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Group-theoretical analysis of octahedral tilting in ferroelectric perovskites

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Group-theoretical methods are used to analyze perovskite structures where both ferroelectric cation displacements and simple tilting of octahedral units are present. This results in a list of 40 different structures, each with a unique space-group symmetry. The list is compared with that of Aleksandrov & Bartolomé [*Phase Transit.* (2001), **74**, 255–335] and a number of differences are found. The group–subgroup relationships between the structures are also determined, along with an indication of those phase transitions that must be first order by Landau theory.

1. Introduction

Structures in the perovskite family ABX_3 have held the interest of crystallographers over many years. Of particular interest have been the description and the classification of their various phases, their group–subgroup relationships with each other, and the distortional mechanisms driving the phase transitions. The ideal perovskite is cubic with space-group symmetry $Pm\bar{3}m$. Most perovskites, however, have lower symmetry owing to distortions.

The most common type of distortion involves the tilting of the BX_6 octahedra relative to one another as nearly rigid corner-linked units. Glazer (1972, 1975) compiled a list of 23 possible tilt systems. More recently, Howard & Stokes (1998), using group-theoretical methods, found 15 possible tilt systems with distinct symmetry. (Some of Glazer's tilt systems have the same symmetry and are in practice indistinguishable.) Also, Howard & Stokes (1998) obtained the group–subgroup relationships between the different tilt systems. This systematic treatment of tilt systems has already proved useful, to varying degrees, in guiding the correct determination of various distorted perovskite structures, for example, $CaFe_xTi_{1-x}O_{3-x/2}$ (Becerro *et al.*, 2000), $SrZrO_3$ (Howard *et al.*, 2000), $PrAlO_3$ (Moussa, Kennedy, Hunter *et al.*, 2001), $CaTiO_3$ (Kennedy, Howard & Chakoumakos, 1999), $LaGaO_3$ (Howard & Kennedy, 1999), $NaTaO_3$ (Kennedy, Prodjosantoso & Howard, 1999), (Ca,Sr)TiO_3 (Carpenter *et al.*, 2001), $Sr_{1-x}Ba_xZrO_3$ (Kennedy *et al.*, 2001), $Pb(Zr_{0.65}Ti_{0.35})O_3$ (Liu *et al.*, 2001), $SrTi_xZr_{1-x}O_3$ (Kam-Yuen *et al.*, 2001) and $BaPbO_3$ (Moussa, Kennedy & Vogt, 2001).

Another common type of perovskite distortion involves the displacement of the B cations within the octahedra, leading to either a ferroelectric or an antiferroelectric structure. Such distortions by themselves have been reasonably well understood for many years, the most well known ferroelectric example being $BaTiO_3$. Recently, Forrester *et al.* (2001) used group-theoretical arguments to help settle questions about ferroelectric phase transitions in lead zinc niobate-lead titanate (PZN-PT).

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The situation becomes more complex when we superimpose octahedral tilting and *B*-cation displacements. Howard *et al.* (2002) superimposed octahedral tilting on the antiferroelectric structure in WO_3, which can be considered a perovskite structure with the *A* cation absent. They obtained all possible subgroups due to the presence of different tilt systems and then used this information to answer some of the lingering questions about the complex phase diagram of WO_3.

Aleksandrov (1978) considered the superposition of octahedral tilting and ferroelectric *B*-cation displacements in perovskites and obtained a list of possible structures and their symmetries. Recently, Aleksandrov & Bartolomé (2001) expanded that list to include additional possible directions of the displacements.

In this paper, we revisit the work of Aleksandrov (1978). We apply group-theoretical methods to perovskite structures in which octahedral tilting and ferroelectric *B*-cation displacements are both present and obtain 40 possible space-group symmetries. We compare our results with those of Aleksandrov & Bartolomé (2001) and find a number of differences, which we discuss below. We also extend the work of Aleksandrov (1978) by determining the group–subgroup relationships between the different structures and indicate which phase transitions are allowed by Landau theory to be continuous.

