \sin\theta_i\}^2. \end{aligned}$$

Now if the undistorted structure has a centre of symmetry, and the origin is taken at this point, $\sum_i f_i \sin\theta_i = 0$; also if superlattice reflexions only are considered, $\sum_i f_i \cos\theta_i = 0$.

The structure amplitude expression now becomes

$$|F|^2_{hkl} = \{\sum_i f_i^{hkl}\Delta_i \sin\theta_i\}^2+\{\sum_i f_i^{hkl}\Delta_i \cos\theta_i\}^2,$$

where all θ_i are known.

This expression can be made more accurate by introducing further approximations for $\cos\Delta_i$ and $\sin\Delta_i$, bringing in terms in $|F|^2$ involving higher powers of Δ_i, but this makes its application difficult. The equation as derived is valid only for Δ_i small, and can be applied only to reflexions of low indices.

Using this equation, the expressions for the structure amplitude for the various classes of superlattice reflexions were calculated for each of the three possible displacement configurations, and a comparison made with the observed values in an attempt to establish the correct configuration and to obtain information concerning the displacements occurring. In most cases a visual examination of the relative intensities of reflexions in a given class was sufficient to enable the relevant structure amplitude equation to be solved.

8. Choice between $Pc2_1n$, $Pcmn(1)$ and $Pcmn(2)$

For the three configurations the structure-amplitude expressions for reflexion class $hk0$ with h and k both odd are:

$$\begin{aligned} Pc2_1n:\quad |F|^2_{hk0} = {} & \{8\pi h(f^{hk0}_{\text{Ca}}\,{}_x\delta^{\text{Ca}}_{0,\frac{3}{4},0}+f^{hk0}_{\text{O}}\,{}_x\delta^{\text{O}}_{0,\frac{3}{4},\frac{1}{2}}) \\ & \pm 8\pi k f^{hk0}_{\text{O}}({}_y\delta^{\text{O}}_{\frac{1}{4},\frac{1}{2},\frac{1}{4}}-{}_y\delta^{\text{O}}_{\frac{3}{4},0,\frac{3}{4}})\}^2 \\ & +\{8\pi h f^{hk0}_{\text{Ti}}\,{}_x\delta^{\text{Ti}}_{0,0,\frac{1}{2}}\}^2. \end{aligned}$$

$$Pcmn\,(1):\quad |F|^2_{hk0} = \{8\pi h f^{hk0}_{\text{Ti}}\,{}_x\delta^{\text{Ti}}_{0,0,\frac{1}{2}}\}^2.$$

$$\begin{aligned} Pcmn\,(2):\quad |F|^2_{hk0} = {} & \{8\pi h(f^{hk0}_{\text{Ca}}\,{}_x\delta^{\text{Ca}}_{0,\frac{3}{4},0}+f^{hk0}_{\text{O}}\,{}_x\delta^{\text{O}}_{0,\frac{3}{4},\frac{1}{2}}) \\ & \pm 16\pi f^{hk0}_{\text{O}}\,k_y\delta^{\text{O}}_{\frac{1}{4},\frac{1}{2},\frac{1}{4}}\}^2. \end{aligned}$$

In these expressions the positive sign is for $h+k = 4n+2$ and the negative sign is for $h+k = 4n$.

The dependence of intensity for these reflexions on the value of $h+k$ predicted for $Pc2_1n$ and $Pcmn\,(2)$ is in fact observed, reflexions with $h+k = 4n$ being much stronger than those with $h+k = 4n+2$. Configuration $Pcmn\,(1)$ is therefore incorrect. No simple dependence on the value of h as predicted by $Pcmn\,(1)$ is observed:

hkl	F^2_{visual}	hkl	F^2_{visual}
110	2	330	2
130	100	350	20
310	40	170	40
150	20	510	1

Between the two remaining configurations an unambiguous determination could not be made, but all observed intensities were consistent with the $Pcmn(2)$ equations. The evidence is discussed below.

The resolved displacements of the group $2a$ and group $2b$ oxygen ions are related by the symmetry elements of $Pcmn(2)$, Table 3, but for $Pc2_1n$, Table 1, they are entirely independent. The relevant structure-amplitude expressions for the reflexion classes which provide information on the displacements of these ions are:

x displacements—reflexions $h0l$ with h even, l odd.

$$Pcmn(2):\quad |F|^2_{h0l} = \{16\pi f^{h0l}_{\text{O}}({}_x\delta^{\text{O}}_{\frac{1}{4},\frac{1}{2},\frac{1}{4}})\}^2.$$

$$Pc2_1n:\quad |F|^2_{h0l} = \{8\pi f^{h0l}_{\text{O}}({}_x\delta^{\text{O}}_{\frac{1}{4},\frac{1}{2},\frac{1}{4}}-{}_x\delta^{\text{O}}_{\frac{3}{4},\frac{1}{2},\frac{3}{4}})\}^2.$$

z displacements—reflexions $h0l$ with h odd, l even.

