

# Ordered double perovskites – a group-theoretical analysis

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Received 14 March 2003

Accepted 7 May 2003

Group-theoretical methods are used to enumerate the structures of ordered double perovskites,  $A_2BB'X_6$ , in which the ordering of cations  $B$  and  $B'$  into alternate octahedra 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 the irreducible representation  $R_1^+$  of the  $Pm\bar{3}m$  space group of the cubic aristotype, while the octahedral tilting is mediated by irreducible representations  $M_3^+$  and  $R_4^+$ . There are 12 different structures identified, and the corresponding group–subgroup relationships are displayed. Known structures are briefly reviewed.

## 1. Introduction

Structures in the  $ABX_3$  perovskite family have long attracted interest, both as challenging problems for crystallographers, on account of subtle structural variations, and for the effects that these variations may have on important physical properties (Megaw, 1973). The occurrence of the  $ABO_3$  perovskite motif in superconducting and magnetoresistive oxides, in microwave dielectric materials, in ferroelectrics, and in piezoelectric materials, including those showing enhanced piezoelectric response (Kuwata *et al.*, 1981; Park & Shrout, 1997), has brought perovskites and their crystal structures to the attention of the wider scientific community. The perovskite family is extended by substitutions, particularly of the  $A$ - and  $B$ -site cations, undertaken (for example) to optimize electronic or magnetic properties for specific applications. Substitution of cation  $B'$  for  $B$  leads, in general, to the solid solution  $AB_{1-x}B'_xX_3$ , but if  $x \simeq 0.5$  and  $B'$  and  $B$  are sufficiently different in charge and/or size,  $B$ -site cation ordering may occur.<sup>1</sup> The formula is then properly written as  $A_2BB'X_6$  and the compound is commonly described as a double perovskite<sup>2</sup> (Anderson *et al.*, 1993). Such double perovskites are currently under investigation for their magnetic and, more particularly, their magnetoresistive properties (Kobayashi *et al.*, 1998). In their comprehensive survey of double perovskite oxides, Anderson *et al.* (1993) identified essentially two

<sup>1</sup> Ordering of the octahedral-site cations may occur at other compositions, giving, for example, 2:1 ordered perovskites,  $A_3B_2B'X_9$ , at  $x \simeq 0.33$ , and 3:1 ordered perovskites,  $A_4B_3B'X_{12}$ , at  $x \simeq 0.25$ , but the 1:1 rock-salt order is by far the most common ordered arrangement.

<sup>2</sup> Some researchers prefer the term double-edge perovskites, in order to distinguish them from oxygen-deficient double-cell perovskites, such as  $YBaFe_2O_5$  (Woodward & Karen, 2003). We shall use the terms 'ordered double perovskites' or the shorter 'double perovskites' for the compounds described here.

patterns of *B*-site ordering. One type, which is exemplified by more than 160 perovskite oxides, is described as rock-salt ordering, in that cations *B* and *B'* order into alternate octahedra, and the other type (only one example given in the Anderson *et al.* review) is a layered ordering of cations *B* and *B'*. This paper concerns the structures of  $A_2BB'X_6$  double perovskites, with rock-salt ordering on the *B* sites.

The ideal simple  $ABX_3$  perovskite is cubic, in space group  $Pm\bar{3}m$ , but distorted variants are the norm. The most common distortion is the tilting of the  $BX_6$  octahedral units as nearly rigid corner-linked units. This tilting is usually driven by a mismatch in the size of the *A*-site cation and the size of the cubo-octahedral cavity in the cubic corner-sharing  $BX_3$  network (Woodward, 1997*b*). Glazer (1972) developed a convenient notation to describe this tilting, and the implications for structure have been considered in detail (Glazer, 1972, 1975; Howard & Stokes, 1998). Doubling of the ideal perovskite by imposition of rock-salt ordering leads to another cubic structure, in space group  $Fm\bar{3}m$ , with a unit-cell edge double that of the  $ABX_3$  perovskite. However, octahedral tilting (that is, of the  $BX_6$  and  $B'X_6$  corner-linked octahedra) is to be expected, and hence lower-symmetry structures will result. In this paper, we use group-theoretical methods to enumerate the structures of the  $A_2BB'X_6$  double perovskites that arise from rock-salt cation ordering combined with simple octahedral tilting. Other frequently encountered distortions, such as displacement of the *B* cations within the  $BX_6$  octahedra (Megaw, 1973; Howard *et al.*, 2002; Stokes *et al.*, 2002), will not be considered in this work. We find 12 structures from our analysis, and for each structure we give the space group, the tilt system using Glazer's notation, the unit cell in terms of the aristotype cubic perovskite  $ABX_3$  cell and the atomic coordinates of various atoms in the new unit cell. The group-subgroup relationships are derived and displayed, and the connection with previous work, both theoretical and experimental, is reviewed. Finally, we note that a number of double perovskites have been described in space groups that do not appear in our list, and we argue that such descriptions cannot be strictly correct.