2. Tilt-system notation

Glazer (1972) introduced a compact notation for tilt systems. His notation consisted of three letters, each with superscript 0, + or −. The three letters refer to the *x*, *y* and *z* axes of the underlying cubic perovskite structure $Pm\bar{3}m$. Two or more letters that are the same refer to axes about which the magnitude of the tilts are equal. The superscripts + and − refer to tilts about an axis in the given *x*, *y* or *z* direction. For +, successive tilts about an axis are equal and in the same direction. For −, successive tilts about an axis are equal in magnitude but in opposite directions. Since the octahedra are corner linked, successive tilts in directions perpendicular to the axis are constrained to be equal in magnitude but in opposite directions. The superscript 0 means that there is no tilt about an axis in that direction. All possible tilt systems can be written as a linear combination of the three + tilt systems $a^+b^0b^0$, $b^0a^+b^0$ and $b^0b^0a^+$, about the *x*, *y* and *z* axes, respectively, and the three − tilt systems $a^-b^0b^0$, $b^0a^-b^0$ and $b^0b^0a^-$, also about the *x*, *y* and *z* axes, respectively. For example, $a^+b^-b^-$ denotes a tilt system with + tilts about the *x* axis and − tilts about both the *y* and the *z* axes. In addition, the repetition of the letter *b* denotes that the tilts about the *y* and *z* directions are equal in magnitude in this structure. We do not consider tilt systems where both + and − tilts occur about the same axis. These would result in structures where the magnitudes of successive tilts are not equal.

3. Group-theoretical analysis

Distortions in crystalline structures are associated with representations of the parent space-group symmetry. Howard & Stokes (1998) find that the + tilt systems in the perovskites are associated with the three-dimensional irreducible representation (IR) M_3^+ of $Pm\bar{3}m$ and the − tilt systems are associated with the three-dimensional IR R_4^+. [We use the IR notation from Miller & Love (1967).]

Distortions caused by ferroelectric displacements of the *B* cation are associated with the three-dimensional IR Γ_4^-. Introduced here is a modified Glazer notation where *subscripts* + and − denote ferroelectric *B*-cation displacements along a given axis. For example, the tetragonal ferroelectric structure of $BaTiO_3$ would be represented by $a_0^0a_0^0c_+^0$, where the single subscript + denotes *B*-cation displacements in the + direction along the *z* axis. Furthermore, $a_0^0a_0^0c_-^0$ would represent a ferroelectric structure with *B*-cation displacements in the − direction along the *z* axis.

In the Landau theory of phase transitions, the magnitude of the distortions present is given by an order parameter $\boldsymbol{\eta}$, which is a vector in representation space. Since the IRs Γ_4^-, M_3^+ and R_4^+ are all three-dimensional, the order parameters associated with each of these IRs are also three-dimensional with the form (a, b, c). Here, we are dealing with three order parameters, $\boldsymbol{\eta}_1$, $\boldsymbol{\eta}_2$ and $\boldsymbol{\eta}_3$, associated with the IRs Γ_4^-, M_3^+ and R_4^+, respectively. The three components a, b, c of $\boldsymbol{\eta}_1$ are the amplitudes of the *B*-cation displacements in the *x*, *y* and *z* directions, *i.e.* $a_+^0b_0^0b_0^0$, $a_0^0b_+^0a_0^0$ and $a_0^0a_0^0c_+^0$, respectively. The three components of $\boldsymbol{\eta}_2$ are the magnitudes of the + tilts, $a_0^+b_0^0b_0^0$, $a_0^0b_0^+a_0^0$ and $a_0^0a_0^0c_0^+$, respectively. The three components of $\boldsymbol{\eta}_3$ are the magnitudes of the − tilts, $a_0^-b_0^0b_0^0$, $a_0^0b_0^-a_0^0$ and $a_0^0a_0^0c_0^-$, respectively.