$$Pcmn(2):\quad |F|^2_{h0l} = \{16\pi f^{h0l}_{\text{O}}({}_z\delta^{\text{O}}_{\frac{1}{4},\frac{1}{2},\frac{1}{4}})\}^2$$

$$Pc2_1n:\quad |F|^2_{h0l} = \{8\pi f^{h0l}_{\text{O}}({}_z\delta^{\text{O}}_{\frac{1}{4},\frac{1}{2},\frac{1}{4}}-{}_z\delta^{\text{O}}_{\frac{3}{4},\frac{1}{2},\frac{3}{4}})\}^2.$$

y displacements—reflexions $hk0$ with h odd, k odd.

$$\begin{aligned} Pcmn(2):\quad |F|^2_{hk0} = {} & \{8\pi h(f^{hk0}_{\text{Ca}}\,{}_x\delta^{\text{Ca}}_{0,\frac{3}{4},0}+f^{hk0}_{\text{O}}\,{}_x\delta^{\text{O}}_{0,\frac{3}{4},\frac{1}{2}}) \\ & \pm 16\pi k f^{hk0}_{\text{O}}({}_y\delta^{\text{O}}_{\frac{1}{4},\frac{1}{2},\frac{1}{4}})\}^2. \end{aligned}$$

$$\begin{aligned} Pc2_1n:\quad |F|^2_{hk0} = {} & \{8\pi h(f^{hk0}_{\text{Ca}}\,{}_x\delta^{\text{Ca}}_{0,\frac{3}{4},0}+f^{hk0}_{\text{O}}\,{}_x\delta^{\text{O}}_{0,\frac{3}{4},\frac{1}{2}}) \\ & \pm 8\pi k f^{hk0}_{\text{O}}({}_y\delta^{\text{O}}_{\frac{1}{4},\frac{1}{2},\frac{1}{4}}-{}_y\delta^{\text{O}}_{\frac{3}{4},\frac{1}{2},\frac{3}{4}})\}^2 \\ & +\{8\pi h f^{hk0}_{\text{Ti}}\,{}_x\delta^{\text{Ti}}_{0,\frac{1}{2},\frac{1}{2}}\}^2. \end{aligned}$$

Now reflexions $h0l$ are quite strong, and the $hk0$ reflexions exhibit the dependence on the value of $h+k$ previously described. This necessitates that

$$_x\delta^{O}_{\frac14,\frac12,\frac14} = -_x\delta^{O}_{\frac34,\frac12,\frac34};\ _y\delta^{O}_{\frac14,\frac12,\frac14} = -_y\delta^{O}_{\frac34,\frac12,\frac34};\ _z\delta^{O}_{\frac14,\frac12,\frac14} = -_z\delta^{O}_{\frac34,\frac12,\frac34}\,.$$

The displacements of the group $2a$ and group $2b$ oxygen ions are therefore consistent with the conditions imposed by the symmetry elements of $Pcmn(2)$.

The remaining differences between the two configurations are that $Pc2_1n$ permits x and z displacements of the Ti ions, and polar y displacements of the Ti, Ca, and group 1 O ions.

The reflexions most sensitive to polar displacements along the y axis are the non-superlattice reflexions $0k0$ with $k = 2, 6, 10, \ldots$. For these reflexions, if no polar displacements occur, the Ti and Ca ions scatter 180° out of phase, and since their atomic scattering factors are almost identical, the ratio $|F|^2_{020}/|F|^2_{060}$ is very sensitive to polar displacements of these ions. The measured value however is precisely that expected from the y displacements of the group 2 O ions previously determined. If polar Ca, Ti, or group 1 O displacements occur, then

$$_y\delta^{Ca} < 0{\cdot}03,\ _y\delta^{Ti} < 0{\cdot}03,\ _y\delta^{O} < 0{\cdot}05\ \text{Å}\,.$$

If simultaneous polar displacements in the same direction of the Ti and Ca ions, or Ti and O ions, occur, then the displacements are more difficult to detect by the above argument, but these displacement types are considered most improbable.

Examination of reflexions $hk0$ with h odd and k odd failed to show any dependence of intensity on the parameter h, although the $Pc2_1n$ structure-factor equation for this class contains a term $\{8\pi h f^{hk0}_{Ti} |_x\delta^{Ti}|\}^2$. A possible z displacement of the Ti ions could not be established or discounted, since its effect is masked by other displacements.

