

Octahedral tilting in cation-ordered perovskites – a group-theoretical analysis

Christopher J. Howard^{a,b*} and
Harold T. Stokes^c^aAustralian Nuclear Science and Technology Organisation, Private Mail Bag 1, Menai, NSW 2234, Australia, ^bSchool of Physics, University of Sydney, NSW 2006, Australia, and ^cDepartment of Physics and Astronomy, Brigham Young University, Provo, Utah 84602-4675, USACorrespondence e-mail: cjh@ansto.gov.au

Group-theoretical methods are used to enumerate the structures of ordered perovskites, in which 1:2 and 1:3 ordering of B and B' cations is considered in combination with the ubiquitous BX_6 (or $B'X_6$) octahedral tilting. The cation ordering on the B -cation site is described by irreducible representations of the $Pm\bar{3}m$ space group of the cubic aristotype: Λ_1 ($\mathbf{k} = 1/3, 1/3, 1/3$) for the cation ordering pattern in the 1:2 compound $A_3BB'_2X_9$ and M_1^+ ($\mathbf{k} = 1/2, 1/2, 0$) for the cation ordering in the 1:3 compound $A_4BB'_3X_{12}$. The octahedral tilting is mediated by the irreducible representations M_3^+ and R_4^+ . Ten distinct structures have been identified in the 1:2 case and 11 structures for 1:3.

Received 10 May 2004
Accepted 11 August 2004

1. Introduction

The ideal perovskite, ABX_3 , which is cubic with space-group symmetry $Pm\bar{3}m$, has been described (Megaw, 1973) as 'probably the simplest example of a structure containing two different cations'. The ideal perovskite is, however, relatively uncommon, most perovskites having lower symmetry owing to distortions. Three different distortions have been identified (Megaw, 1973): distortions of the BX_6 octahedral units, B -cation displacements within these octahedra and the tilting of the BX_6 octahedra relative to one another as corner-linked, practically rigid units. These different kinds of distortion can occur separately or in combination. If we add the possibilities of more than one cation on the A or B sites, and more than one anion on the X site, and of the ordering of these different cations/anions in the pertinent sites, then a bewildering array of different structures can result (Mitchell, 2002).

Of the three types of distortion mentioned above, the most common is that involving octahedral tilting. Octahedral tilting alone can lead to a significant number of different structures, with different space-group symmetries. A lasting contribution to the understanding of these structures was made by Glazer (1972), who developed a description of the different possible patterns of octahedral tilting and then obtained the space groups by inspection. Glazer found 23 different tilt systems, accommodated in 15 different space groups. Glazer also introduced a very convenient symbolic description for the tilt system, now almost universally adopted. The problem of octahedral tilting in simple perovskites has been revisited by a number of authors (Aleksandrov, 1976; Bärnighausen, 1980; Howard & Stokes, 1998, 2002), using more formal group-theoretical methods. Howard and Stokes listed 15 possible space groups for perovskites with octahedral tilting, but considered that only one distinct tilt system would be found in each. The group-subgroup relationships were derived and

displayed, and the corresponding phase transitions were analysed to examine whether they might be continuous.

Howard & Stokes (1998, 2002) carried out group-theoretical analyses with the aid of a computer program, and perhaps the most significant aspect of their work was to demonstrate the power of this approach in enumerating and analysing the structures arising as a result of distortions. The same methods have been used to enumerate the structures arising from ferroelectric patterns of *B*-cation displacement combined with (possible) octahedral tilting (Stokes *et al.*, 2002), and from certain patterns of antiferroelectric *B*-cation displacement combined with octahedral tilting (Howard *et al.*, 2002). The combinations of a rock-salt pattern of *B*-site cation ordering with octahedral tilting in the double perovskites $A_2BB'X_6$ have been considered in detail (Howard *et al.*, 2003). The layered ordering of different cations onto the perovskite *A*-sites has also been considered (Howard & Zhang, 2004), although it will merit further comment in this paper. Howard and co-workers have demonstrated the usefulness of the group-theoretical arguments in the practical determination of difficult perovskite-related structures. Recent determinations of the structures of SrZrO₃ at 1073 K (Howard *et al.*, 2000), Ca_{0.5}Sr_{0.5}TiO₃ at room temperature (Howard *et al.*, 2001), WO₃ at 1033 K (Howard *et al.*, 2002) and La_{0.6}Sr_{0.1}TiO₃ at room temperature (Howard & Zhang, 2003) were all greatly assisted by group theory.

This work is an extension to consider cation ordering beyond the 1:1 rock-salt pattern on the *B* sites that was examined earlier (Howard *et al.*, 2003). We consider 1:2 ordering on the *B* site in $A_3BB'_2X_9$, as occurs for example in Ba₃ZnTa₂O₉ (Galasso & Pyle, 1963) and the 1:3 ordering on the *B* sites in $A_4BB'_3X_{12}$, such as Ba₄LiSb₃O₁₂ (Jacobson *et al.*, 1974).¹ The structures of Ba₃ZnTa₂O₉ and Ba₄LiSb₃O₁₂ are illustrated in Figs. 1 and 2, respectively. We use group-theoretical methods to enumerate the structures arising from these different patterns of *B*-site cation ordering in combination with simple octahedral tilting, but no account is taken of the other distortions that are possible. We find ten distinct structures arising from the 1:2 cation ordering in combination with (possible) octahedral tilting and 11 structures for 1:3 cation ordering. The group-subgroup relationships are derived and displayed. The connection with previous work, both theoretical and experimental, is reviewed. In the course of the work on the 1:3 system, we found it necessary to clarify our arguments on which tilt systems and space groups actually occur. In previous work (Howard & Stokes, 1998, 2002), we argued that only the most general tilt system allowed in a particular space group would ever occur. For example, tilt angles not required to be equal by the space-group symmetry would in fact be different. However, for reasons of kinetics, a cation arrangement of higher symmetry than allowed by the space

group will normally be preserved. This has minor implications for our previous work on perovskites with *A*-site cation ordering (Howard & Zhang, 2004).

2. Group-theoretical analysis

The analysis starts from a consideration of the parent perovskite, ABX_3 , in space group $Pm\bar{3}m$. Cation (or anion) ordering and distortions are all associated with the repre-

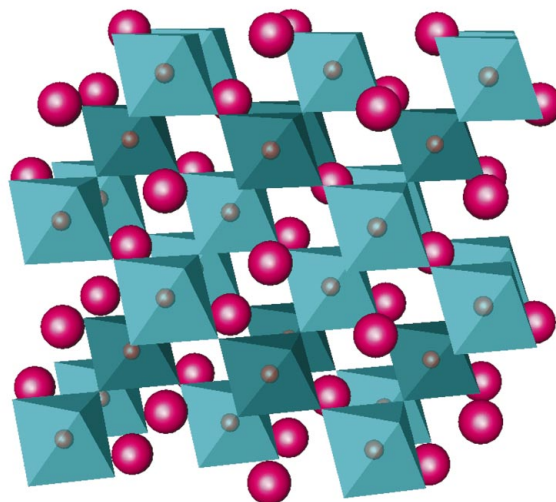


Figure 1

Representation of the structure of Ba₃ZnTa₂O₉. ZnO₆ and TaO₆ are shown as the darker and lighter octahedra, respectively, with the Zn and Ta ions being visible within them. The Ba ions are represented by the spheres seen between these octahedra. The figure was prepared from the coordinates published by Jacobson *et al.* (1976) using the computer program *ATOMS* (Dowty, 1999).

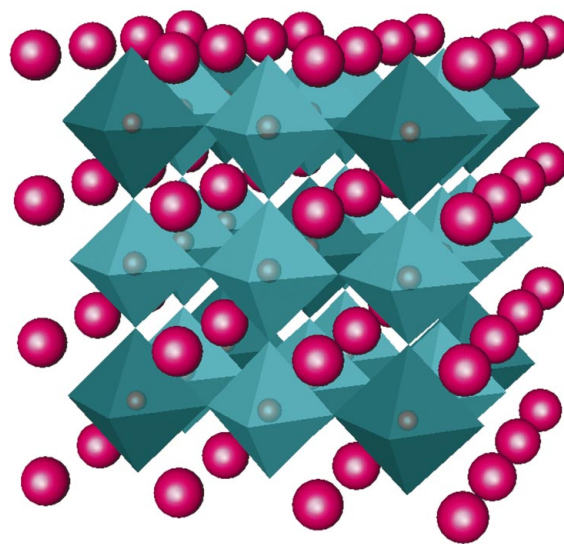


Figure 2

The structure of Ba₄LiSb₃O₁₂ prepared from the published data of Jacobson *et al.* (1974). The darker and lighter octahedra represent units of LiO₆ and SbO₆, respectively.