## 2. Group-theoretical analysis

The analysis starts from a consideration of the parent perovskite,  $ABX_3$ , in space group  $Pm\bar{3}m$ . The analysis is aided throughout by use of the computer program *ISOTROPY* ([www.physics.byu.edu/~stokesh/isotropy.html](http://www.physics.byu.edu/~stokesh/isotropy.html)). In the parent structure, atoms *A*, *B* and *X* are at  $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$  (Wyckoff position 1*b*), 0,0,0 (1*a*) and  $\frac{1}{2}, 0, 0$  (3*d*), respectively. The  $A_2BB'X_6$  double perovskite with rock-salt ordering is generated if the translations 1,0,0, 0,1,0 and 0,0,1 lead to occupancy of the octahedral site by alternate *B* and *B'* cations, while other operations of the parent space group leave the occupancies unchanged. The one-dimensional irreducible representation (irrep)  $R_1^+$  ( $\mathbf{k} = \frac{1}{2}, \frac{1}{2}, \frac{1}{2}$ ) of  $Pm\bar{3}m$ , taking the values  $-1$  under the unit translations of the parent space group and  $+1$  under the other operations, is identified as the representation associated with the rock-salt cation ordering. The subgroup of  $Pm\bar{3}m$  that

leaves the ordered double perovskite unchanged, an isotropy subgroup, is as stated above  $Fm\bar{3}m$ .

We intend in this paper to enumerate the structures occurring in double perovskites as a result of the cation ordering in combination with the corner-linked tilting of the  $BX_6$  (or  $B'X_6$ ) octahedral units. A full analysis of corner-linked tilting in perovskites, without cation ordering, has been given previously by Howard & Stokes (1998). The relevant irreps of the parent space group [we use the notation of Miller & Love (1967)] are  $R_4^+$  ( $\mathbf{k} = \frac{1}{2}, \frac{1}{2}, \frac{1}{2}$ ), which corresponds to modes with out-of-phase tilting of octahedra in successive layers, and  $M_3^+$  ( $\mathbf{k} = \frac{1}{2}, \frac{1}{2}, 0$ ), which is associated with in-phase octahedral tilting. This previous analysis was completed using the *ISOTROPY* computer program. *ISOTROPY* was used again in the present study in order to examine the different possible structures produced by  $R_1^+$  cation ordering followed by  $M_3^+$  and/or  $R_4^+$  octahedral tilting, and the results are presented in Table 1. An order parameter is associated with each of these irreps. For  $R_1^+$ , the order parameter is a scalar that corresponds to the degree of cation ordering, which we take to be essentially fixed. Although the degree of cation ordering may depend on sample history and on temperature, the symmetries of the resulting structures do not depend on the value of the order parameter, provided that at least partial ordering occurs. The order parameters associated with irreps  $M_3^+$  and  $R_4^+$  are vectors, and the three components of each vector correspond to the magnitudes of the tilts around the three axes of the parent perovskite, these tilts being in-phase for  $M_3^+$  and out-of-phase for  $R_4^+$ . Structures from *ISOTROPY* showing both in-phase and out-of-phase tilting around the same axis were removed before preparation of Table 1, since the tilts in successive layers of such structures would differ in magnitude and could not be considered as 'simple' tilts. However, 12 distinct structures remain. Table 1 includes the order parameters associated with  $M_3^+$  and  $R_4^+$  for each valid structure, and from these parameters we obtain the Glazer symbol for the tilt system. This symbol, of the form  $a^{\#}b^{\#}c^{\#}$ , is used to indicate no tilt, in-phase octahedral tilting or out-of-phase octahedral tilting around the  $\langle 001 \rangle$  axes of the parent  $Pm\bar{3}m$  perovskite by showing the superscript # as 0, + or  $-$ , respectively. Three of the structures, namely those in  $P2_1/c$ ,  $C2/m$  and  $P\bar{1}$ , are shown in Table 1 in both the standard settings provided by *ISOTROPY* and the alternative settings on more convenient nearly orthogonal cells. More details about irreps, order parameters, isotropy subgroups and the methods for their enumeration, the elimination of other than simple tilt systems, and the Glazer notation for tilts can be found in previous publications (Glazer, 1972; Stokes & Hatch, 1984; Howard & Stokes, 1998; Stokes *et al.*, 2002).

