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The Classification of Tilted Octahedra in Perovskites

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A simple method for describing and classifying octahedral tilting in perovskites is given and it is shown how the tilts are related to the unit-cell geometries. Several examples from the literature are listed and predictions about hitherto unknown structures of some materials are made.

Introduction

The perovskite structure is very commonly found in compounds of general formula ABX_3 and many of these materials have interesting and important properties, such as ferroelectricity, piezoelectricity, non-linear optical behaviour and so on.

Fig. 1 shows the basic unit, which consists of corner-linked octahedra of X anions (usually oxygen or fluorine) with B cations at their centres and A cations between them; the cations have been left out of the diagram since, in this paper, only the octahedra will be considered. The ideal structure thus depicted is found in some materials, for example $SrTiO_3$ at room temperature; more usually the structure is modified by cation displacements as in $BaTiO_3$, or by the tilting of octahedra as in $CaTiO_3$, or by a combination of both as in $NaNbO_3(P)$. The cation displacements, which are directly linked with ferroelectricity and antiferroelectricity, are relatively simple to deal with and in any case do not directly affect the lattice parameters except by a relatively small distortion of the octahedra. The tilting of the octahedra has usually a far greater effect on lattice parameters but is more difficult to describe. However, attempts have been made to discuss these phenomena (Megaw, 1966, 1969) and it is as a result of these studies that the present work has evolved.* It

* A scheme very similar to the one described here has recently been derived independently by J. K. Brandon (private communication) in connexion with the structure of $Ca_2Nb_2O_7$.

is the aim of this paper to show how the various tilt systems may be classified and how they affect the crystal symmetries. Displacements of cations are not discussed here at any length. The derived results are based on the assumption that the octahedra are regular throughout. Very commonly the overall symmetry follows that of the tilts in spite of displacements and distortions; and even when it does not, the symmetry due to the tilts can be considered separately.

This classification has already proved useful in a recent study of the $T_2 \rightarrow$ cubic transition in $NaNbO_3$ (Glazer & Megaw, 1972), in which it readily suggested a likely model for the T_2 structure. More recently, it has also been successfully used in studying the $T_1 \rightarrow T_2$ transition (Ahtee, Glazer & Megaw, 1972). In connexion with phase transitions, dynamic (as opposed to static) tilting of octahedra can be interpreted in terms of lattice modes. In fact, it seems probable that the most obvious tilt configurations generally correspond to some of the most important modes associated with phase transitions in perovskites. The present classification should therefore find some use in the lattice dynamical studies of these transitions.

Effect of octahedral tilts

When an octahedron in the perovskite structure is tilted in some particular way it causes tilting of the neighbouring octahedra. However, it is, in practice, extremely difficult to visualize the total effect, and in

any case, there are several possibilities for the final structure.

Physically it is useful to consider the tilting of an octahedron about any one of its symmetry axes. For the purposes of a general classification, however, it is preferable to consider all tilts as combinations of

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* A note of caution must be sounded here. The three separate tilt operations about the tetrad axes do not belong to an Abelian group. In other words, the final tilt arrangement depends on the order in which the tilt operations are carried out. This does not greatly affect the arguments of the present paper, since the scheme outlined here is intended for the description of structures and not their derivation. In any case, for small tilt angles ($< 15°$) the dependence of the result on the sequence of operations is only a second-order effect.
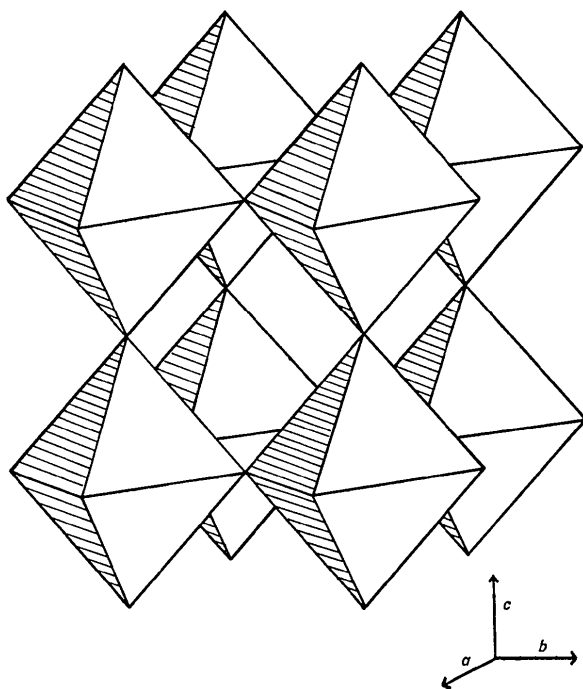

Fig. 1. Octahedral framework of cubic perovskite. The A cation is in the interstice formed by the anion octahedra; the B cation is at the centre of each octahedron.

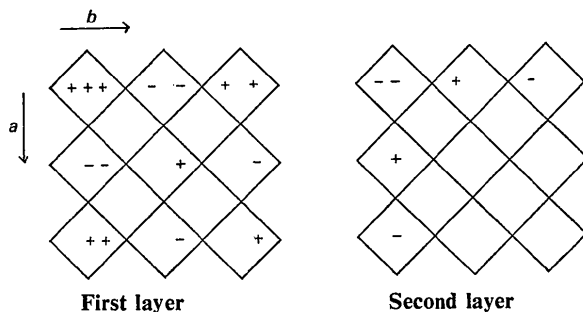Fig. 2. Schematic diagram of two adjacent layers of octahedra. The + and − signs indicate the relative senses of tilt in the octahedra (see text).

component tilts about the three tetrad axes.* For small angles of tilt, the component tilts can be taken to be about the pseudocubic axes prior to tilting, the magnitudes of the tilts being indicated symbolically by a set of three letters which refer to the axes in the order [100], [010], [001], and which in the general case of unequal tilts are denoted abc. Equality of tilts is denoted by repeating the appropriate letter, e.g. aac means equal tilts about [100] and [010] with a different tilt about [001]. We consider only those tilts that are 'freely variable' and independent.

In Fig. 2 two adjacent layers of octahedra are shown schematically. Consider the octahedron at the top-left position in the first layer and let it be tilted in an arbitrarily defined positive sense about the pseudocubic [100], [010] and [001] axes. This is indicated on the diagram by + + +.