¹ These perovskites have been classified as 'double perovskites' by some authors (Mitchell, 2002), because they contain two species of cation on the *B* site. Perovskites $A_3BB'_2X_9$ have also been described as 'triple perovskites' (Ting *et al.*, 2004). Other patterns of 1:2 and 1:3 *B*-site cation ordering are possible, but a search of the literature (Mitchell, 2002) suggests they have not been observed.

sentations of the parent space-group symmetry. In this paper we intend to consider the combination of two different patterns of *B*-site cation ordering with BX_6 octahedral tilting. A full analysis of corner-linked tilting, in the absence of any cation ordering, has been presented by Howard & Stokes (1998, 2002). The relevant irreducible representations (irreps) [we use the notation of Miller & Love (1967)] were R_4^+ ($\mathbf{k} = \frac{1}{2}, \frac{1}{2}, \frac{1}{2}$), corresponding to modes with out-of-phase tilting of the octahedra in successive layers, and M_3^+ ($\mathbf{k} = \frac{1}{2}, \frac{1}{2}, 0$), associated with in-phase octahedral tilting. The previous analyses (Howard & Stokes, 1998, 2002) were completed using group-theoretical methods for enumerating the isotropy subgroups of a parent space group (Hatch, 1984; Stokes & Hatch, 1984*a,b*; Hatch & Stokes, 1985, 1986, 1987*a,b*) is implemented in the computer program *ISOTROPY* (www.physics.byu.edu/~stokes/isyropy.html).

It is found in this work, with the help of *ISOTROPY*, that the irreps corresponding to the 1:2 and 1:3 *B*-site ordering patterns of interest are Λ_1 ($\mathbf{k} = \frac{1}{3}, \frac{1}{3}, \frac{1}{3}$) and M_1^+ ($\mathbf{k} = \frac{1}{2}, \frac{1}{2}, 0$), respectively. The computer program *ISOTROPY* was used again to examine the collection of isotropy subgroups associated with irreps Λ_1 , M_3^+ and R_4^+ in the first case, and M_1^+ , M_3^+ and R_4^+ in the second. Compared with the analysis (Howard *et al.*, 2003) of the rock-salt ordering pattern associated with irrep R_1^+ , the present work involves a greater complexity. Whereas R_1^+ was a one-dimensional irrep, defining a single-scalar order parameter, the cation ordering here involves Λ_1 or M_1^+ , which are eight- and three-dimensional irreps, respectively. In our discussion of R_1^+ (Howard *et al.*, 2003), we declared the order parameter to be essentially fixed in the preparation. We shall declare the (respectively eight or three) components of the order parameter to be similarly fixed in the present case. The irreps M_3^+ and R_4^+ associated with octahedral tilting are three-dimensional, and the order parameters are thus three-component vectors. As has been detailed previously (Howard & Stokes, 1998, 2002; Howard *et al.*, 2003), the three components correspond to the magnitudes of the tilts around the three axes of the perovskite parent, these tilts being in-phase for M_3^+ and out-of-phase for R_4^+ . As usual, we consider only 'simple' tilts by removing structures that allow both in-phase and out-of-phase tilting around the same axis.

2.1. Perovskites $A_3BB'_2X_9 - 1:2$ (Λ_1) *B*-site cation ordering

Since the 1:2 *B*-site cation ordering, as occurs in $Ba_3ZnTa_2O_9$ and a number of other compounds (Galasso & Pyle, 1963), is rather more complicated than the ordering we have considered previously (Howard *et al.*, 2003; Howard & Zhang, 2004), the identification of the associated irrep might have been expected to present a challenge. In fact, it was already known that the ordered structure (in the absence of octahedral tilting) is associated with $\mathbf{k} = \frac{1}{3}, \frac{1}{3}, \frac{1}{3}$ or the Λ line (Mitchell, 2002), and that the space-group symmetry of that structure is $P\bar{3}m1$. We find using *ISOTROPY* that for the irreps associated with $\mathbf{k} = \frac{1}{3}, \frac{1}{3}, \frac{1}{3}$, the isotropy subgroup $P\bar{3}m1$ only appears once: irrep Λ_1 with the order parameter

($a, 0, 0, 0, 0, 0, 0$). The same result can be obtained using the related computer program *COPL* (complete order parameter listing; Stokes & Hatch, 2002), which requires as input only the space groups of the parent and subgroup, and the lattice vectors of the latter in terms of those of the former. Noting that the unit cell in $P\bar{3}m1$ has the dimensions $2^{1/2} \times 2^{1/2} \times 3^{1/2}$ (with $\gamma = 120^\circ$) relative to the edge of the parent cell (Jacobson *et al.*, 1976), and assuming initially that there is no origin shift involved, it takes very little time to come up with a combination of lattice vectors such as $(1, 0, \bar{1})$, $(\bar{1}, 1, 0)$, $(1, 1, 1)$ that will yield the same result.

ISOTROPY was used again to list the different possible structures produced by Λ_1 ($\mathbf{k} = \frac{1}{3}, \frac{1}{3}, \frac{1}{3}$) cation ordering followed by M_3^+ and/or R_4^+ octahedral tilting. The lists were long (*e.g.* 64 resulting from Λ_1 followed by M_3^+), but only those structures (four in the case just considered) showing an order parameter for Λ_1 as ($a, 0, 0, 0, 0, 0$) were retained. When both M_3^+ and R_4^+ tilting were invoked, structures showing both positive and negative tilts around the same axis were (as explained above) removed. This left just 10 distinct structures, including that structure with the space-group symmetry $P\bar{3}m1$ formed in the absence of octahedral tilting, and details are given in Table 1. This table shows for each valid structure, along with space groups, origin, lattice vectors *etc.*, the order parameters associated with M_3^+ and R_4^+ , and the Glazer symbol for the tilt system derived from these order parameters. This symbol, of the form $a^\#b^\#c^\#$, is used to indicate no tilt ($\# = 0$), in-phase octahedral tilting ($\# = +$) or out-of-phase octahedral tilting ($\# = -$) around the $\langle 001 \rangle$ axes of the parent $Pm\bar{3}m$ perovskite.

The group-subgroup relationships can be obtained from the order parameters recorded in Table 1. Such relationships would be expected to be useful in connection with any studies of the structural phase transitions that might be undertaken. If the order parameters in one isotropy subgroup span a space of greater dimension than those of another subgroup, and if the order parameters of the former can be obtained from those of the latter by infinitesimal changes, then the former is a subgroup of the latter. The group-subgroup relationships obtained are summarized in Fig. 3. This figure also indicates, by broken lines, the phase transitions between group-subgroup pairs that are required by Landau theory (Landau & Lifshitz, 1980) to be first order.

It may be appropriate to comment on the appearance in Table 1 and Fig. 3 of order parameters with negative components, such as shown for entries at $a^0b^-b^-$ ($A2/m$) and $a^+b^-b^-$ ($P2_1/c$). For R_4^+ octahedral tilting, the order parameters $(0, b, b)$ and $(0, \bar{b}, b)$ correspond to the tilting of the octahedra about axes parallel to the $[011]$ and $[0\bar{1}1]$ directions (of the parent perovskite), respectively. In most cases it would not be necessary to distinguish these possibilities, but here the *B*-site cation ordering, irrep Λ_1 order parameter ($a, 0, 0, 0, 0, 0$) makes the $[111]$ direction unique, and hence the directions $[011]$ and $[0\bar{1}1]$ inequivalent. We have incorporated the distinction into the Glazer symbols written just above. The same distinction must also be considered in determining group-subgroup relationships and is the reason that here $A2/n$ is not a subgroup of $A2/m$.

Table 1

Isotropy subgroups of $Pm\bar{3}m$ for the irrep Λ_1 ($\mathbf{k} = \frac{1}{3}\frac{1}{3}\frac{1}{3}$) in combination with irreps M_3^+ and/or R_4^+ .