An IR *i* maps space-group operators *g* onto matrices $D^i(g)$ (three-dimensional matrices in the cases of Γ_4^-, M_3^+ and R_4^+). In Landau theory, the effect of a space-group operator on an order parameter is given simply by the multiplication of the matrix: $g\boldsymbol{\eta} = D(g)\boldsymbol{\eta}$. The symmetry of a distorted structure is defined by all those operators *g* for which $D^i(g)\boldsymbol{\eta}_i = \boldsymbol{\eta}_i$ is satisfied for every IR *i* of the distortions present. The operators form an isotropy subgroup of the parent group. A complete collection of isotropy subgroups associated with Γ_4^-, M_3^+ and R_4^+ includes every possible symmetry that can be realized by combining *B*-cation displacements and octahedral tilts. [See Howard & Stokes (1998) for more details about IRs, order parameters and isotropy subgroups.]

Group-theoretical methods for enumerating isotropy subgroups have been developed by Hatch and Stokes (Hatch, 1984; Stokes & Hatch, 1984; Hatch & Stokes, 1985, 1986, 1987) and have been implemented in the computer program *ISOTROPY* (www.physics.byu.edu/~stokesh/isotropy.html).

4. Results

Using *ISOTROPY*, we have generated the list of isotropy subgroups given in Table 1. [For an example of how this is done, see Case Study 1 in Stokes & Hatch (2002); see also

Table 1
Isotropy subgroups of $Pm\bar{3}m$ for the IRs Γ_4^-, M_3^+ and R_4^+.

For each subgroup, we give (i) an arbitrary reference number, (ii) the space-group symmetry, (iii)–(v) the order parameters for the IRs Γ_4^-, M_3^+ and R_4^+, respectively, (vi) the tilt-displacement system using a modified notation of Glazer (1972, 1975), (vii)–(viii) the lattice vectors and origin of the subgroup with respect to the parent group $Pm\bar{3}m$, and (ix) the entries in this table that are minimal supergroups of this subgroup. Phase transitions from supergroups marked with an asterisk (*) are required by Landau theory to be first order. Entries 2–15 are from Howard & Stokes (1998). The lattice vectors and origins are given using the conventional settings of space groups in the *International Tables for Crystallography* (Hahn, 1983). The hexagonal setting is used for rhombohedral groups. The second origin choice is used for groups with two origin choices. The setting with unique axis *b*, cell choice 1, is used for the monoclinic space groups.