We must now see how this affects the surrounding octahedra. If we choose any particular axis, then in directions *perpendicular* to it, successive octahedra are constrained to have opposite tilts about that axis. Thus, the positive tilt about [100] of magnitude a in the first octahedron makes a negative tilt about [100] of equal magnitude in the nearest-neighbour octahedra along [010] and [001]. This operation can be carried through to all the octahedra and the final result is shown in this figure. It is obvious that there are some missing signs, indicating some choice in how to complete the structure. This arises because successive octahedra *along* an axis can have either the same or opposite sense of tilt. We can then indicate the particular choice by the superscripts +, − or 0, to show whether successive octahedra along an axis have the same tilt, opposite tilt or no tilt about that axis. Assuming no repeat period consists of more than two octahedra, there are 10 distinct possibilities:

$a^+b^+c^+$	$a^+b^+c^-$	$a^+b^-c^-$	$a^-b^-c^-$	3 tilts
$a^0b^+c^+$	$a^0b^+c^-$	$a^0b^-c^-$		2 tilts
$a^0a^0c^+$	$a^0a^0c^-$			1 tilt
$a^0a^0a^0$				no tilts

where the repetition of the symbol a^0 is used when there is zero tilt about more than one axis.

In the above scheme, combinations such as $a^+a^+c^+$, $a^+a^-a^+$ etc. have been omitted, since, for the moment, we shall deal only with the senses of tilt. In Fig. 3 these arrangements are drawn out in full. It can be seen that each case gives a self-consistent structure, *i.e.* there are now no missing signs and each structure has a regular repeat. This simple diagram permits the lattice-centring conditions to be obtained merely by inspection. For example, $a^+b^+c^+$ is body-centred and $a^-b^-c^-$ is all-face-centred.

In order to demonstrate that all these structures are physically possible and that the predicted centring does occur, a flexible model was constructed. In Fig. 4 a series of stereo-photographs of the eight representative octahedra of each arrangement is shown. The correctness of the prediction can easily be verified. With

some experience, it is also a simple matter from Fig. 4 to find other symmetry elements, such as mirror planes and rotation axes.

We must now go on to discuss the relation between the tilts and the crystal systems, and here the magnitude of the tilts becomes important. Any tilt, as defined here, results in a decrease in the distances between octahedron centres (pseudocubic subcell edges) *perpendicular* to the tilt axis. The corresponding distance *along* the tilt axis is unchanged by the tilt operation. Denoting the angles of tilt about [100], [010] and [001] by α, β and γ respectively (less than 15°, say) the pseudocubic axial lengths are given by

$$a_p = \xi \cos \beta \cos \gamma$$
$$b_p = \xi \cos \alpha \cos \gamma$$
$$c_p = \xi \cos \alpha \cos \beta$$

where ξ is the anion–anion distance through the centre of the octahedron.

These equations show that three unequal tilts produce three unequal pseudocubic spacings, two equal tilts produce two equal spacings and one different and three equal tilts produce three equal spacings. Thus

$$a^i b^j c^k \text{ has 3 unequal spacings}$$
$$a^i b^j b^k \text{ has 2 equal spacings}$$
$$a^i a^j a^k \text{ has 3 equal spacings}$$

where superscripts i, j, k refer to the senses of tilt about [100], [010] and [001] respectively, and may stand for $+$, $-$, or 0. It should be noted that three equal tilts correspond to tilting about one of the triad axes of the octahedron and two equal tilts correspond to tilting about one of its diad axes, provided that the tilt angles are small; or, with larger tilt angles, that the operations are carried out in an alternating sequence of small steps.

In order to deal with the interaxial angles it is useful to note that whenever a superscript is 0 or $+$ this implies the existence of a mirror plane perpendicular to the relevant axis.

For the one-tilt systems $a^0 a^0 c^+$ and $a^0 a^0 c^-$, therefore, there are respectively three and two mutually perpendicular mirror planes and hence both tilt systems give rise to orthogonal axes; it is also obvious that a single tilt about [001] must leave a 4-fold axis and therefore both cases have tetragonal symmetry.

For the two-tilt systems it is clear that whenever the superscripts are $0++$ or $0+-$ (in any order) the unit cell must have orthogonal axes, since the $+$'s and 0's necessarily imply at least two mirror planes mutually perpendicular. When two superscripts are $-$ the problem becomes a little more difficult. Fig. 5(a) shows part of the unit cell of $a^0 b^- c^-$. A, B and C are three anion atoms of one octahedron. Here A lies above the (001) plane through $z=0$ and B lies on it; C is at a height $z=\frac{1}{4}$. The next octahedron along [001] is denoted by A', B' and C'. A' lies below the (001) plane through $z=\frac{1}{2}$ and B' lies on it. C' is the atom at the bottom vertex of this octahedron and must therefore

be the same atom as C. Since the diagram has been drawn as if the c_p axis were perpendicular to (001) we see that there is a displacement vector along [010] between C' and C. Therefore in order that C' and C be the same atom the c_p axis must be inclined to b_p but must remain perpendicular to a_p. A special case arises in $a^0 b^- b^-$. Here the equality of tilts about [010] and [001] implies equality between b_p and c_p, whence it is possible to construct an orthogonal unit cell by transforming from the axes $a_o = 2a_p$, $b_o = 2b_p$, $c_o = 2c_p$ to a new set a_n, b_n, c_n defined by

$$
\begin{array}{c c c c}
 & a_o & b_o & c_o \\
a_n & 1 & 0 & 0 \\
b_n & 0 & \frac{1}{2} & -\frac{1}{2} \\
c_n & 0 & \frac{1}{2} & \frac{1}{2}
\end{array}
$$