For each subgroup, we give the space-group symmetry (and number), with the lattice vectors and origin of the subgroup with respect to the parent cell in $Pm\bar{3}m$, and also the positions of the atoms relative to the new cell. The order parameters associated with the irreps M_3^+ and R_4^+ are shown, along with the tilt system described using the notation of Glazer (1972). The order parameter for irrep Λ_1 is $(a,0,0,0,0,0,0)$ in every case. The lattice vectors and origins are given for the conventional settings of space groups in the *International Tables for Crystallography* (Hahn, 1983). The setting with the unique b axis, cell choice 1, is used for the monoclinic space groups, although the atomic coordinates are given for cell choice 2 in cases, tilt systems $a^0\bar{b}^-b^-$ and $a^-b^-b^-$, where this yields a nearly orthogonal cell.

Space group	M_3^+	R_4^+	Tilts	Lattice vectors	Origin	Atomic positions in $A_3BB_2X_9$ (Wyckoff symbol, coordinates)			
						A	B	B'	X
$P\bar{3}m1$ (#164)	(0,0,0)	(0,0,0)	$a^0a^0a^0$	$(1,0,\bar{1}),(\bar{1},1,0),$ $(1,1,1)$	(0,0,0)	$1(b), 0,0,\frac{1}{2}$ $2(d), 1/3,2/3,z$ $z \simeq 5/6$	$1(a), 0,0,0$	$2(d), 1/3,2/3,z$ $z \simeq 1/3$	$3(f), 1/2,0,1/2$ $6(i), x, \bar{x},z$ $x,z \simeq 1/6,1/6$
$P2_1/c$ (#14)	(0,0, b)	(0,0,0)	$a^0a^0c^+$	$(1,1,\bar{1}),(\bar{1},1,0),$ $(\bar{1},1,2)$	(0,0,0)	$2(b), 1/2,0,0$ $4(e), x,y,$ $z \simeq 1/6,1/2,1/6$	$(a), 0,0,0$	$4(e), x,y,$ $z \simeq 2/3,1/2,1/6$	$2(d), 1/2,0,1/2$ $4(e), x,y,$ $z \simeq 1/6,0,1/6$ $4(e), x,y,$ $z \simeq 1/6,1/4,11/12$ $4(e), x,y,$ $z \simeq 1/6,3/4,11/12$ $4(e), x,y,$ $z \simeq 1/2,3/4,1/4$
$C2/m$ (#12)	(0, b , b)	(0,0,0)	$a^0b^+b^+$	$(4,\bar{2},\bar{2}), (0,2,\bar{2}),$ $(1,1,1)$	$(\bar{1},0,1)$	$2(c), 0,0,1/2$ $2(d), 0,1/2,1/2$ $4(f), 1/4,1/4,1/2$ $4(i), x,0,z$ $x,z \simeq 2/3,5/6$ $4(i), x,0,z$ $x,z \simeq 1/6,5/6$ $8(j), x,y,$ $z \simeq 11/12,3/4,5/6$	$2(a), 0,0,0$ $4(i), x,0,z$ $x,z \simeq 1/6,1/3$ $8(j), x,y,$ $z \simeq 11/12,3/4,1/3$	$4(i), x,0,z$ $x,z \simeq 2/3,1/3$ $2(b), 0,1/2,0$ $4(e), 1/4,1/4,0$	$4(h), 0,y,1/2$ $y \simeq 3/4$ $4(i), x,0,z$ $x,z \simeq 1/12,1/6$ $4(i), x,0,z$ $x,z \simeq 7/12,1/6$ $4(i), x,0,z$ $x,z \simeq 3/4,1/2$ $8(j), x,y,$ $z \simeq 5/6,3/4,1/6$ $8(j), x,y,$ $z \simeq 1/8,3/8,1/2$ $8(j), x,y,$ $z \simeq 3/8,3/8,1/2$ $8(j), x,y,$ $z \simeq 5/24,3/8,1/6$ $8(j), x,y,$ $z \simeq 17/24,5/8,1/6$ $8(j), x,y,$ $z \simeq 23/24,3/8,1/6$ $8(j), x,y,$ $z \simeq 23/24,7/8,1/6$
$P\bar{3}$ (#147)	(b,b,b)	(0,0,0)	$a^+a^+a^+$	$(2,0,\bar{2}),(\bar{2},2,0),$ $(1,1,1)$	(0,0,0)	$1(b), 0,0,1/2$ $3(f), 1/2,0,1/2$ $2(d), 1/3,2/3,z$ $z \simeq 1/6$ $6(g), x,y,$ $z \simeq 1/6,1/3,5/6$	$1(a), 0,0,0$ $3(e), 1/2,0,0$	$2(d), 1/3,2/3,z$ $z \simeq 2/3$ $6(g), x,y,$ $z \simeq 1/6,1/3,1/3$	$6(g), x,y,$ $z \simeq 1/12,11/12,1/6$ $6(g), x,y,$ $z \simeq 1/12,5/12,1/6$ $6(g), x,y,$ $z \simeq 1/12,2/3,1/6$ $6(g), x,y,$ $z \simeq 5/6,5/12,1/6$ $6(g), x,y,$ $z \simeq 1/4,1/4,1/2$ $6(g), x,y,$ $z \simeq 1/4,1/2,1/2$
$P\bar{1}$ (#2)	(b,c,d)	(0,0,0)	$a^+b^+c^+$	$(2,0,\bar{2}),(\bar{2},2,0),$ $(1,1,1)$	(0,0,0)	$1(b), 0,0,1/2$ $1(f), 1/2,0,1/2$ $1(g), 0,1/2,1/2$ $1(h), 1/2,1/2,1/2$ $2(i), x,y,$ $z \simeq 1/6,1/3,5/6$ $2(i), x,y,$ $z \simeq 1/6,5/6,5/6$ $2(i), x,y,$ $z \simeq 1/3,1/6,1/6$	$1(a), 0,0,0$ $1(c), 0,1/2,0$ $1(d), 1/2,0,0$ $1(e), 1/2,1/2,0$	$2(i), x,y,$ $z \simeq 1/6,1/3,1/3$ $2(i), x,y,$ $z \simeq 1/6,5/6,1/3$ $2(i), x,y,$ $z \simeq 1/3,1/6,2/3$ $2(i), x,y,$ $z \simeq 1/3,2/3,2/3$	$2(i), x,y,$ $z \simeq 1/12,11/12,1/6$ $2(i), x,y,$ $z \simeq 5/6,11/12,1/6$ $2(i), x,y,$ $z \simeq 1/12,1/6,1/6$ $2(i), x,y,$ $z \simeq 1/12,5/12,1/6$ $2(i), x,y,$ $z \simeq 5/6,5/12,1/6$ $2(i), x,y,$ $z \simeq 1/12,2/3,1/6$ $2(i), x,y,$ $z \simeq 1/4,1/4,1/2$

Table 1 (continued)