Ref	Space group	Γ_4^-	M_3^+	R_4^+	System	Lattice vectors	Origin	Supergroups
1	221 $Pm\bar{3}m$	(0, 0, 0)	(0, 0, 0)	(0, 0, 0)	$a_0^0a_0^0a_0^0$	(1, 0, 0)(0, 1, 0)(0, 0, 1)	(0, 0, 0)	
2	127 $P4/mbm$	(0, 0, 0)	(0, 0, a)	(0, 0, 0)	$a_0^0a_0^0c_0^+$	(1, 1, 0)($\bar{1}$, 1, 0)(0, 0, 1)	(0, 0, 0)	1
3	139 $I4/mmm$	(0, 0, 0)	(0, a, a)	(0, 0, 0)	$a_0^0b_0^+b_0^+$	(0, 2, 0)(0, 0, 2)(2, 0, 0)	(1/2, 1/2, 3/2)	1*
4	204 $Im\bar{3}$	(0, 0, 0)	(a, a, a)	(0, 0, 0)	$a_0^+a_0^+a_0^+$	(2, 0, 0)(0, 2, 0)(0, 0, 2)	(1/2, 1/2, 1/2)	1
5	71 $Immm$	(0, 0, 0)	(a, b, c)	(0, 0, 0)	$a_0^+b_0^+c_0^+$	(2, 0, 0)(0, 2, 0)(0, 0, 2)	(1/2, 1/2, 1/2)	2, 3, 4*
6	140 $I4/mcm$	(0, 0, 0)	(0, 0, 0)	(0, 0, a)	$a_0^0a_0^0c_0^-$	(1, 1, 0)($\bar{1}$, 1, 0)(0, 0, 2)	(0, 0, 0)	1
7	74 $Imma$	(0, 0, 0)	(0, 0, 0)	(0, a, a)	$a_0^0b_0^-b_0^-$	(0, 1, 1)(2, 0, 0)(0, 1, $\bar{1}$)	(0, 0, 0)	1*
8	167 $R\bar{3}c$	(0, 0, 0)	(0, 0, 0)	(a, a, a)	$a_0^-a_0^-a_0^-$	($\bar{1}$, 1, 0)(0, $\bar{1}$, 1)(2, 2, 2)	(0, 0, 0)	1
9	12 $C2/m$	(0, 0, 0)	(0, 0, 0)	(0, a, b)	$a_0^0b_0^-c_0^-$	(0, 2, 0)(2, 0, 0)(0, 1, 1)	(1/2, 1/2, 0)	6, 7
10	15 $C2/c$	(0, 0, 0)	(0, 0, 0)	(a, b, b)	$a_0^-b_0^-b_0^-$	(2, $\bar{1}$, $\bar{1}$)(0, 1, $\bar{1}$)(0, 1, 1)	(1/2, 1/2, 0)	6, 7, 8*
11	2 $P\bar{1}$	(0, 0, 0)	(0, 0, 0)	(a, b, c)	$a_0^-b_0^-c_0^-$	(0, 1, 1)(1, 0, 1)(1, 1, 0)	(0, 0, 0)	9, 10
12	63 $Cmcm$	(0, 0, 0)	(0, a, 0)	(0, 0, b)	$a_0^0b_0^+c_0^-$	(2, 0, 0)(0, 0, $\bar{2}$)(0, 2, 0)	(1/2, 0, 1/2)	2, 6
13	62 $Pnma$	(0, 0, 0)	(a, 0, 0)	(0, b, b)	$a_0^-b_0^-b_0^-$	(0, 1, 1)(2, 0, 0)(0, 1, $\bar{1}$)	(0, 0, 0)	2, 7
14	11 $P2_1/m$	(0, 0, 0)	(a, 0, 0)	(0, b, c)	$a_0^+b_0^-c_0^-$	(0, $\bar{1}$, 1)(2, 0, 0)(0, 1, 1)	(0, 0, 0)	9, 12, 13
15	137 $P4_2/nmc$	(0, 0, 0)	(a, a, 0)	(0, 0, b)	$a_0^+a_0^+c_0^-$	(2, 0, 0)(0, 2, 0)(0, 0, 2)	(0, 0, −1)	3, 6
16	99 $P4mm$	(0, 0, a)	(0, 0, 0)	(0, 0, 0)	$a_0^0a_0^0c_+^0$	(1, 0, 0)(0, 1, 0)(0, 0, 1)	(0, 0, 0)	1
17	38 $Amm2$	(a, a, 0)	(0, 0, 0)	(0, 0, 0)	$a_+^0a_+^0c_0^0$	(0, 0, 1)(1, $\bar{1}$, 0)(1, 1, 0)	(0, 0, 0)	1*
18	160 $R3m$	(a, a, a)	(0, 0, 0)	(0, 0, 0)	$a_+^0a_+^0a_+^0$	(1, $\bar{1}$, 0)(0, 1, $\bar{1}$)(1, 1, 1)	(0, 0, 0)	1
19	6 Pm	(a, b, 0)	(0, 0, 0)	(0, 0, 0)	$a_+^0b_+^0c_0^0$	(0, 1, 0)(0, 0, 1)(1, 0, 0)	(0, 0, 0)	16, 17