	First Layer			Second Layer			Symbol	Lattice
	+++	-+-	+++	--+	+--	--+		
	+--	--+	+--	-+-	+++	-+-	a·b·c⁻	I
	+++	-+-	+++	--+	+--	--+		
	+++	-+-	+++	---	+-+	---		
	+--	--+	+--	-++	++-	-++	a·b·c	P
	+++	-+-	+++	---	+-+	---		
	+++	---	+++	---	+++	---		
	+--	-++	+--	-++	+--	-++	a·b·c⁻	A
	+++	---	+++	---	+++	---		
	+++	---	+++	---	+++	---		
	---	+++	---	+++	---	+++	a b c	F
	+++	---	+++	---	+++	---		
	0++	0+-	0++	0-+	0--	0-+		
	0--	0-+	0--	0+-	0++	0+-	a⁰b·c⁻	I
	0++	0+-	0++	0-+	0--	0-+		
	0++	0+-	0++	0--	0-+	0--		
	0--	0-+	0--	0++	0+-	0++	a⁰b·c	B
	0++	0+-	0++	0--	0-+	0--		
	0++	0--	0++	0--	0++	0--		
	0--	0++	0--	0++	0--	0++	a⁰b c	F
	0++	0--	0++	0--	0++	0--		
	00+	00-	00+	00+	00-	00+		
	00-	00+	00-	00-	00+	00-	a⁰a⁰c⁻	C
	00+	00-	00+	00+	00-	00+		
	00+	00-	00+	00-	00+	00-		
	00-	00+	00-	00+	00-	00+	a⁰a⁰c	F
	00+	00-	00+	00-	00+	00-		
	000	000	000	000	000	000		
	000	000	000	000	000	000	a⁰a⁰a⁰	P
	000	000	000	000	000	000		

Fig. 3. Schematic diagram illustrating all the possible senses of tilt. Each set of three symbols refers to one octahedron; nine octahedra make up one layer as shown in Fig. 2, but the outline of the octahedral framework has been omitted for simplicity.
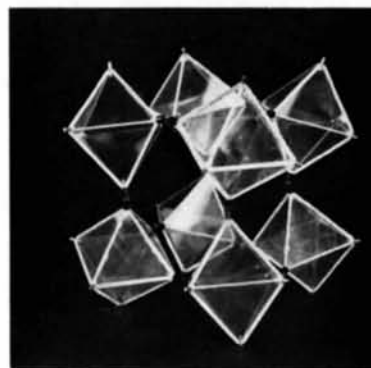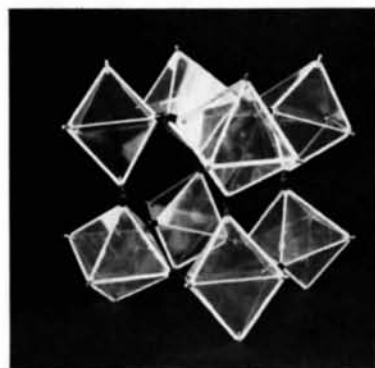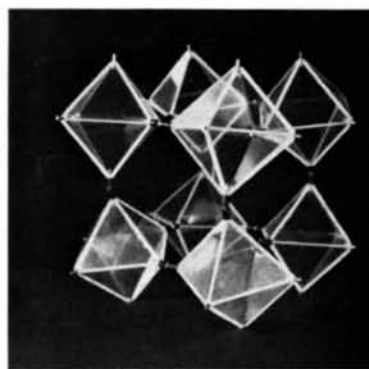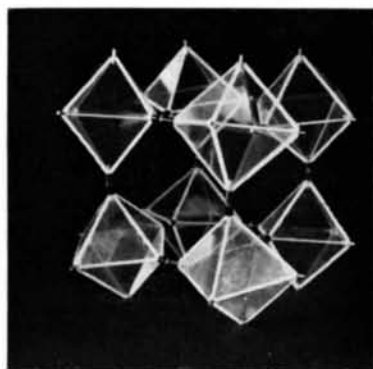
THREE TILTS
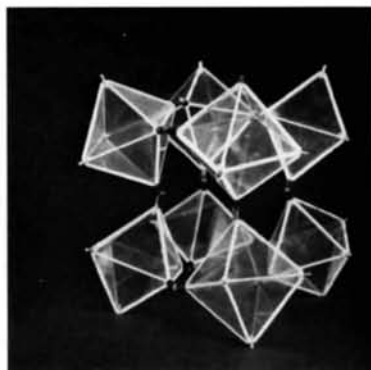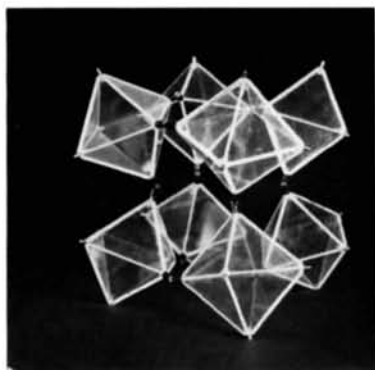
$a^+b^+c^+$
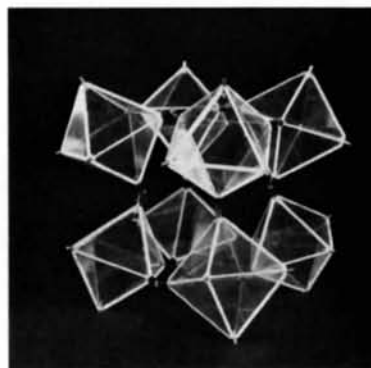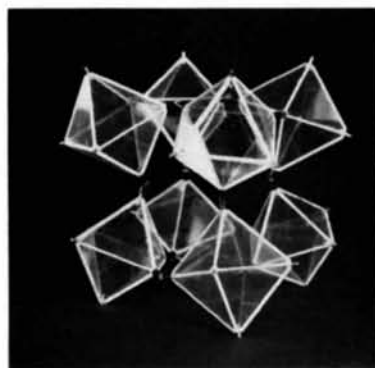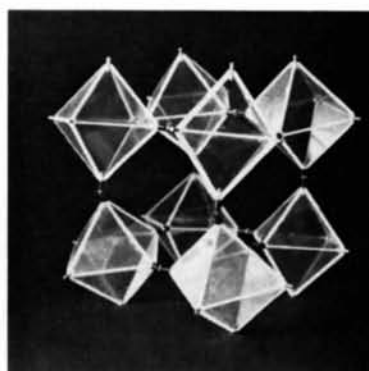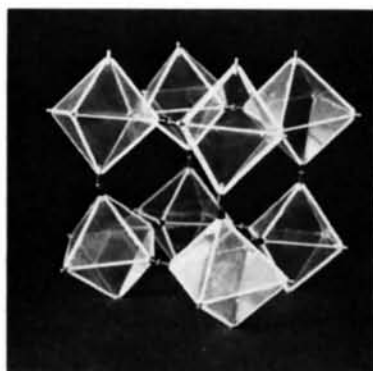
$a^+b^+c^-$