Space group	M_3^+	R_4^+	Tilts	Lattice vectors	Origin	Atomic positions in $A_3BB_2X_9$ (Wyckoff symbol, coordinates)			
						<i>A</i>	<i>B</i>	<i>B'</i>	<i>X</i>
						2(<i>i</i>), <i>x,y</i> , $z \simeq 1/3, 2/3, 1/6$			2(<i>i</i>), <i>x,y</i> , $z \simeq 0, 1/4, 1/2$ 2(<i>i</i>), <i>x,y</i> , $z \simeq 1/4, 1/2, 1/2$ 2(<i>i</i>), <i>x,y</i> , $z \simeq 1/4, 3/4, 1/2$ 2(<i>i</i>), <i>x,y</i> , $z \simeq 1/4, 0, 1/2$ 2(<i>i</i>), <i>x,y</i> , $z \simeq 5/12, 1/12, 5/6$ 2(<i>i</i>), <i>x,y</i> , $z \simeq 5/12, 1/3, 5/6$ 2(<i>i</i>), <i>x,y</i> , $z \simeq 5/12, 7/12, 5/6$ 2(<i>i</i>), <i>x,y</i> , $z \simeq 5/12, 5/6, 5/6$ 2(<i>i</i>), <i>x,y</i> , $z \simeq 1/3, 11/12, 1/6$ 2(<i>i</i>), <i>x,y</i> , $z \simeq 1/3, 5/12, 1/6$ 2(<i>i</i>), <i>x,y</i> , $z \simeq 1/2, 1/4, 1/2$
$P\bar{3}c1$ (#165)	(0,0,0)	(<i>b,b,b</i>)	$a^-a^-a^-$	(1,0, $\bar{1}$),($\bar{1}$,1,0), (2,2,2)	(0,0,0)	2(<i>a</i>), 0,0,1/4 4(<i>d</i>), 1/3,2/3, z $z \simeq 5/12$	2(<i>b</i>), 0,0,0	4(<i>d</i>), 1/3,2/3, z $z \simeq 1/6$	6(<i>f</i>), <i>x,0,1/4</i> $x \simeq 1/2$ 12(<i>g</i>), <i>x,y</i> , $z \simeq 1/6, 5/6, 1/12$
$C2/m$ (#12)	(0,0,0)	(0, \bar{b} , <i>b</i>)	$a^0\bar{b}^-b^-$	(2, $\bar{1}$, $\bar{1}$), (0,1, $\bar{1}$), (4,1,1)	(0,0,0)				
$A2/m$ (#12)			$a^0\bar{b}^-b^-$	(2,2,2), (0,1, $\bar{1}$), (2,1,1)	(0,0,0)	4(<i>i</i>), <i>x,0,z</i> $x,z \simeq 1/4, 0$ 4(<i>i</i>), <i>x,0,z</i> $x,z \simeq 1/12, 1/3$ 4(<i>i</i>), <i>x,0,z</i> $x,z \simeq 7/12, 1/3$	2(<i>a</i>), 0,0,0 2(<i>d</i>), 1/2,0,0	4(<i>i</i>), <i>x,0,z</i> $x,z \simeq 1/3, 1/3$ 4(<i>i</i>), <i>x,0,z</i> $x,z \simeq 5/6, 1/3$	4(<i>i</i>), <i>x,0,z</i> $x,z \simeq 3/4, 1/2$ 4(<i>i</i>), <i>x,0,z</i> $x,z \simeq 1/12, 5/6$ 4(<i>i</i>), <i>x,0,z</i> $x,z \simeq 7/12, 5/6$ 8(<i>j</i>), <i>x,y</i> , $z \simeq 1/4, 1/4, 1/4$ 8(<i>j</i>), <i>x,y</i> , $z \simeq 1/12, 1/4, 1/12$ 8(<i>j</i>), <i>x,y</i> , $z \simeq 7/12, 1/4, 7/12$
$C2/c$ (#15)	(0,0,0)	(<i>b,c,c</i>)	$a^-b^-b^-$	(2, $\bar{1}$, $\bar{1}$), (0,1, $\bar{1}$), (4,1,1)	($\frac{1}{2}$, 0, $\frac{1}{2}$)				
$A2/n$ (#15)			$a^-b^-b^-$	(2,2,2), (0,1, $\bar{1}$), (2,1,1)	($\frac{1}{2}$, 0, $\frac{1}{2}$)	4(<i>e</i>), 3/4, <i>y</i> ,3/4 $y \simeq 1/4$ 8(<i>f</i>), <i>x,y</i> , $z \simeq 1/12, 1/4, 1/12$	4(<i>d</i>), 0,1/4,3/4	8(<i>f</i>), <i>x,y</i> , $z \simeq 5/6, 1/4, 1/12$	4(<i>e</i>), 3/4, <i>y</i> ,3/4 $y \simeq 3/4$ 8(<i>f</i>), <i>x,y</i> , $z \simeq 3/4, 1/2, 0$ 8(<i>f</i>), <i>x,y</i> , $z \simeq 1/12, 3/4, 1/12$ 8(<i>f</i>), <i>x,y</i> , $z \simeq 1/12, 1/2, 1/3$ 8(<i>f</i>), <i>x,y</i> , $z \simeq 1/12, 1/2, 5/6$
$P\bar{1}$ (#2)	(0,0,0)	(<i>b,c,d</i>)	$a^-b^-c^-$	(3,2,1), (0,1, $\bar{1}$), ($\bar{1}$,1,0)	(0,0,0)	2(<i>i</i>), <i>x,y</i> , $z \simeq 1/4, 3/4, 1/4$ 2(<i>i</i>), <i>x,y</i> , $z \simeq 5/12, 11/12, 3/4$ 2(<i>i</i>), <i>x,y</i> , $z \simeq 11/12, 5/12, 1/4$	1(<i>h</i>), 0,0,0 1(<i>h</i>), 1/2,1/2,1/2	2(<i>i</i>), <i>x,y</i> , $z \simeq 1/3, 1/3, 0$ 2(<i>i</i>), <i>x,y</i> , $z \simeq 1/6, 1/6, 1/2$	2(<i>i</i>), <i>x,y</i> , $z \simeq 1/4, 1/4, 1/4$ 2(<i>i</i>), <i>x,y</i> , $z \simeq 1/4, 1/4, 3/4$ 2(<i>i</i>), <i>x,y</i> , $z \simeq 1/4, 3/4, 3/4$ 2(<i>i</i>), <i>x,y</i> , $z \simeq 1/12, 1/12, 1/4$ 2(<i>i</i>), <i>x,y</i> , $z \simeq 5/12, 5/12, 1/4$ 2(<i>i</i>), <i>x,y</i> , $z \simeq 1/12, 7/12, 1/4$ 2(<i>i</i>), <i>x,y</i> , $z \simeq 5/12, 11/12, 1/4$ 2(<i>i</i>), <i>x,y</i> , $z \simeq 1/12, 1/12, 3/4$ 2(<i>i</i>), <i>x,y</i> , $z \simeq 5/12, 5/12, 3/4$

Table 1 (continued)

Space group	M_3^+	R_4^+	Tilts	Lattice vectors	Origin	Atomic positions in $A_3BB_2X_9$ (Wyckoff symbol, coordinates)			
						A	B	B'	X
$P2_1/c$ (#14)	$(b,0,0)$	$(0,c,\bar{c})$	$a^+b^-\bar{b}^-$	$(2,2,2), (0,1,\bar{1}), (\bar{2},1,1)$	$(0,0,0)$	$4(e), x,y,$ $z \simeq 1/4,0,0$ $4(e), x,y,$ $z \simeq 1/12,0,1/3$ $4(e), x,y,$ $z \simeq 7/12,0,1/3$	$2(a), 0,0,0$ $2(b), 1/2,0,0$	$4(e), x,y,$ $z \simeq 1/3,0,1/3$ $4(e), x,y,$ $z \simeq 5/6,0,1/3$ $4(e), x,y,$ $z \simeq 7/12,0,5/6$ $4(e), x,y,$ $z \simeq 1/4,1/4,1/4$ $4(e), x,y,$ $z \simeq 1/4,3/4,1/4$ $4(e), x,y,$ $z \simeq 1/12,1/4,1/12$ $4(e), x,y,$ $z \simeq 1/12,3/4,1/12$ $4(e), x,y,$ $z \simeq 7/12,1/4,1/12$ $4(e), x,y,$ $z \simeq 7/12,3/4,1/12$	$4(e), x,y,$ $z \simeq 3/4,0,1/2$ $4(e), x,y,$ $z \simeq 1/12,0,5/6$ $4(e), x,y,$ $z \simeq 7/12,0,5/6$ $4(e), x,y,$ $z \simeq 1/4,1/4,1/4$ $4(e), x,y,$ $z \simeq 1/4,3/4,1/4$ $4(e), x,y,$ $z \simeq 1/12,1/4,1/12$ $4(e), x,y,$ $z \simeq 1/12,3/4,1/12$ $4(e), x,y,$ $z \simeq 7/12,1/4,1/12$ $4(e), x,y,$ $z \simeq 7/12,3/4,1/12$

2.2. Perovskites $A_4BB'_3X_{12} - 1:3 (M_1^+)$ B-site cation ordering

The irrep associated with the 1:3 B-site cation ordering as occurs in $Ba_4LiSb_3O_{12}$ (cubic, in space group $Im\bar{3}m$ on a $2 \times 2 \times 2$ cell) was identified using methods similar to those described in the previous section. The irrep is M_1^+ ($\mathbf{k} = \frac{1}{2}, \frac{1}{2}, 0$) and the order parameter is (a,a,a) . The computer program *COPL* rapidly yielded the same result.