The evidence obtained, therefore, is consistent with the $Pcmn(2)$ configuration, the displacement relationships being given by Table 3.

9. The ion displacements of *Pcmn*(2)

The parameters to be determined are the x, y and z displacements of the group 2 O ions, and the x and z displacements of the Ca and group 3 O ions. The structure-amplitude equations relevant to the various displacements have been discussed, with the exception of that which involves the z displacements of the Ca and group 1 O ions. Information concerning these displacements is given by reflexions $0kl$ with l even, k odd. The structure-amplitude equation is

$$|F|^2_{hk0} = \{8\pi l\,(f^{0kl}_{Ca}\ _z\delta^{Ca}_{0,\frac34,0} + f^{0kl}_{O}\ _z\delta^{O}_{0,\frac34,\frac12})\}^2\,.$$

This equation, in conjunction with that for the non-superlattice reflexion 020, which contains a term involving the y displacement of the group 2 O ions as the only unknown, were solved, making use of the observed relative structure amplitudes of certain reflexions of these classes, and the following absolute displacement values were obtained:

Oxygen ions (group 2)

$$|\Delta_x| = 0{\cdot}10\pm0{\cdot}05,\ |\Delta_y| = 0{\cdot}20\pm0{\cdot}05,\ |\Delta_z| = 0{\cdot}10\pm0{\cdot}05\ \text{Å}\,.$$

Calcium ions and oxygen ions (group 1)

$$|3_x\Delta^{Ca}_{0,\frac34,0} + {}_x\Delta^{O}_{0,\frac34,\frac12}| = 0{\cdot}20\pm0{\cdot}05\,,$$

$$|3_z\Delta^{Ca}_{0,\frac34,0} + {}_z\Delta^{O}_{0,\frac34,\frac12}| = 0{\cdot}38\pm0{\cdot}05\ \text{Å}\,.$$

The factor 3 in the expression for the Ca and group 1 O displacements arises from the ratio f_{Ca}/f_O; for the reflexions analysed this value was ~ 3.

From the above analysis, the individual displacements of the Ca and group 1 O ions cannot be unambiguously determined. To attempt to obtain more information about these and to determine the relative phases of the various displacements, use is made of packing considerations.

10. Packing of ions in the unit cell of $CaTiO_3$

The Goldschmidt radii for the O, Ti and Ca ions are 1·32, 0·64 and 1·15 Å respectively. The last is corrected for 12-fold oxygen coordination. The radius sums are therefore

$$R_{Ca}+R_O = 2{\cdot}47,\ R_O+R_{Ti} = 1{\cdot}96\ \text{Å}\,.$$

If the ions retain their undisplaced positions in the orthorhombic unit cell, then the nearest-neighbour distances of the Ca and group 1 O ions are 2·72 Å

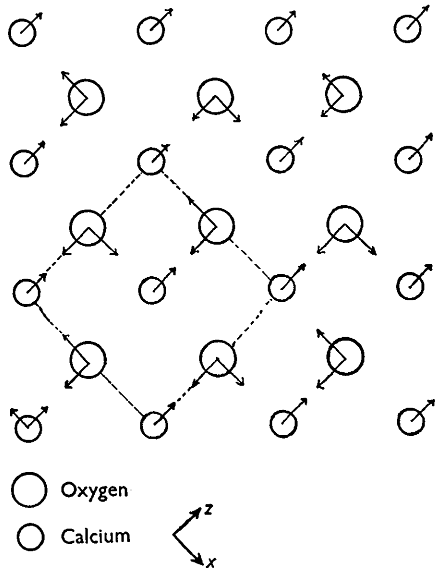

Fig. 2. Oxygen and calcium displacements in the plane perpendicular to the b axis.