$a^+b^-c^-$

$a^-b^-c^-$

Fig. 4. Stereo-photographs of the eight representative octahedra in each arrangement. The axes used are right-handed with [001] vertical and [010] to the right. The origin is taken at the centre of any octahedron.
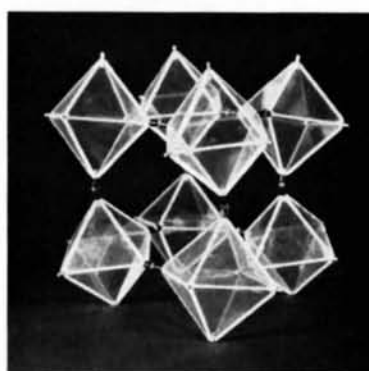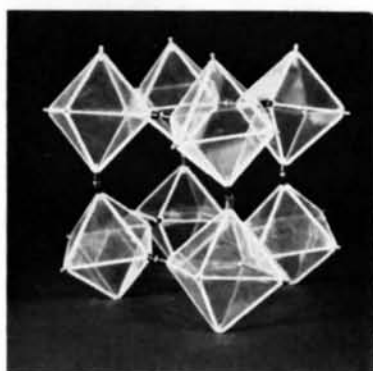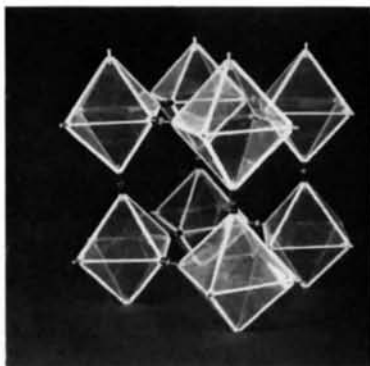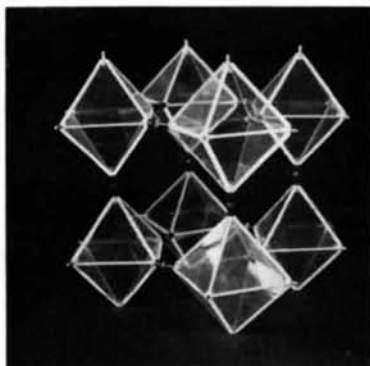
TWO TILTS

$a^0b^+c^+$

$a^0b^+c^-$

$a^0b^-c^-$
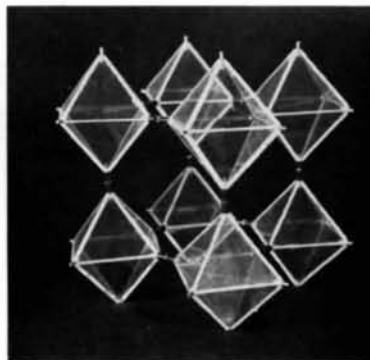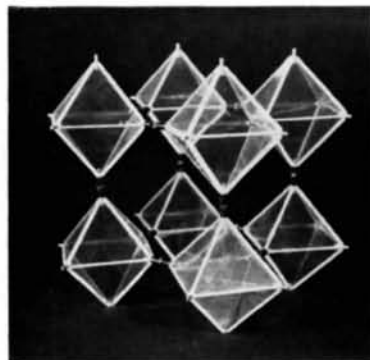
Fig. 4 (cont.)

PLATE 10

ONE TILT

$a^0a^0c^+$

$a^0a^0c^-$
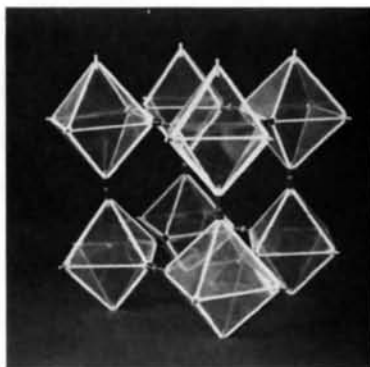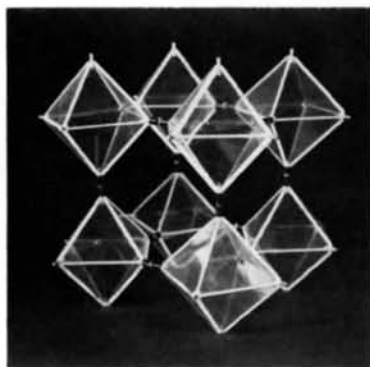
NO TILTS

$a^0a^0a^0$

Fig. 4 (cont.)

For the three-tilt systems, similar arguments can be applied. Thus $a^+b^+c^+$ and $a^+b^+c^-$ are orthogonal systems, since they have at least two mutually-perpendicular mirror planes, while $a^+b^-c^-$ must have two axes b_p and c_p inclined and one (a_p) perpendicular, as in $a^0b^-c^-$. When all three superscripts are − it is therefore reasonable to expect all three axes to be inclined to one another. Fig. 5(b) shows the interesting case of $a^-b^-b^-$. Since the tilts about [010] and [001] are of the − type, the b_p and c_p axes are shown inclined to one another. In this case we see that the displacement vector $\overrightarrow{A'A}$ lies along $[0\bar{1}1]$ and as expected all three axes are inclined to one another. In this particular example, transformation by the above matrix gives a unit cell with c_n perpendicular to a_n and b_n and with a_n and b_n inclined to one another. The special case of $a^-a^-a^-$ has three axes equal in length and equally inclined to one another. Since three equal tilts correspond to tilting of the octahedra about their triad axes, this system must be rhombohedral.
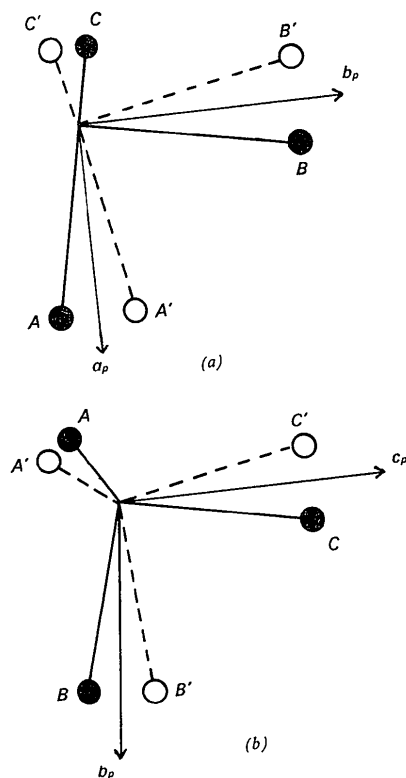

Fig. 5. (a) Projection on (001) of part of the unit cell of $a^0b^-c^-$, showing the anions in two successive octahedra along [001]. The relative coordinates of the anions are indicated in the key to the diagram. The vector $\overrightarrow{C'C}$ implies that c_p is inclined to (001) (see text). z coordinates: A, $+z$; A', $\frac{1}{2}-z$; B, 0; B', $\frac{1}{2}$; C, C', $\frac{1}{4}$. (b) Projection on (100) of part of the unit cell of $a^-b^-b^-$, showing the anions in two successive octahedra along [100]. The vector $\overrightarrow{A'A}$ implies that a_p is inclined to (100). x coordinates; A, A', $\frac{1}{4}$; B, $+x$; B', $\frac{1}{2}-x$; C, $+x$; C', $\frac{1}{2}-x$.