ISOTROPY was used in this case to list the different possible structures produced by M_1^+ ($\mathbf{k} = \frac{1}{2}, \frac{1}{2}, 0$) cation ordering followed by M_3^+ and/or R_4^+ octahedral tilting. There were very few structures with the M_1^+ order parameter (a,a,a) , but we also retained certain structures showing B-cation ordering of lower symmetry. The argument here is that these structures

would allow for a less symmetric cation arrangement, but because cation rearrangement is dependent on diffusive processes that are very slow except at high temperatures, the higher-symmetry arrangement would normally be retained. For a given tilt system, however, when assuming the retention of the high-symmetry cation arrangement, only the highest symmetry structure need be retained.² Consider, as a specific example, the entry in Table 2 for tilt system $a^0a^0c^+$. The space-group symmetry is $I4/m$. The order parameter for M_1^+ is (a,a,b) . The distortion caused by the tilts has lowered the space-group symmetry from $Im\bar{3}m$ to $I4/m$, which permits a cation ordering that is more general than the 3:1 ordering we have been considering. Note that we obtain $I4/m$ for $a^0a^0c^+$ even if the M_1^+ order parameter is constrained to remain at (a,a,a) . The *ISOTROPY* output shows another entry for the tilt system $a^0a^0c^+$, where the order parameter for M_1^+ is (a,b,c) and the space-group symmetry is $C2/m$, a subgroup of $I4/m$. We do not include this entry in Table 2 since the lowering of the symmetry to $C2/m$ is caused by a change in cation ordering and not by octahedral tilts. The situation for cation ordering contrasts with that for tilts in that, as we have argued previously (Howard & Stokes, 1998, 2002), the lowest-symmetry tilt system consistent with a particular space-group symmetry is the one that will occur. Retaining the structures in different tilt systems as just explained, but removing as usual those showing both positive and negative tilts around the same axis, leads to 11 distinct structures, including that with space group $Im\bar{3}m$ arising from the B-site cation ordering alone. The details of these structures are given in Table 2, which in this case includes the order parameter for the cation ordering irrep M_1^+ . The corresponding group-subgroup relationships are summarized in Fig. 4.

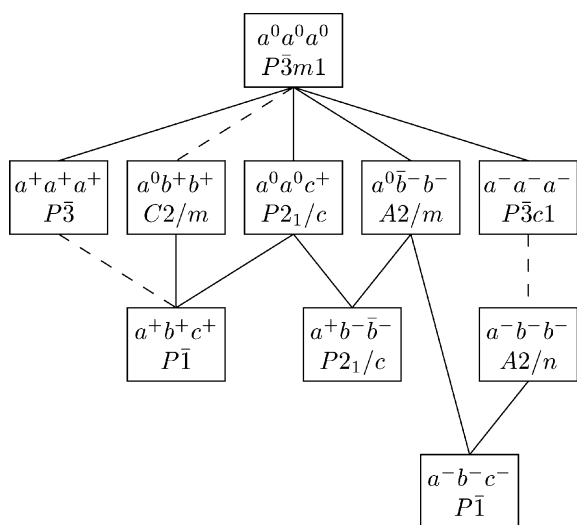


Figure 3 A schematic diagram showing the group-subgroup relationships among the 10 space groups appearing in Table 1. A dashed line joining a group to its subgroup indicates that the corresponding phase transition is required by Landau theory to be first order.

² The same considerations have been applied in §2.1, but in retaining only the highest symmetry structures for every tilt system, only those structures with cation arrangements at the full symmetry, order parameter $(a,0,0,0,0,0,0)$, appear.

Table 2

Isotropy subgroups of $Pm\bar{3}m$ for the irrep M_1^+ in combination with irreps M_3^+ and/or R_4^+ .

The entries in this table include the order parameter associated with the cation ordering, irrep M_1^+ , since the space-group symmetries associated with certain of the tilt systems permit, but do not require, a B -site cation distribution of lower symmetry than is considered in this work. For tilt systems $a^+b^+c^+$ (in $P\bar{1}$) and $a^+b^-c^-$ (in $P2_1/c$) we show atomic coordinates in settings corresponding to nearly orthogonal cells.

Space group	M_1^+	M_3^+	R_4^+	Tilts	Lattice vectors	Origin	Atomic positions in $A_4BB_3X_{12}$ (Wyckoff symbol, coordinates)			
							A	B	B'	X
$Im\bar{3}m$ (#229)	(a,a,a)	$(0,0,0)$	$(0,0,0)$	$a^0a^0a^0$	$(2,0,0),(0,2,0),$ $(0,0,2)$	$(0,0,0)$	$8(c), 1/4,1/4,1/4$	$2(a), 0,0,0$	$6(b), 0,1/2,1/2$	$12(d), 1/4,0,1/2$
$I4/m$ (#87)	(a,a,b)	$(0,0,c)$	$(0,0,0)$	$a^0a^0c^+$	$(2,0,0),(0,2,0),$ $(0,0,2)$	$(0,0,0)$	$8(f), 1/4,1/4,1/4$	$2(a), 0,0,0$	$2(b), 0,0,1/2$ $4(c), 0,1/2,0$	$12e, x,0,0 \ x \simeq 1/4$ $4(d), 0,1/2,1/4$ $4(e), 0,0,z$ $z \simeq 1/4$ $8(h), x,y,0 \ x,$ $y \simeq 1/4,0$ $8(h), x,y,0$ $x,y \simeq 1/2,1/4$
$R\bar{3}$ (#148)	(a,a,a)	(b,b,b)	$(0,0,0)$	$a^+a^+a^+$	$(2,0,\bar{2}),(\bar{2},2,0),$ $(1,1,1)$	$(0,0,0)$	$3(b), 0,0,1/2$ $9(d), 1/2,0,1/2$	$3(a), 0,0,0$	$9(e), 1/2,0,0$	$18(f), x,y,$ $z \simeq 1/12,11/12,1/6$ $18(f), x,y,$ $z \simeq 3/4,3/4,1/2$
$C2/m$ (#12)	(b,a,a)	$(0,c,c)$	$(0,0,0)$	$a^0b^+b^+$	$(2,0,0),(0,2,2),$ $(\bar{1},\bar{1},1)$	$(0,0,0)$	$2(c), 0,0,1/2$	$2(a), 0,0,0$ $2(d), 0,1/2,1/2$ $4(e), 1/4,1/4,0$	$2(b), 0,1/2,0$	$4(h), 0,y,1/2$ $y \simeq 1/4$ $4(i), x,0,z$ $x,z \simeq 1/4,0$ $8(j), x,y,$ $z \simeq 1/8,1/8,1/4$ $8(j), x,y,$ $z \simeq 1/8,5/8,1/4$
$P\bar{1}$ (#2)	(a,b,c)	(d,e,f)	$(0,0,0)$	$a^+b^+c^+$	$(\bar{1},1,1),(\bar{1},\bar{1},1),$ $(1,1,1)$	$(0,0,0)$				
$\bar{1}$ (#2)				$a^+b^+c^+$	$(2,0,0),(0,2,0),$ $(0,0,2)$	$(0,0,0)$	$2(b), 1/4,1/4,3/4$	$2(a), 0,0,0$ $2(c), 1/4,3/4,1/4$ $2(d), 3/4,1/4,1/4$ $2(h), 1/4,1/4,1/4$	$2(e), 0,0,1/2$	$4(i), x,y,$ $z \simeq 1/4,0,0$ $4(i), x,y,$ $z \simeq 0,1/4,0$ $4(i), x,y,$ $z \simeq 0,0,1/4$ $4(i), x,y,$ $z \simeq 1/4,1/2,0$ $4(i), x,y,$ $z \simeq 0,1/4,1/2$ $4(i), x,y,$ $z \simeq 0,1/2,1/4$
$R\bar{3}c$ (#167)	(a,a,a)	$(0,0,0)$	(b,b,b)	$a^-a^-a^-$	$(2,\bar{2},0),(0,2,\bar{2}),$ $(2,2,2)$	$(0,0,0)$	$6(a), 0,0,1/4$ $18(e), x,0,1/4$ $x \simeq 1/2$	$6(b), 0,0,0$	$18(d), 1/2,0,0$	$18(e), x,0,1/4$ $x \simeq 3/4$ $36(f), x,y,$ $z \simeq 1/6,1/12,1/12$
$P4/mnc$ (#128)	(a,a,b)	$(0,0,0)$	$(0,0,c)$	$a^0a^0c^-$	$(2,0,0),(0,2,0),$ $(0,0,2)$	$(0,0,0)$	$8(g), x,x + 1/2,$ $1/4 \ x \simeq 1/4$	$2(a), 0,0,0$	$2(b), 0,0,1/2$ $4(c), 0,1/2,0$	$4(d), 0,1/2,1/4$ $4(e), 0,0,$ $z \simeq 1/4$ $8(h), x,y,0 \ x,$ $y \simeq 1/4,0$ $8(h), x,y,0$ $x,y \simeq 1/4,1/2$
$Cmca$ (#64)	(b,a,a)	$(0,0,0)$	$(0,c,c)$	$a^0b^-b^-$	$(0,2,2),(0,\bar{2},2),$ $(2,0,0)$	$(0,0,0)$	$8(e), 1/4,y,1/4$ $y \simeq 0$ $8(f), 0,y,z \ y,$ $z \simeq 3/4,1/4$	$4(a), 0,0,0$	$4(b), 1/2,0,0$ $8(c), 1/4,1/4,0$	$8(e), 1/4,y,1/4$ $y \simeq 1/4$ $8(f), 0,y,z \ y,$ $z \simeq 0,1/4$ $16(g), x,y,$ $z \simeq 1/8,1/8,0$ $16(g), x,y,$ $z \simeq 1/8,1/8,1/2$
$C2/c$ (#15)	(b,a,a)	$(0,0,0)$	(c,d,d)	$a^-b^-b^-$	$(0,2,2),(0,\bar{2},2),$ $(2,0,0)$	$(0,1,0)$	$4(e), 0,y,1/4$ $y \simeq 1/4$ $4(e), 0,y,1/4$ $y \simeq 3/4$ $8(f), x,y,$ $z \simeq 1/4,1/2,1/4$	$4(c), 1/4,1/4,0$	$4(a), 0,0,0$ $4(b), 0,1/2,0$	$4(e), 0,y,1/4$ $y \simeq 0$ $4(e), 0,y,1/4$ $y \simeq 1/2$ $4(d), 1/4,1/4,1/2$ $8(f), x,y,$ $z \simeq 3/4,1/4,1/4$