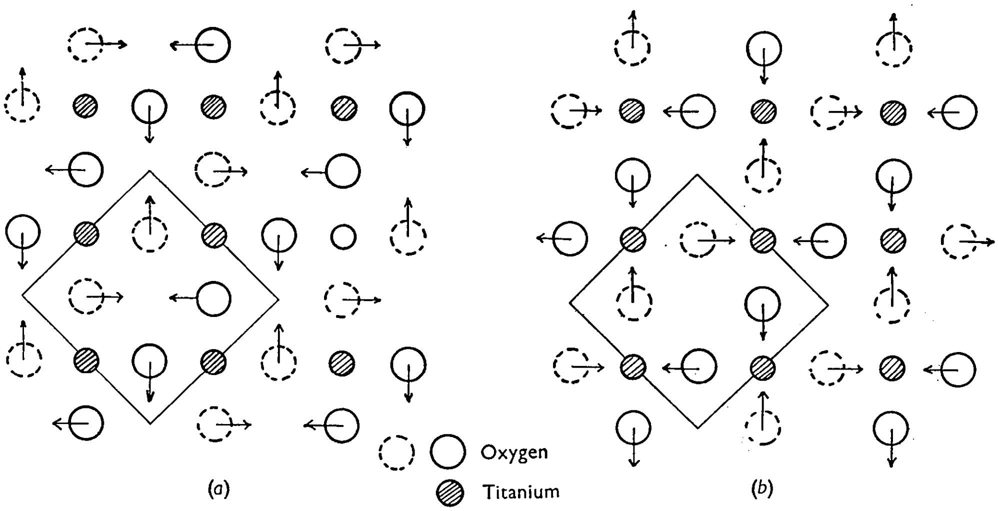

Fig. 3. The two possible displacement configurations of the Ti and coplanar O ions in the planes perpendicular to the b axis.

along the z axis, and 2·68 Å in the x direction. Displacements of these ions in the x and z directions are therefore to be expected.

If the combined displacements of these ions are considered to be those imposed by the packing of hard spheres, then the expressions for the Ca and group 1 O displacements are satisfied with

$$|_x\Delta^{\mathrm{Ca}}| \sim 0,\ |_x\Delta^{\mathrm{O}}| \sim 0{\cdot}20,\ |_z\Delta^{\mathrm{Ca}}| \sim 0{\cdot}16,\ |_z\Delta^{\mathrm{O}}| \sim 0{\cdot}10\ \text{Å},$$

and with the displacement of the Ca ions at $0, \frac{1}{4}, 0$; $\frac{1}{2}, \frac{1}{4}, \frac{1}{2}$ being opposite to those of the O ions at $\frac{1}{2}, \frac{1}{4}, 0$; $0, \frac{1}{4}, \frac{1}{2}$; and similarly for the Ca ions at $0, \frac{3}{4}, 0$; $\frac{1}{2}, \frac{3}{4}, \frac{1}{2}$ and the O ions at $\frac{1}{2}, \frac{3}{4}, 0$; $0, \frac{3}{4}, \frac{1}{2}$.

The displacements in planes $(0, \frac{1}{4}, 0)$, $(0, \frac{3}{4}, 0)$ are shown in Fig. 2, the directions in alternate planes being reversed.

11. Displacements of the group 2 O ions

Two possibilities exist for the combined x, y, z displacements of these ions. Fig. 3 shows the x and z displacement combinations in planes $(x, \frac{1}{2}, z)$ and $(x, 0, z)$. The x and z displacements have the same direction in these planes, the y displacement being reversed. Positive and negative y displacements are indicated by full and broken outlines for the ions.

In Fig. 3(a) the O ions move to increase the Ti–O nearest-neighbour distances to a common value of 1·93 Å, compared with 1·91 Å for this distance when the ions are in undisplaced positions, and 1·96 Å for the Goldschmidt radii sum. The displacement type of Fig. 3(b), on the other hand, produces a long and a short Ti–O nearest-neighbour distance of 2·08 Å and 1·78 Å. From packing considerations, therefore, the former type (Fig. 3(a)) is to be expected.

The Ti–O (group 1) distance is also increased by these oxygen displacements from 1·91 Å to 1·92 Å. The $\mathrm{Ti{-}O_6}$ groups therefore remain almost perfect octahedra, the effect of the displacements being to rotate and tilt them slightly about the y axis as the Ca and O ions rearrange themselves to produce better packing.

The displacements in the complete unit cell are shown in Fig. 4, the ion positions being those of space group D_{2h}^{16}–$Pcmn$, with:

4 Ti in 4(a): $\frac{1}{2}, 0, 0$; $0, 0, \frac{1}{2}$; $\frac{1}{2}, \frac{1}{2}, 0$; $0, \frac{1}{2}, \frac{1}{2}$.
4 Ca in 4(c): $x, \frac{1}{4}, z$; $\bar{x}, \frac{3}{4}, \bar{z}$; $\frac{1}{2}+x, \frac{3}{4}, \frac{1}{2}-z$; $\frac{1}{2}-x, \frac{1}{4}, \frac{1}{2}+z$;
with $x = 0$, $z = 0{\cdot}030$.
4 O in 4(c): with $x = \frac{1}{2}-0{\cdot}037$, $z = -0{\cdot}018$.
8 O in 8(d): x, y, z; $\frac{1}{2}-x, \frac{1}{2}-y, \frac{1}{2}+z$;
$\bar{x}, \frac{1}{2}+y, \bar{z}$; $\frac{1}{2}+x, \bar{y}, \frac{1}{2}-z$;
$\bar{x}, \bar{y}, \bar{z}$; $\frac{1}{2}+x, \frac{1}{2}+y, \frac{1}{2}-z$;
$x, \frac{1}{2}-y, z$; $\frac{1}{2}-x, y, \frac{1}{2}+z$;
with $x = \frac{1}{4}-0{\cdot}018$, $y = -0{\cdot}026$, $z = \frac{1}{4}-0{\cdot}018$.