In this way it is possible to formulate some general rules to help in correlating the tilt systems with the relative lattice parameters.

(1) Equality of tilts about two or more pseudocubic axes leads to equality in the respective pseudocubic axial lengths, e.g. $a^+a^+a^+$ has $a_p=b_p=c_p$.

(2) If, in the symbolic notation used here, two or more superscripts are + or 0, the pseudocubic axes are orthogonal.

(3) If two, and only two, superscripts are −, then the two respective pseudocubic axes are inclined to one another whilst the third is perpendicular to them both.

(4) If all three superscripts are −, then all three pseudocubic axes are inclined to one another.

It finally remains necessary to determine the space-group symmetry of the tilt systems. The simplest way to do this is to draw a plan of the structure and then fill in the symmetry elements. As an example, Fig. 6 shows two (001) layers of the system $a^-b^+c^+$ and the presence of mirror and n-glide planes shows that its space group is *Pnmm* (No. 63).

In Table 1, the resulting tilt systems have been summarized together with the relevant symmetry information. The different tilt systems are numbered serially from 1 to 23. The lattice-centring refers to a unit cell $a_o=ma_p$, $b_o=nb_p$, $c_o=qc_p$ as given in the fourth column. The space-group symbol in each case refers to the axes a_o, b_o, c_o except where this would give lower symmetry than the true crystal symmetry. In these cases, indicated by an asterisk, the true space group has been given, the axes a_n, b_n, c_n being defined by the matrix given above.

This Table enables many of the structures to be determined uniquely from X-ray evidence. For example, the systems $a^+b^-b^-$, $a^+a^-a^-$ and $a^0b^-b^-$, which are orthorhombic, are all distinguishable from one another either because of their pseudocubic axial lengths or because of their lattice-centring when referred to the pseudocubic multiple-cell axes a_o, b_o, c_o. Similarly, the three tetragonal systems $a^0b^+b^+$, $a^0a^0c^+$ and $a^0a^0c^-$ are distinguishable from one another; use of this was made in the derivation of the $NaNbO_3(T_2)$ structure (Glazer & Megaw, 1972).

Experimental determination of the lattice-centring can be difficult, since the X-ray reflexions that characterize it are very weak in intensity. Because the tilts produce doubling of the pseudocubic axial lengths, these reflexions are found on half-integral reciprocal lattice planes, if the original subcell axes are used. Unless specifically looked for, they can easily be missed, particularly in studies on powdered materials. Nevertheless, from the observation of very few half-integral reflexions it is possible to derive a trial model for the structure.

The scheme of simple tilt systems outlined so far has relied on the condition that no repeat period consists of more than two octahedra. It is obvious that more complicated compound tilt systems can be built up by stacking the simple systems together in an infinite variety of ways. In practice only two different com-

pound tilt systems have been observed up till now, the stacking being found to occur along one crystallographic direction, [010]. For this reason we consider only this kind of compound tilt, the others being beyond the scope of the present work. The structures may best be described by considering them in terms of successive pairs of octahedron layers, each sharing a layer in common, or single layers when the tilt about [010] is zero.

In one of the two cases the repeat period along [010] is $4b_p$. Numbering the layers 1 to 4, the structure is described by $a^-b^+a^-$ for layers 1 and 2, $a^-b^-a^-$ for layers 2 and 3, $a^-b^+a^-$ for layers 3 and 4. This can be written thus

$$(a^-b^+a^-)^2_1 \quad (a^-b^-a^-)^3_2 \quad (a^-b^+a^-)^4_3.$$

In the other case the repeat period along [010] is $6b_p$. Here the structure consists of $a^-b^+c^+$ for layers 1 and 2, $a^-b^0c^+$ for layer 3, $a^-b^+c^+$ for layers 4 and 5, $a^-b^0c^+$ for layer 6, thus:

$$(a^-b^+c^+)^2_1 \quad (a^-b^0c^+)^3_3 \quad (a^-b^+c^+)^5_4 \quad (a^-b^0c^+)^6_6.$$

The actual multiplicities of $4b_p$ and $6b_p$ in these cases are consequences of the tilts about [100] and [001].

Symmetry-determination for compound tilt systems is more difficult than for the simple systems and will not be attempted here. In any case, the known examples of such tilt systems (NaNbO$_3$, phases P and R) also have cation displacements to further complicate matters. In fact, it has only been possible to determine their structures by carrying out a complete refinement using many reflexions (Sakowski-Cowley, Łukaszewicz & Megaw, 1969; Sakowski-Cowley, 1967).

Examples of tilt systems

A search of the literature has revealed many perovskite structures with octahedral tilts and these are summarized in Table 2. The assignment of the tilt systems was made usually by reference to the published atomic coordinates supplied by the various authors. Sometimes, as in AgNbO$_3$ for example, the structures have not actually been determined except by analogy with already known structures; as there is no reason to doubt their correctness, they too have been included in the Table, but are marked with an asterisk.

In Table 2 the materials are arranged according to tilt system, together with an indication of which cations, if any, are displaced. The observed space groups are also given for comparison with the space groups that would be expected from the anion framework alone.