20	8 Cm	(a, a, b)	(0, 0, 0)	(0, 0, 0)	$a_+^0a_+^0c_+^0$	(1, 1, 0)($\bar{1}$, 1, 0)(0, 0, 1)	(0, 0, 0)	16, 17, 18*
21	1 $P1$	(a, b, c)	(0, 0, 0)	(0, 0, 0)	$a_+^0b_+^0c_+^0$	(1, 0, 0)(0, 1, 0)(0, 0, 1)	(0, 0, 0)	19, 20
22	38 $Amm2$	(0, 0, a)	(b, 0, 0)	(0, 0, 0)	$a_0^+b_0^0c_+^0$	(1, 0, 0)(0, 2, 0)(0, 0, 2)	(0, 1/2, 0)	2, 16
23	100 $P4bm$	(0, 0, a)	(0, 0, b)	(0, 0, 0)	$a_0^0a_0^0c_+^+$	(1, 1, 0)($\bar{1}$, 1, 0)(0, 0, 1)	(0, 0, 0)	2, 16
24	26 $Pmc2_1$	(a, a, 0)	(0, 0, b)	(0, 0, 0)	$a_+^0a_+^0c_0^+$	(0, 0, 1)(1, $\bar{1}$, 0)(1, 1, 0)	(1/4, −1/4, 0)	2, 17
25	7 Pc	(a, a, b)	(0, 0, c)	(0, 0, 0)	$a_+^0a_+^0c_+^+$	(0, 0, 1)(1, $\bar{1}$, 0)(1, 1, 0)	(1/4, −1/4, 0)	20, 23, 24
26	6 Pm	(a, b, 0)	(0, 0, c)	(0, 0, 0)	$a_+^0b_+^0c_0^+$	($\bar{1}$, 1, 0)(0, 0, 1)(1, 1, 0)	(0, 0, 0)	19, 22, 24
27	8 Cm	(0, a, b)	(0, 0, c)	(0, 0, 0)	$a_0^0b_+^0c_+^+$	(0, 2, 0)(2, 0, 0)(0, 0, $\bar{1}$)	(1/2, 0, 0)	19, 22, 23
28	1 $P1$	(a, b, c)	(0, 0, d)	(0, 0, 0)	$a_+^0b_+^0c_+^+$	(0, 0, 1)(1, 1, 0)($\bar{1}$, 1, 0)	(0, 0, 0)	21, 25, 26, 27
29	146 $R3$	(a, a, a)	(b, b, b)	(0, 0, 0)	$a_+^+a_+^+a_+^+$	(2, 0, $\bar{2}$)($\bar{2}$, 2, 0)(1, 1, 1)	(0, 0, 0)	4, 18
30	107 $I4mm$	(0, 0, a)	(b, b, 0)	(0, 0, 0)	$a_0^+a_0^+c_+^0$	(2, 0, 0)(0, 2, 0)(0, 0, 2)	(−1/2, 1/2, 0)	3, 16
31	42 $Fmm2$	(a, a, 0)	(b, b, 0)	(0, 0, 0)	$a_+^+a_+^+c_0^0$	(0, 0, 2)(2, $\bar{2}$, 0)(2, 2, 0)	(−1/2, 1/2, 1/2)	3, 17
32	8 Cm	(a, a, b)	(c, c, 0)	(0, 0, 0)	$a_+^+a_+^+c_+^+$	(0, 0, 2)(2, $\bar{2}$, 0)(1, 1, 1)	(0, 1, 0)	20, 30, 31
33	44 $Imm2$	(0, 0, a)	(b, c, d)	(0, 0, 0)	$a_0^+b_0^+c_+^+$	(2, 0, 0)(0, 2, 0)(0, 0, 2)	(1/2, 1/2, 0)	5, 22, 23*, 30
34	8 Cm	(0, a, b)	(c, d, e)	(0, 0, 0)	$a_0^+b_+^+c_+^+$	(0, 2, $\bar{2}$)(2, 0, 0)(0, 0, $\bar{2}$)	(1/2, 0, 0)	26, 27, 31, 33
35	1 $P1$	(a, b, c)	(d, e, f)	(0, 0, 0)	$a_+^+b_+^+c_+^+$	(1, 1, 1)(1, 1, $\bar{1}$)($\bar{1}$, 1, 1)	(0, 0, 0)	28, 29*, 32, 34
36	161 $R3c$	(a, a, a)	(0, 0, 0)	(b, b, b)	$a_+^-a_+^-a_+^-$	($\bar{1}$, 1, 0)(0, $\bar{1}$, 1)(2, 2, 2)	(0, 0, 0)	8, 18
37	42 $Fmm2$	(0, 0, a)	(0, 0, 0)	(b, 0, 0)	$a_0^-b_0^0c_+^0$	(2, 0, 0)(0, 2, 0)(0, 0, 2)	(0, 1/2, 0)	6, 16
38	108 $I4cm$	(0, 0, a)	(0, 0, 0)	(0, 0, b)	$a_0^0a_0^0c_+^-$	(1, 1, 0)($\bar{1}$, 1, 0)(0, 0, 2)	(0, 0, 0)	6, 16
39	46 $Ima2$	(a, a, 0)	(0, 0, 0)	(0, 0, b)	$a_+^0a_+^0c_0^-$	(0, 0, 2)(1, $\bar{1}$, 0)(1, 1, 0)	(0, 0, 1/2)	6, 17