12. Temperature variations

By analogy with many other perovskite-type minerals it was expected that at higher temperatures the symmetry of $\mathrm{CaTiO_3}$ might increase. Earlier workers have indicated that optically dissimilar areas change in outline on heating to redness. This was checked on our own mineral sections, which on heating and cooling showed slightly different twin arrangements, possibly by annealing out of the less common twins of the type shown in Fig. 1(d). Preliminary high-temperature X-ray photographs were taken of a natural crystal heated in a small blowpipe flame to about 1200° C. or more, and these showed unmistakable reduction of twin spot complexity. Further evidence was found in rather poor quality powder photographs taken at high temperatures, where the results indicated that the shear angle β varied from 90°±48′ at room temperature to very close to 90° at 600° C.; the large cell of eight pseudo-cubic primitive sub-cells, however, remained, certainly up to 1000° C. Von Hippel, Breckenridge, Chesley & Tisza (1946) have stated that synthetic $CaTiO_3$ (ceramic) showed no change of thermal expansion up to 1200° C.; but Nurse (1951) has found inversion of the heating curve at 1250° C., which is consistent with our X-ray photographs taken at very high temperatures.

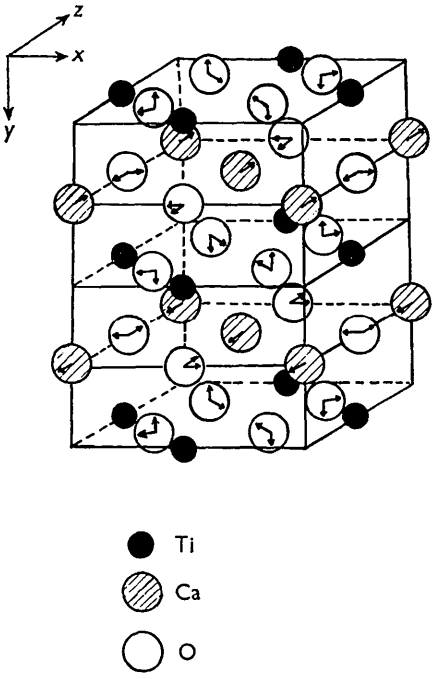

Fig. 4. Ionic displacement in a unit cell of perovskite.

Measurements were made on a crystal possessing two twin components twinned by rotation of 180° about the normal to (101) so that the shear angle β could be easily detected by the separation of $h00$ and $00h$ reflexions. The measurements were made from room temperature down to −150° C. on a liquid-air camera previously described (Kay & Vousden, 1949); above room temperature, a conical β-filter heater furnace, as described by Steward (1949), was built into a standard type of single-crystal camera. A nitrogen atmosphere was used to extend the range of this to 600° C. and a platinum coil extended this to 800° C.

Throughout this range, odd layer lines $0k0$ were seen to be present, indicating that the cell retains the doubled b axis up to 800° C., and the continued presence of 601 and 106 reflexions up to this temperature shows that no change of the cell occurs in the xz plane. Fig. 5 shows the variation of a and c and the shear departure from 90° of β over the range −150° C. to 800° C. The gradual variation of parameters suggests that at higher temperatures a change to higher symmetry probably occurs, and also that heating to dull red heat would make only small changes to the actual twin arrangement, as was observed in practice.

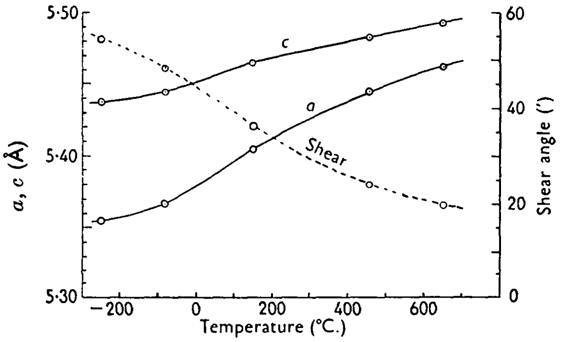

Fig. 5. Variation of orthorhombic a and c and pseudo-cubic β parameters of perovskite with temperature.

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