It is immediately apparent that the majority of tilted structures belong to the systems (10) $a^-b^+a^-$ and (14) $a^-a^-a^-$. It is not clear why this should be; in fact, it is surprising that out of the 23 possible tilt systems only 9 have been found to occur. It would be extremely interesting to find some of the other structures, in particular the cubic (3) $a^+a^+a^+$ and the tetragonal (16) $a^0b^+b^+$ with axial ratio less than unity.
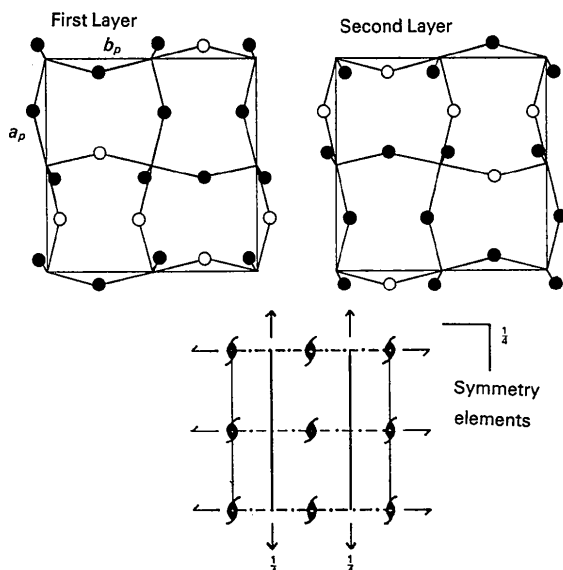

Fig. 6. Plan of two (001) layers of octahedra for the tilt system (4) $a^-b^+c^+$. Closed and open circles indicate whether the anions are above or below the planes through the centres of the octahedra; the centres of the octahedra of the first layer are at height 0 and those of the second layer at height $\frac{1}{4}$. The symmetry elements, shown below the plan, indicate that the space group is $Pnmm$.

The differences between the observed space groups and those due to the tilted framework alone arise out of the cation displacements. For example, we find that there are two space groups for $a^-a^-a^-$ materials; when there are no B cation displacements the space group is $R\bar{3}c$, whereas when the B cation is displaced the centre of symmetry is lost and the space group becomes $R3c$. Again, in PrAlO$_3$ below 135° K, the observed space group (with reference to pseudocubic axial directions) is $F\bar{1}$ as opposed to $F12/m1$ for the framework alone. Here the Pr displacements are responsible for imposing triclinic symmetry on a monoclinic framework.

One example of an untilted structure has been given in Table 2, namely KCuF$_3$, since it sounds a note of caution. In this material the observed space group is $F4/mmc$, as in $a^0a^0c^-$, and yet the axial ratio is less than 1. It is therefore very difficult to ascertain by the arguments of the present paper whether the structure is one with no tilts plus *large* distortion of the octahedra or whether it is one with tilts as in $a^0a^0c^-$ plus *small* distortions. In fact it is known to be the former; this is hardly surprising in view of the large Jahn–Teller effects that are normally shown by copper compounds.

Distortions of the octahedra, then, can lead to ambiguities, although it appears that in the majority of cases they do not. Because of them the actual magnitudes of the lattice parameters may not lead to an accurate measure of the tilts, although there is evidence that they do, at least, provide a reasonable estimate of them (Megaw, 1971, with reference to the rare-earth ortho-

ferrites). In $LaAlO_3$, which is $a^-a^-a^-$, the flattening of the oxygen octahedra (Megaw, 1971) actually leads to a rhombohedral angle greater than 90°. Nevertheless, this still does not affect the nature of the tilt system: the lattice-centring conditions and relative pseudo-cubic lattice parameters would still lead to the correct assignment of $a^-a^-a^-$.

$SrTiO_3$ and $KMnF_3$ possess the $a^0a^0c^-$ structure and this has been shown to be associated with the condensation of a Γ_{25} soft-phonon mode at $q=\frac{1}{2},\frac{1}{2},\frac{1}{2}$ on transforming from the cubic phase (Shirane & Yamada, 1969; Shirane, Minkiewicz & Linz, 1970). This mode has components consisting of rigid oscillations of the anion octahedra about [001] with successive octahedra along this direction oscillating in antiphase. It is for this reason that, when the mode condenses at the transition temperature, $a^0a^0c^-$ results.

On the other hand, $NaNbO_3(T_2)$ possesses the $a^0a^0c^+$ structure (determined with the present technique, using three reflexions), and condensation of an M_3 soft-phonon mode at $q=\frac{1}{2},\frac{1}{2},0$ has been postulated to explain the transition from the cubic phase (Glazer & Megaw, 1972). This mode consists of successive octahedra along [001] oscillating in phase about this direction, thus giving rise to the $a^0a^0c^+$ structure on condensation.

More recent work on the T_1 phase of $NaNbO_3$ (Ahtee, Glazer & Megaw, 1972) showed that its structure could be described by $a^-b^0c^+$, and the transition from T_2 to T_1 has been explained in terms of condensation of a Γ_{25} mode. The two transitions can then be summarized thus:

$$a^0a^0a^0 \text{ (cubic)} \xrightarrow{M_3} a^0a^0c^+ \ (T_2) \xrightarrow{\Gamma_{25}} a^-b^0c^+ \ (T_1)$$
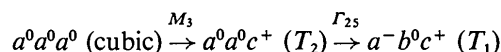
and we see that condensation of soft-modes produces a sequence of transitions to give the scheme: zero-tilt system → one-tilt system → two-tilt system.

The simple tilt systems derived in this paper are therefore of importance in the discussion of soft-phonon modes in connexion with phase transitions in perovskites, since rigid oscillations of the octahedra constitute important modes near the transitions.

As mentioned earlier, there are not many known examples of compound tilts. Actually, only $NaNbO_3$ is definitely known to possess such complicated tilt systems, although it is very likely that $AgNbO_3$ is isomorphous with it. The evidence for this (Francombe & Lewis, 1958) is based on the presence of superlattice lines corresponding to a unit cell of $2a_p \times 4b_p \times 2c_p$, with $a_p=c_p$ and $\beta>90°$, as is found in $NaNbO_3(P)$.