40	46 $Ima2$	(0, 0, a)	(0, 0, 0)	(b, b, 0)	$a_0^-a_0^-c_+^0$	(1, 1, 0)($\bar{1}$, 1, 0)(0, 0, 2)	(0, 1/2, 0)	7, 16
41	46 $Ima2$	(a, a, 0)	(0, 0, 0)	(b, b, 0)	$a_+^-a_+^-c_0^0$	(0, 0, 2)(1, $\bar{1}$, 0)(1, 1, 0)	(0, 0, 0)	7, 17
42	44 $Imm2$	(a, $\bar{a}$, 0)	(0, 0, 0)	(b, b, 0)	$a_+^-a_-^-c_0^0$	(1, 1, 0)(0, 0, 2)(1, $\bar{1}$, 0)	(0, 0, 1/2)	7, 17
43	5 $C2$	(a, $\bar{a}$, 0)	(0, 0, 0)	(b, b, c)	$a_+^-a_-^-c_0^-$	(1, $\bar{1}$, 2)(1, $\bar{1}$, 0)(1, 1, 0)	(0, 0, 1/2)	10, 39, 42
44	5 $C2$	(0, 0, a)	(0, 0, 0)	(b, c, 0)	$a_0^-b_0^-c_+^0$	($\bar{2}$, 0, 0)(0, 0, 2)(1, 1, 0)	(1/2, 0, 0)	9, 37, 40
45	8 Cm	(a, b, 0)	(0, 0, 0)	(0, 0, c)	$a_+^0b_+^0c_0^-$	(2, 0, 0)(0, 0, 2)(1, $\bar{1}$, 0)	(0, 0, 0)	19, 37, 39
46	8 Cm	(a, $\bar{a}$, b)	(0, 0, 0)	(c, c, 0)	$a_+^-a_-^-c_+^0$	(1, $\bar{1}$, 2)(1, 1, 0)($\bar{1}$, 1, 0)	(0, 0, 0)	20, 40, 42
47	9 Cc	(a, a, b)	(0, 0, 0)	(c, c, d)	$a_+^-a_+^-c_+^-$	(1, 1, 2)(1, $\bar{1}$, 0)(1, 1, 0)	(1/2, 0, 0)	10, 20, 36*, 38, 39, 40, 41
48	8 Cm	(a, b, 0)	(0, 0, 0)	(c, d, 0)	$a_+^-b_+^-c_0^0$	(2, 0, 0)(0, 0, 2)(1, $\bar{1}$, 0)	(0, 0, 1/2)	9, 19, 37, 38, 41, 42
49	1 $P1$	(a, b, c)	(0, 0, 0)	(d, e, f)	$a_+^-b_+^-c_+^-$	(1, 0, 1)(1, 1, 0)($\bar{1}$, 1, 0)	(0, 0, 0)	11, 21, 43, 44, 45, 46, 47, 48
50	40 $Ama2$	(0, 0, a)	(0, b, 0)	(c, 0, 0)	$a_0^-b_0^+c_+^0$	(0, 2, 0)(2, 0, 0)(0, 0, $\bar{2}$)	(1/2, 0, 0)	12, 22, 37
51	38 $Amm2$	(0, 0, a)	(0, b, 0)	(0, 0, c)	$a_0^0b_0^+c_+^-$	(0, 2, 0)(2, 0, 0)(0, 0, $\bar{2}$)	(1/2, 1/2, 0)	12, 22, 38
52	36 $Cmc2_1$	(0, 0, a)	(0, 0, b)	(0, c, 0)	$a_0^0b_0^-c_+^+$	(2, 0, 0)(0, 2, 0)(0, 0, 2)	(1/2, 1/2, 0)	12, 23, 37
53	9 Cc	(a, b, 0)	(0, c, 0)	(0, 0, d)	$a_+^0b_+^+c_0^-$	(2, 0, 0)(0, 0, 2)(0, $\bar{2}$, 0)	(0, 0, 1/2)	27, 45, 50, 52
54	105 $P4_2mc$	(0, 0, a)	(b, b, 0)	(0, 0, c)	$a_0^-a_0^+c_+^-$	(2, 0, 0)(0, 2, 0)(0, 0, 2)	(1/2, 1/2, 0)	15, 30, 38
55	41 $Aba2$	(a, a, 0)	(b, b, 0)	(0, 0, c)	$a_+^+a_+^+c_0^-$	(0, 0, 2)($\bar{2}$, 2, 0)(2, 2, 0)	(1, 0, 1/2)	15, 31, 39
56	33 $Pna2_1$	(0, 0, a)	(0, 0, b)	(c, c, 0)	$a_0^-a_0^-c_+^+$	(1, 1, 0)($\bar{1}$, 1, 0)(0, 0, 2)	(0, 0, 0)	13, 23, 40
57	26 $Pmc2_1$	(a, a, 0)	(0, 0, b)	(c, c, 0)	$a_+^-a_+^-c_0^+$	(0, 0, 2)(1, $\bar{1}$, 0)(1, 1, 0)	(1/4, −1/4, 1/2)	13, 24, 41