Table 2 (continued)

Space group	M_1^+	M_3^+	R_4^+	Tilts	Lattice vectors	Origin	Atomic positions in $A_4BB_3X_{12}$ (Wyckoff symbol, coordinates)			
							A	B	B'	X
$P\bar{1}(\#2)$	(<i>a,b,c</i>)	(0,0,0)	(<i>d,e,f</i>)	$a^-b^-c^-$	(2,0,0),(0,2,0), (0,0,2)	(0,0,0)	2(<i>i</i>), <i>x,y</i> , $z \simeq 1/4,1/4,1/4$	1(<i>a</i>), 0,0,0 1(<i>h</i>), 1/2,1/2,1/2	1(<i>b</i>), 0,0,1/2	8(<i>f</i>), <i>x,y</i> , $z \simeq 1/8,1/8,0$ 8(<i>f</i>), <i>x,y</i> , $z \simeq 1/8,3/8,0$ 8(<i>f</i>), <i>x,y</i> , $z \simeq 7/8,1/8,0$ 8(<i>f</i>), <i>x,y</i> , $z \simeq 7/8,3/8,0$
							2(<i>i</i>), <i>x,y</i> , $z \simeq 1/4,1/4,3/4$		1(<i>c</i>), 0,1/2,0	2(<i>i</i>), <i>x,y</i> , $z \simeq 0,1/4,0$
							2(<i>i</i>), <i>x,y</i> , $z \simeq 1/4,3/4,1/4$		1(<i>d</i>), 1/2,0,0	2(<i>i</i>), <i>x,y</i> , $z \simeq 0,0,1/4$
							2(<i>i</i>), <i>x,y</i> , $z \simeq 1/4,3/4,3/4$		1(<i>e</i>), 1/2,1/2,0	2(<i>i</i>), <i>x,y</i> , $z \simeq 1/4,0,1/2$
									1(<i>f</i>), 1/2,0,1/2	2(<i>i</i>), <i>x,y</i> , $z \simeq 1/2,0,1/4$
									1(<i>g</i>), 0,1/2,1/2	2(<i>i</i>), <i>x,y</i> , $z \simeq 1/2,1/4,0$
										2(<i>i</i>), <i>x,y</i> , $z \simeq 1/4,1/2,0$
										2(<i>i</i>), <i>x,y</i> , $z \simeq 0,1/4,1/2$
										2(<i>i</i>), <i>x,y</i> , $z \simeq 0,1/2,1/4$
										2(<i>i</i>), <i>x,y</i> , $z \simeq 1/4,1/2,1/2$
										2(<i>i</i>), <i>x,y</i> , $z \simeq 1/2,1/4,1/2$
										2(<i>i</i>), <i>x,y</i> , $z \simeq 1/2,1/2,1/4$
$P2_1/c$ (#14)	(<i>a,b,c</i>)	(<i>d</i> ,0,0)	(0, <i>e</i> , <i>f</i>)	$a^+b^-c^-$	(0,2,0),($\bar{2}$,0,0), (0,2,2)	(0,0,0)				
$P2_1/n$ (#14)	(<i>a,b,c</i>)	(0, <i>d</i> ,0)	(<i>e</i> ,0, <i>f</i>)	$a^-b^+c^-$	(2,0,0),(0,2,0), (0,0,2)	(0,0,0)	4(<i>e</i>), <i>x,y</i> , $z \simeq 1/4,1/4,1/4$	2(<i>a</i>), 0,0,0	2(<i>b</i>), 0,0,1/2	4(<i>e</i>), <i>x,y</i> , $z \simeq 1/4,0,0$
							4(<i>e</i>), <i>x,y</i> , $z \simeq 1/4,1/4,3/4$		2(<i>c</i>), 1/2,0,1/2	4(<i>e</i>), <i>x,y</i> , $z \simeq 0,1/4,0$
									2(<i>d</i>), 1/2,0,0	4(<i>e</i>), <i>x,y</i> , $z \simeq 0,0,1/4$
										4(<i>e</i>), <i>x,y</i> , $z \simeq 1/4,1/2,0$
										4(<i>e</i>), <i>x,y</i> , $z \simeq 0,1/4,1/2$
										4(<i>e</i>), <i>x,y</i> , $z \simeq 0,1/2,1/4$

3. Discussion

We first compare the results obtained here with those presented in similar analyses of the same system. The (limited) experimental data are briefly reviewed, as are the prospects for practical identification of the different structures presented here.

3.1. Previous analyses

Nagai *et al.* (1997) have attempted to enumerate the structures arising from the 1:2 *B*-site cation ordering (irrep Λ_1) in combination with the tilting of the corner-linked $B(B')X_6$ octahedra. These authors examined the symmetry operations of the parent perovskite remaining after both the 1:2 *B*-site cation ordering and the introduction of octahedral tilting, and determined the space group from the list of these

remaining symmetry operations. The detailed argument was given in two example cases. For the tilt system $a^0a^0c^+$ their result is just as given in our Table 1.³ For the tilt system $a^0a^0c^-$, they find a structure in the space group $C2/c$, on just the same cell (after allowing for their different setting) as our structure for the tilt system $a^-b^-b^-$. We conclude that they have correctly identified the structure and symmetry of a 1:2 perovskite with $a^0a^0c^-$ tilts, but this tilt system does not appear on our list (Table 1) because the symmetry can and will support tilts about the other axes, leading to $a^-a^-c^-$ (previously written as $a^-b^-b^-$). Regarding the tilt systems appearing in our Table 1, we obtain results in agreement with Nagai *et al.* (1997), except for the tilt systems $a^0b^-b^-$ (we

³ Note, however, that these authors describe their monoclinic structures in settings with the *c* axis unique.

obtain $C2/m$ rather than $C2/c$) and the above-mentioned $a^-b^-b^-$ (we have $C2/c$ not $P2/c$). Nagai *et al.* (1997) also list structures for a number of tilt systems (e.g. $a^0a^0c^-$ as explained above, $a^0b^+c^+$, $a^+a^+a^-$) which we argue could not in practice occur.