Table 1. *Complete list of possible simple tilt systems*

Serial number	Symbol	Lattice centring	Multiple cell	Relative pseudocubic subcell parameters	Space group
3-tilt systems					
(1)	$a^+b^+c^+$	I	$2a_p \times 2b_p \times 2c_p$	$a_p \neq b_p \neq c_p$	$Immm$ (No. 71)
(2)	$a^+b^+b^+$	I		$a_p \neq b_p = c_p$	$Immm$ (No. 71)
(3)	$a^+a^+a^+$	I		$a_p = b_p = c_p$	$Im3$ (No. 204)
(4)	$a^+b^+c^-$	P		$a_p \neq b_p \neq c_p$	$Pmmn$ (No. 59)
(5)	$a^+a^+c^-$	P		$a_p = b_p \neq c_p$	$Pmmn$ (No. 59)
(6)	$a^+b^+b^-$	P		$a_p \neq b_p = c_p$	$Pmmn$ (No. 59)
(7)	$a^+a^+a^-$	P		$a_p = b_p = c_p$	$Pmmn$ (No. 59)
(8)	$a^+b^-c^-$	A		$a_p \neq b_p \neq c_p \alpha \neq 90°$	$A2_1/m11$ (No. 11)
(9)	$a^+a^-c^-$	A		$a_p = b_p \neq c_p \alpha \neq 90°$	$A2_1/m11$ (No. 11)
(10)	$a^+b^-b^-$	A		$a_p \neq b_p = c_p \alpha \neq 90°$	$Pnma$ (No. 62)*
(11)	$a^+a^-a^-$	A		$a_p = b_p = c_p \alpha \neq 90°$	$Pnma$ (No. 62)*
(12)	$a^-b^-c^-$	F		$a_p \neq b_p \neq c_p \alpha \neq \beta \neq \gamma \neq 90°$	$F\bar{1}$ (No. 2)
(13)	$a^-b^-b^-$	F		$a_p \neq b_p = c_p \alpha \neq \beta \neq \gamma \neq 90°$	$I2/a$ (No. 15)*
(14)	$a^-a^-a^-$	F		$a_p = b_p = c_p \alpha = \beta = \gamma \neq 90°$	$R\bar{3}c$ (No. 167)
2-tilt systems					
(15)	$a^0b^+c^+$	I	$2a_p \times 2b_p \times 2c_p$	$a_p < b_p \neq c_p$	$Immm$ (No. 71)
(16)	$a^0b^+b^+$	I		$a_p < b_p = c_p$	$I4/m$ (No. 78)
(17)	$a^0b^+c^-$	B		$a_p < b_p \neq c_p$	$Bmmb$ (No. 63)
(18)	$a^0b^+b^-$	B		$a_p < b_p = c_p$	$Bmmb$ (No. 63)
(19)	$a^0b^-c^-$	F		$a_p < b_p \neq c_p \alpha \neq 90°$	$F2/m11$ (No. 12)
(20)	$a^0b^-b^-$	F		$a_p < b_p = c_p \alpha \neq 90°$	$Imcm$ (No. 74)*
1-tilt systems					
(21)	$a^0a^0c^+$	C	$2a_p \times 2b_p \times c_p$	$a_p = b_p < c_p$	$C4/mmb$ (No. 127)
(22)	$a^0a^0c^-$	F	$2a_p \times 2b_p \times 2c_p$	$a_p = b_p < c_p$	$F4/mmc$ (No. 140)
Zero-tilt system					
(23)	$a^0a^0a^0$	P	$a_p \times b_p \times c_p$	$a_p = b_p = c_p$	$Pm3m$ (No. 221)

* These space group symbols refer to axes chosen according to the matrix transformation

$$\begin{pmatrix} 1 & 0 & 0 \\ 0 & \frac{1}{2} & -\frac{1}{2} \\ 0 & \frac{1}{2} & \frac{1}{2} \end{pmatrix}.$$

Table 2. *Examples of known tilt systems*

Tilt system	Substance	Cation displacements	Observed space group	Space group of tilted framework alone	Reference
(4) $a^-b^+c^+$	NaNbO₃(S)	Na?	Pmmm	Pmmm	Ahtee, Glazer & Megaw (1972)
(10) $a^-b^+a^-$	YAlO₃	Y	Pbnm	Pbnm	Geller & Wood (1956)
	SmAlO₃	Sm	Pbnm	Pbnm	Marezio, Dernier & Remeika (1972)
	EuAlO₃*	Eu? }	Pbnm	Pbnm	Geller & Bala (1956)
	GdAlO₃*	Gd? }			
	DyAlO₃	Dy	Pbnm	Pbnm	Bidaux & Mériel (1968)
	BaCeO₃	Ba	Pbnm	Pbnm	Jacobson, Tofield & Fender (1972)
	YCrO₃, YFeO₃, LaFeO₃, PrFeO₃, NdFeO₃, SmFeO₃, EuFeO₃, GdFeO₃	Y; Y, La, Pr, Nd, Sm, Eu, Gd	Pbnm	Pbnm	Geller & Wood (1956)
	TbFeO₃, DyFeO₃, HoFeO₃, ErFeO₃, TmFeO₃, YbFeO₃, LuFeO₃	Tb, Dy, Ho, Er, Tm, Yb, Lu	Pbnm	Pbnm	Marezio, Remeika & Dernier (1970)
	NaMgF₃ (<760°C)*		Pbnm	Pbnm	Chao, Evans, Skinner & Milton (1961)
	YNiO₃, SmNiO₃, EuNiO₃, GdNiO₃, DyNiO₃, HoNiO₃, ErNiO₃, TmNiO₃, YbNiO₃, LuNiO₃	Y, Sm, Eu, Gd, Dy, Ho, Er, Tm, Yb, Lu	Pbnm	Pbnm	Demazeau, Marbeuf, Pouchard & Hagenmuller (1971)
	BaPrO₃	Ba	Pbnm	Pbnm	Jacobson, Tofield & Fender (1972)
	CaTiO₃		Pbnm	Pbnm	Kay & Bailey (1957)
	CdTiO₃	Cd, Ti	Pbn2₁	Pbnm	Kay & Miles (1957)
(14) $a^-a^-a^-$	LaAlO₃	La	R3̄c	R3̄c	Derighetti, Drumheller, Laves, Müller & Waldner (1965); de Rango, Tsoucaris & Zelwer (1966)
	PrAlO₃(172–293 °K)		R3̄c	R3̄c	Burbank (1970)
	NdAlO₃		R3̄c	R3̄c	Derighetti, Drumheller, Laves, Müller & Waldner (1965); Marezio, Dernier & Remeika (1972)
	LaCoO₃		R3̄c	R3̄c	Menyuk, Dwight & Raccah (1967)
	FeF₃, CoF₃, RuF₃, RhF₃, PdF₃, IrF₃, VF₃		R3̄c	R3̄c	Hepworth, Jack, Peacock & Westland (1957)
	BiFeO₃	Bi, Fe	R3c	R3̄c	Jack & Gutmann (1951); Michel, Moreau, Achenbach, Gerson & James (1969a)
	LiNbO₃	Li, Nb	R3c	R3̄c	Abrahams, Reddy & Bernstein (1966); Megaw (1968)
	NaNbO₃(N)	Na, Nb	R3c	R3̄c	Darlington (1971)
	LiTaO₃	Li, Ta	R3c	R3̄c	Abrahams & Bernstein (1967)
	BaTbO₃		R3c	R3̄c	Jacobson, Tofield & Fender (1972)
	PbZr₀.₉Ti₀.₁O₃	Pb, (Zr, Ti)	R3c	R3̄c	Michel, Moreau, Achenbach, Gerson & James (1969b)