Table 1 (continued)

Ref	Space group	Γ_4^-	M_3^+	R_4^+	System	Lattice vectors	Origin	Supergroups
58	31 $Pmn2_1$	$(\bar{a}, a, 0)$	$(0, 0, b)$	$(c, c, 0)$	$a^-a^-c_0^+$	$(0, 0, 2)(1, 1, 0)(\bar{1}, 1, 0)$	$(1/4, 1/4, 1/2)$	13, 24, 42
59	7 Pc	$(\bar{a}, a, b)$	$(0, 0, c)$	$(d, d, 0)$	$a^-a^-c_+^+$	$(1, \bar{1}, 0)(1, 1, 0)(\bar{1}, 1, 2)$	$(1/4, 1/4, 0)$	25, 46, 56, 58
60	4 $P2_1$	$(0, 0, a)$	$(0, 0, b)$	$(c, d, 0)$	$a_0^-b_0^-c_+^+$	$(\bar{1}, 1, 0)(0, 0, 2)(1, 1, 0)$	$(0, 0, 0)$	14, 44, 52, 56
61	6 Pm	$(a, b, 0)$	$(0, 0, c)$	$(d, e, 0)$	$a_+^-b_+^-c_0^+$	$(\bar{1}, 1, 0)(0, 0, 2)(1, 1, 0)$	$(0, 0, 1/2)$	14, 26, 48, 50, 51, 57, 58