There has been no systematic consideration of the structures that might arise from octahedral tilting in the 1:3 B -site ordered perovskites. Indeed to date only one compound, $Sr_4NaSb_3O_{12}$, has been reported to show both 1:3 ordering and octahedral tilting. Alonso *et al.* (1990) used X-ray diffraction to establish the cation-ordering pattern, but concluded from the neutron pattern that the tilt system might be as in $GdFeO_3$, namely $a^-a^-c^+$. Introducing the 1:3 B -site cation ordering into the $GdFeO_3$ structure, they concluded that the structure would have space-group symmetry $P2_1/n$ on a $2 \times 2 \times 2$ cell. We find their structure to be correct (see entry in Table 2⁴), apart from the fact that the space-group symmetry can and will support the tilt system $a^-b^-c^+$.

3.2. Experimental situation

In their early studies Galasso & Pyle (1963) were able to prepare a considerable number of barium and strontium tantalates ($A = Ba$; $B = Mg, Ni, Co, Zn, Mn, Ca, Sr$; $B' = Ta$; $X = O$; $A = Sr$; $B = Mg, Ni, Co, Zn, Ca$; $B' = Ta$; $X = O$) showing 1:2 B -site cation ordering. Subsequently, the same ordering was reported in a number of barium, strontium and calcium niobates ($A = Ba$; $B = Mg, Ni, Co, Zn, Ca$; $B' = Nb$; $X = O$; $A = Sr$; $B = Mg, Ni, Co$; $B' = Nb$; $X = O$; $A = Ca$; $B = Mg, Co, Ca$; $B' = Nb$; $X = O$), as well as in their A -site substituted variants, and in the bismuthate $Ba_3TeBi_2O_9$. We note that it should be relatively easy to identify the 1:2 ordering from X-ray diffraction patterns, provided only that the B and B' cations give a reasonable contrast in scattering. The ordering will generate what we will term Λ -point reflections that index on the cell of the parent perovskite as $h \pm 1/3 k \pm 1/3 l \pm 1/3$.

The occurrence of octahedral tilting in perovskites with 1:2 B -site cation ordering has been recognized by Reaney and co-workers (Reaney *et al.*, 1994), and by Nagai *et al.* (1997). In-phase (M -point) octahedral tilting gives rise to superlattice reflections with one integral, two half-integral indices and out-of-phase (R -point) tilting gives reflections with all indices half-integral when referred to the parent perovskite cell. It is an experimental advantage that these do not coincide with the Λ -point reflections associated with cation ordering, but the relatively weak scattering from oxygen means that in X-ray diffraction patterns these additional reflections are expected to be weak. Reaney *et al.* employed electron diffraction in the study of octahedral tilting and found a greater propensity to tilting when the smaller Sr cation (as in $Sr_3ZnTa_2O_9$, tilting observed) is substituted for the larger Ba cation (as in $Ba_3ZnTa_2O_9$, no tilting).⁵ In their work on $Sr_3MgTa_2O_9$, Nagai *et al.* (1997) employed X-ray as well as electron diffraction

techniques. In fact, they did find one R -point reflection in the X-ray powder pattern, as well as splitting of the main peaks due to the reduction from hexagonal to monoclinic symmetry. No M -point features were detected, so a structure (that in $C2/c$) showing only out-of-phase tilting was proposed. The same structure has been proposed for $Sr_3MgNb_2O_9$ (Lee *et al.*, 2001). Park & Woodward (2000) synthesized the ordered perovskite $Ba_3TeBi_2O_9$ and carried out a careful structural determination using both synchrotron X-ray and neutron powder diffraction, along with results from the *ISOTROPY* computer program. The structure of $Ba_3TeBi_2O_9$ is that in the space group $P3c1$, with tilt system $a^-a^-a^-$, Reaney *et al.* (1994) reported that for a number of these ordered perovskites, for example $Sr_3CaTa_2O_9$, the electron diffraction pattern showed Λ -, M - and R -point superlattice reflections. Our analysis (Table 1) suggests that for such perovskites (showing both + and - octahedra tilting) there is only one possible structure, the tilt system $a^+b^-b^-$, in space group $P2_1/c$. The space group $P2_1/c$ has in fact been reported for $Ca_3CaNb_2O_9$ (Hervieu *et al.*, 1977; Levin *et al.*, 2000) and $A_3CoNb_2O_9$, $A = Ca, Sr$ (Ting *et al.*, 2004). All these authors show carefully indexed electron diffraction patterns from single domain samples and a detailed comparison with our work indicates that the tilt system is not the $a^+b^-b^-$, with a tilt component about $[0\bar{1}1]$, that we show in our table, but rather the tilt system $a^\pm b^-b^-$, with the tilt component about $[011]$. This structure was listed by *ISOTROPY*, but was rejected because it showed in-phase (+) and out-of-phase (-) tilts around the same axis. The structures of $Ca_3CaNb_2O_9$ and $A_3CoNb_2O_9$, $A = Ca, Sr$, may represent the first manifestations of such complex tilts.

It appears that 1:3 B -site cation ordering has been observed only in the antimonates, $Ba_4LiSb_3O_{12}$, $Ba_4NaSb_3O_{12}$ and $Sr_4NaSb_3O_{12}$ (Jacobson *et al.*, 1974; Alonso *et al.*, 1987, 1990). Octahedral tilting (out-of-phase) has been noted only in the strontium compound. The fact that the cation ordering and in-phase octahedral tilting are both associated with the M -point

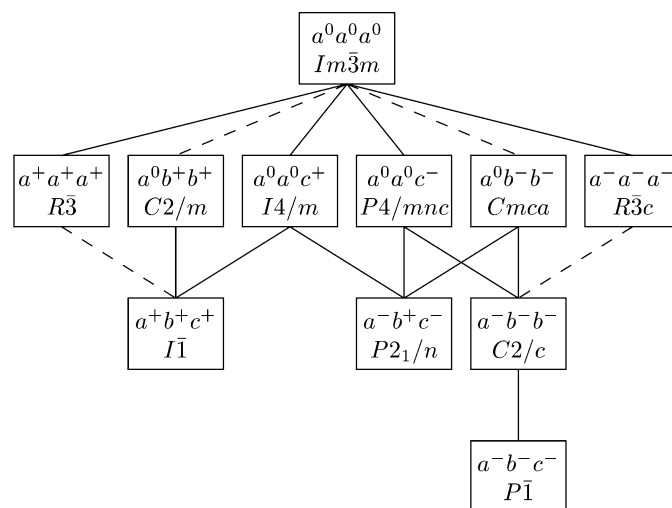
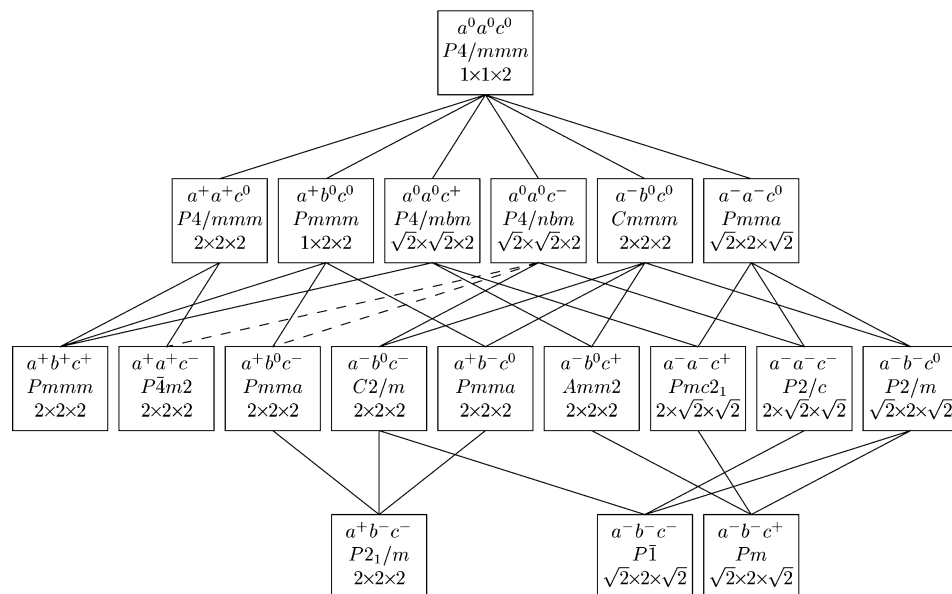


Figure 4
A schematic account of the group-subgroup relationships among the 11 space groups appearing in Table 2. The dashed lines have the same meaning as in Fig. 1.

⁴ The agreement goes beyond the cell and space-group symmetry. The atom positions tabulated by Alonso *et al.* also correspond with the entries in our table.