Table 2 (cont.)

		tilt	cation			reference
(17)	NaNbO₃(T₁)	$a^-b^0c^+$	Na?	Ccmm	Ccmm	Ahtee, Glazer & Megaw (1972)
(19)	PrAlO₃(<135 °K)	$a^-b^0c^-$	Pr	F1	F1	Burbank (1970)
(20)	PrAlO₃(135–172 °K)	$a^-b^0a^-$	Pr	I12/m1	F12/m1	Burbank (1970)
(21)	NaNbO₃(T₂)	$a^0a^0c^+$		C4/mmb	C4/mmb	Glazer & Megaw (1972)
(22)	KMnF₃(88–184 °K)	$a^0a^0c^-$		F4/mmc	F4/mmc	Minkiewicz, Fujii & Yamada (1970)
	SrTiO₃(<110 °K)			F4/mmc	F4/mmc	Unoki & Sakudo (1967)
(23)	KCuF₃	$a^0a^0a^0$		F4/mmc	Pm3m	Okazaki & Suemune (1961)
Compound tilts						
(10) (13)	AgNbO₃(<325 °C)*	$(a^-b^+a^-)\tfrac{1}{3}\tfrac{1}{4}(a^-b^-a^-)\tfrac{1}{3}(a^-b^+a^-)\tfrac{4}{3}$	Ag, Nb	Not given	Ccmm	Francombe & Lewis (1958)
	NaNbO₃(P)		Na, Nb	Pbma	F12/m1	Sakowski-Cowley, Łukaszewicz & Megaw (1969)
	AgTaO₃(<370 °C)*		Ag? Ta?	Not given	Icmm	Francombe & Lewis (1958)
(4) (17)	NaNbO₃(R)	$(a^-b^+c^+)\tfrac{1}{3}\tfrac{1}{4}(a^-b^0c^+)\tfrac{1}{3}(a^-b^+c^+)\tfrac{1}{4}\tfrac{3}{4}(a^-b^0c^+)\tfrac{1}{6}$	Na, Nb	Pmnm	Pn3m	Sakowski-Cowley (1967)

* Structures that have been determined by analogy with already-known structures and for which no atomic coordinates have been given.

In the case of AgTaO₃, the evidence for the compound system is even more tenous since there has been no observation of the necessary superlattice lines.

It is tempting to make some predictions about the nature of the tilts in hitherto undetermined structures by making use of the known lattice parameters and symmetries; examples are shown in Table 3.

SrZrO₃ below 730 °C has pseudocubic subcell parameters $a_p = c_p > b_p$, $\beta \neq 90°$ and is consistent, therefore, with $a^-b^+a^-$ or $a^-b^0a^-$. If the lattice type were known it would be possible to decide between these two possibilities, since they are B-face-centred and all-face-centred respectively; the former structure is the most likely in view of the high frequency with which it is found in practice. Between 730 and 860 °C the unit cell is tetragonal with axial ratio less than 1, indicating that the structure may be $a^+a^+c^0$. Similar considerations apply to NaMgF₃ between 760 and 900 °C, to KCoF₃ at 78 °K and to RbCoF₃ below 101 °K.* Between 860 and 1170 °C, SrZrO₃ is tetragonal with axial ratio greater than 1 and therefore may be $a^0a^0c^+$ or $a^0a^0c^-$. The presence or absence of difference reflexions on half-integral reciprocal lattice planes has not been explicitly reported in these compounds. The predictions, therefore, must be viewed with caution, since in making them it has been assumed that there are no distortions of the octahedra.

It is clear that, when studying the structures of perovskites, a special effort must be made to record the very weak difference reflexions found on half-integral reciprocal lattice planes. Very often in the past, the perovskite structures have been 'determined' by observing that the X-ray powder patterns are very similar to those of already-known structures. The present study has shown that this is unreliable and some of the structures quoted in Table 3, therefore, may be subject to reconsideration. It is to be hoped that the interpretation of future studies of these materials will be made more reliable and simpler by the use of the scheme reported here.

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* One must bear in mind that the original workers with these materials have assigned tetragonal symmetry to these phases from the measured lattice parameters and not from direct observations of symmetry. This means that the structures could, in fact, be orthorhombic with $a_p = b_p \neq c_p$ and would be then consistent with $a^+a^+c^+$, $a^+a^+c^-$, $a^+a^-c^+$ or $a^+a^-c^0$.

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Table 3. *Tilt systems suggested by known lattice parameters (and symmetry, when known)*

Tilt system	Substance	Observed space group	Reference
(10) $a^-b^+a^-$	BaPbO$_3$ ⎫ SrPbO$_3$ ⎰	?	Shuvaeva & Fesenko (1970)
	PrRhO$_3$, NdRhO$_3$, SmRhO$_3$, EuRhO$_3$, GdRhO$_3$, TbRhO$_3$, DyRhO$_3$, HoRhO$_3$, ErRhO$_3$, TmRhO$_3$, LuRhO$_3$	*Pbnm*	Shannon (1970)
	SrZrO$_3$(<730 °C)	?	Carlsson (1967)
(14) $a^-a^-a^-$	KFeF$_3$(78°K)	?	Okazaki, Suemune & Fuchikami (1959)
	LaNiO$_3$	$R\bar{3}c$	Demazeau, Marbeuf, Pouchard & Hagenmuller (1971)
(16) $a^+a^+c^0$	KCoF$_3$(78 °K)	?	Okazaki, Suemune & Fuchikami (1959)
	RbCoF$_3$(< 101 °K)	?	Nouet, Kleinberger & de Kouchkovsky (1969)
	NaMgF$_3$(760–900°C)	?	Chao, Evans, Skinner & Milton (1961)
	SrZrO$_3$(730–860 °C)	?	Carlsson (1967)
(21) $a^0a^0c^+$ or (22) $a^0a^0c^-$	SrZrO$_3$(860–1170 °C)	?	Carlsson (1967)

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