Howard & Stokes (1998).] The first entry in Table 1 is simply the cubic structure of the parent group $Pm\bar{3}m$. Entries 2–15 are structures with tilts but no *B*-cation displacements and are identical to those in Howard & Stokes (1998). Entries 16–21 are structures with *B*-cation displacements but no tilts. The remaining 40 entries are structures with both tilts and *B*-cation displacements.

The last column of Table 1 provides a list of minimal supergroups, which allow tracing of a given structure through successive phase transitions back to the cubic structure. The asterisks indicate phase transitions that are required by Landau theory to be first order. This information was also obtained using *ISOTROPY*.

To ensure the accuracy of Table 1, we wrote a computer program, *TABLE*, that checked the consistency between the order parameters and the symmetry of the subgroups and generated the information about supergroups. *TABLE* also typeset the table directly so that there would be no typographical errors. In addition, *TABLE* drew Fig. 1, which is a subgroup tree for the structures with *B*-cation displacements.

5. Comparison with previous work

We first compared our results for pure tilt systems with Howard & Stokes (1998). We found one difference. In their Fig. 1, a line should be drawn connecting $a^0a^0c^-$ and $a^-b^-b^-$,

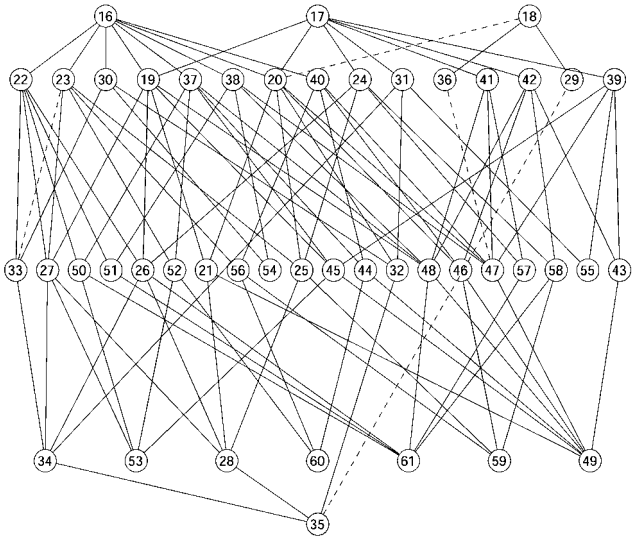

Figure 1
A schematic diagram indicating the group–subgroup relationships among entries 16–61 in Table 1. A dashed line joining a group with its subgroup indicates that the corresponding phase transition is required by Landau theory to be first order.

showing a group–subgroup relationship that they missed (the erratum reports this error). This illustrates how difficult it is to obtain accurate results 'by hand', even for a relatively small number of structures and with the aid of *ISOTROPY*.

We also compared our results with Table II of Aleksandrov & Bartolomé (2001). We found a number of errors in space-group symmetries, for example (their notation followed by our Table 1 entry in parentheses) $p_1p_1p_2/000$ (20), $0p0/00\psi$ (22), $pp0/00\psi$ (24), $p_1p_1p_2/00\psi$ (25), $0p0/00\phi$ (37), $pp0/00\phi$ (39), $00p/\phi\phi0$ (40), $pp0/\phi\phi0$ (41), $pp0/\psi\psi\phi$ (55), $00p/\phi\phi\psi$ (56), $pp0/\phi\phi\psi$ (57).

Their table is also incomplete. There are 15 entries in our Table 1 that do not appear in theirs: entries 11, 21, 27, 28, 35, 42, 43, 46, 47, 48, 49, 53, 58, 59, 61.

Many of the structures in the table of Aleksandrov & Bartolomé (2001) are also redundant from the standpoint of symmetry. For example, the superposition of $\psi\psi0$ and $0p0$ is $a_0^+b_+^+c_0^0$, which is not listed in our Table 1. The symmetry *Imm*2 of this structure also allows tilts to appear about the *z* axis, so the structure is actually $a_0^+b_+^+c_0^+$, the superposition of $\psi_1\psi_2\psi_3$ and $0p0$, which also appears in their table (and is equivalent to entry 33, $a_0^+b_0^+c_+^+$, in our Table 1). We also see in their table that the superposition of $\psi_1\psi_2\psi_3$ and $00p$, $0p0$ and $p00$ results in three identical structures that are simply rotated so that the displacement is along the *z*, *y* and *x* axes, respectively. Their table does not indicate which structures are distinct and which are reorientations of the same structure.

Recently, the $a_+^0a_+^0c_+^-$ structure was observed in $Pb(Ti_{0.48}Zr_{0.52})O_3$ (Ranjan *et al.*, 2002). The space-group symmetry was reported incorrectly as *Pc*. [Aleksandrov & Bartolomé (2001) report this structure as *Cm*, which is also incorrect.] The correct symmetry is *Cc* (Hatch *et al.*, 2002). This symmetry allows additional tilts about the *x* and *y* axes as well, so that the correct structure is actually $a_+^-a_+^-c_+^-$ (entry 47 in our Table 1), which is one of the structures missing from the table of Aleksandrov & Bartolomé (2001). This is an example of how our Table 1 could help prevent errors in the space-group determination of new structures.

6. Summary

We have found by group-theoretical methods the space-group symmetries of all possible structures that can result from simple octahedral tilts in a ferroelectric perovskite. Our results are reliable and comprehensive. We hope that the data presented in Table 1 will be of assistance to those studying perovskite structures and the transformations between them.

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