⁵ Such trends are well known in simple ABX_3 perovskites.


Figure 5

A corrected version (cf. Fig. 1 in Howard & Zhang, 2004) of the schematic drawing showing the different possible structures generated by the layered ordering of cations on the perovskite *A*-site, followed by the corner-linked tilting of the BX_6 octahedra. Included in this diagram are the approximate cell dimensions in terms of the cell edge of the $Pm\bar{3}m$ aristotype. The lines have the same meaning as previously.

may make the occurrence of in-phase (+) tilting difficult to detect. The situation parallels that encountered and discussed in the case of perovskites with 1:1 *B*-site cation ordering (Howard *et al.*, 2003), where the cation ordering and out-of-phase octahedral tilting are both associated with the *R*-point.

4. Some previous analyses revisited

As was realised in the enumeration of structures for perovskites with M_1^+ cation ordering (§2.2), structures permitting a lower-symmetry cation arrangement but corresponding to a distinct tilt system might need to be retained. It is thus necessary to check what structures might have been inadvertently omitted in our previous studies of perovskites with cation ordering (Howard *et al.*, 2003; Howard & Zhang, 2003, 2004).

The irrep of $Pm\bar{3}m$ associated with the 1:1 rock-salt pattern of *B*-site cation ordering (Howard *et al.*, 2003) is R_1^+ ($\mathbf{k} = \frac{1}{2}, \frac{1}{2}, \frac{1}{2}$). Since this is a one-dimensional irrep, order parameter (*a*), the possibility of a lower-symmetry cation arrangement does not arise. However, a footnote (footnote 3) in the paper by Howard *et al.* (2003), referring to layered ordering mediated by the three-dimensional irrep X_1^+ , is found to be in error.

Howard & Zhang (2003, 2004) have shown an analysis for layered ordering of *A*-site cations mediated by the three-dimensional irrep X_3^- ($\mathbf{k} = 0, 0, \frac{1}{2}$). Seven structures have been inadvertently omitted in this case. The corrected version of the schematic diagram, now incorporating these seven structures,

is shown here as Fig. 5. The arguments used by Howard & Zhang for structure solution remain unaffected.

5. Summary

Group-theoretical methods implemented in the computer program *ISOTROPY* have been used to enumerate the structures of double perovskites with 1:2 and 1:3 *B*-site cation ordering combined with octahedral tilting. Details on these structures have been tabulated, and in Figs. 3 and 4 group-subgroup relationships are displayed. The pertinent literature has been briefly reviewed. In the determination of structures involving cation ordering in combination with octahedral tilting, a greater use of neutron diffraction (along with X-ray and electron diffraction) might prove beneficial. Analysis of the perovskites with 1:3 ordering led to a reconsideration of the criteria used

to determine the acceptable structures (from the many listed by *ISOTROPY*); previous work on perovskites with cation ordering has been accordingly reviewed.

This work developed from discussions on the structure of $\text{Ca}_3\text{CoNb}_2\text{O}_9$ with Associate Professor B. J. Kennedy during a visit to the Australian National Beamline Facility in Tsukuba, Japan. Travel to Japan was supported by the Australian Synchrotron Research Program, which is funded by the Commonwealth of Australia under the Major National Research Facilities Program.

References

- Aleksandrov, K. S. (1976). *Ferroelectrics*, **14**, 801–805.
- Alonso, J. A., Mzyayek, E. & Rasines, I. (1987). *Mater. Res. Bull.* **22**, 69–74.
- Alonso, J. A., Mzyayek, E. & Rasines, I. (1990). *J. Solid State Chem.* **84**, 16–22.
- Bärnighausen, H. (1980). *MATCH, Commun. Math. Chem.* **9**, 139–175.
- Dowty, E. (1999). *ATOMS*, Version 5.0.7. Shape Software, Kingsport, Tennessee 37663, USA.
- Galasso, F. & Pyle, J. (1963). *Inorg. Chem.* **2**, 482–484.
- Glazer, A. M. (1972). *Acta Cryst.* **B28**, 3384–3392.
- Hahn, Th. (1983). Editor. *International Tables for X-ray Crystallography*, Vol. A. Birmingham: Kynoch Press. (Present distributor: Kluwer Academic Publishers, Dordrecht.)
- Hatch, D. M. (1984). *Lecture Notes in Physics*, edited by G. Denardo, G. Ghirardi & T. Weber, pp. 390–393. New York: Springer.
- Hatch, D. M. & Stokes, H. T. (1985). *Phys. Rev. B*, **31**, 2908–2912.

- Hatch, D. M. & Stokes, H. T. (1986). *Computer Modeling of Phase Diagrams*, edited by L. H. Bennett, pp. 145–162. Warrendale: Metallurgical Society.
- Hatch, D. M. & Stokes, H. T. (1987a). *Phys. Rev. B*, **35**, 8509–8516.
- Hatch, D. M. & Stokes, H. T. (1987b). *Phys. Rev. B*, **36**, 7185.
- Hervieu, M., Studer, F. & Raveau, B. (1977). *J. Solid State Chem.* **22**, 273–289.
- Howard, C. J., Kennedy, B. J. & Woodward, P. M. (2003). *Acta Cryst.* **B59**, 463–471.
- Howard, C. J., Knight, K. S., Kennedy, B. J. & Kisi, E. H. (2000). *J. Phys. Condens. Matter*, **12**, L677–L683.
- Howard, C. J., Luca, V. & Knight, K. S. (2002). *J. Phys. Condens. Matter*, **14**, 377–387.
- Howard, C. J. & Stokes, H. T. (1998). *Acta Cryst.* **B54**, 782–789.
- Howard, C. J. & Stokes, H. T. (2002). *Acta Cryst.* **B58**, 565.
- Howard, C. J., Withers, R. L. & Kennedy, B. J. (2001). *J. Solid State Chem.* **160**, 8–12.
- Howard, C. J. & Zhang, Z. (2003). *J. Phys. Condens. Matter*, **15**, 4543–4553.
- Howard, C. J. & Zhang, Z. (2004). *Acta Cryst.* **B60**, 249–251.
- Jacobson, A. J., Collins, B. M. & Fender, B. E. F. (1974). *Acta Cryst.* **B30**, 1705–1711.
- Jacobson, A. J., Collins, B. M. & Fender, B. E. F. (1976). *Acta Cryst.* **B32**, 1083–1087.
- Landau, L. D. & Lifshitz, E. M. (1980). *Statistical Physics*, 3rd ed., ch. XIV. New York: Pergamon Press.
- Lee, H. J., Park, H. M., Cho, Y. K., Song, Y. W., Nahm, S. & Byun, J.-D. (2001). *J. Am. Ceram. Soc.* **84**, 3032–3036.
- Levin, I., Bendersky, L. A., Cline, J. P., Roth, R. S. & Vanderah, T. (2000). *J. Solid State Chem.* **150**, 43–61.
- Megaw, H. D. (1973). *Crystal Structures – A Working Approach*. Philadelphia: W. B. Saunders.
- Miller, S. C. & Love, W. F. (1967). *Tables of Irreducible Representations of Space Groups and Co-representations of Magnetic Space Groups*. Boulder: Pruett.
- Mitchell, R. H. (2002). *Perovskites – Modern and Ancient*. Thunder Bay, Ontario: Almaz Press.
- Nagai, T., Sugiyama, M., Sando, M. & Niihara, K. (1997). *Jpn. J. Appl. Phys.* **36**, 1146–1153.
- Park, J.-H. & Woodward, P. M. (2000). *Intl J. Inorg. Mater.* **2**, 153–166.
- Reaney, I. M., Colla, E. L. & Setter, N. (1994). *Jpn. J. Appl. Phys.* **33**, 3984–3990.
- Stokes, H. T. & Hatch, D. M. (1984a). *Phys. Rev. B*, **30**, 4962–4967.
- Stokes, H. T. & Hatch, D. M. (1984b). *Phys. Rev. B*, **31**, 4700.
- Stokes, H. T. & Hatch, D. M. (2002). *J. Appl. Cryst.* **35**, 379.
- Stokes, H. T., Kisi, E. H., Hatch, D. M. & Howard, C. J. (2002). *Acta Cryst.* **B58**, 934–938.
- Ting, V., Liu, Y., Withers, R. L. & Norén, L. (2004). *J. Solid State Chem.* **177**, 2295–2304.