The group-subgroup relationships can be obtained from the order parameters recorded in Table 1. These relationships are particularly useful in connection with studies of structural phase transitions. Briefly, 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. For

**Table 1**

ISOTROPY subgroups of  $Pm\bar{3}m$  for the irrep  $R_1^+$  in combination with irreps  $M_3^+$  and/or  $R_4^+$ .

For each subgroup, we give the space-group symmetry (and number), along with lattice vectors and the origin of the subgroup with respect to the parent cell in  $Pm\bar{3}m$ . The positions of the atoms relative to the new cell are also shown, as are the order parameters associated with the irreps  $M_3^+$  and  $R_4^+$ , along with the tilt system described using the notation of Glazer (1972). The lattice vectors and origins are given for the conventional settings of space groups in the *International Tables for Crystallography* (1983, Vol. A). The hexagonal setting is used for  $R\bar{3}$ . The setting with unique axis  $b$ , cell choice 1, is used for the monoclinic space groups, and the second origin choice is used for space groups with two origin choices. For space groups  $C2/m$  (No. 12),  $P\bar{1}$  (No. 2) and  $P2_1/c$  (No. 14), a second entry shows a setting on a nearly orthogonal cell, which is a more convenient and popular choice in the study of double perovskites.

Space group	$M_3^+$	$R_4^+$	Tilts	Lattice vectors	Origin	Atomic positions (Wyckoff symbol, coordinates)			
						A	B	B'	X
$Fm\bar{3}m$ (No. 225)	(0,0,0)	(0,0,0)	$a^0a^0a^0$	(2,0,0),(0,2,0),(0,0,2)	(0,0,0)	8c, $\frac{1}{4}\frac{1}{4}\frac{1}{4}$	4a, 0,0,0	4b, $\frac{1}{2}\frac{1}{2}\frac{1}{2}$	24e, x,0,0 $x \simeq \frac{1}{4}$
$P4/mnc$ (No. 128)	(0,0,c)	(0,0,0)	$a^0a^0c^+$	(1,1,0), $(\bar{1},1,0)$ ,(0,0,2)	(0,0,0)	4d, $0,\frac{1}{2}\frac{1}{4}$	2a, 0,0,0	2b, $0,0,\frac{1}{2}$	4e, 0,0,z $z \simeq \frac{1}{4}$ 8h, x,y,0 $x \simeq \frac{1}{4}, y \simeq \frac{3}{4}$
$P4_2/nm$ (No. 134)	(0,b,b)	(0,0,0)	$a^0b^+b^+$	(0,2,0),(0,0,2),(2,0,0)	(0,0,0)	2a, $\frac{1}{4}\frac{3}{4}\frac{1}{4}$ 2b, $\frac{3}{4}\frac{1}{4}\frac{1}{4}$ 4c, $\frac{1}{4}\frac{1}{4}\frac{1}{4}$	4f, 0,0,0	4e, $0,0,\frac{1}{2}$	8m, x,x,z $x \simeq 0, z \simeq \frac{1}{4}$ 16n, x,y,z $x \simeq 0, y \simeq \frac{1}{4}, z \simeq 0$
$Pn\bar{3}$ (No. 201)	(a,a,a)	(0,0,0)	$a^+a^+a^+$	(2,0,0),(0,2,0),(2,0,0)	(0,0,0)	2a, $\frac{1}{4}\frac{1}{4}\frac{1}{4}$ 6d, $\frac{1}{4}\frac{3}{4}\frac{3}{4}$	4b, 0,0,0	4c, $\frac{1}{2}\frac{1}{2}\frac{1}{2}$	24h, x,y,z $x \simeq \frac{1}{4}, y \simeq 0, z \simeq 0$
$Pnnn$ (No. 48)	(a,b,c)	(0,0,0)	$a^+b^+c^+$	(2,0,0),(0,2,0),(2,0,0)	(0,0,0)	2a, $\frac{1}{4}\frac{1}{4}\frac{1}{4}$ 2b, $\frac{3}{4}\frac{1}{4}\frac{1}{4}$ 2c, $\frac{1}{4}\frac{1}{4}\frac{3}{4}$ 2d, $\frac{1}{4}\frac{3}{4}\frac{1}{4}$	4f, 0,0,0	4e, $\frac{1}{2}\frac{1}{2}\frac{1}{2}$	8m, x,y,z $x \simeq \frac{3}{4}, y \simeq 0, z \simeq 0$ 8m, x,y,z $x \simeq 0, y \simeq \frac{1}{4}, z \simeq 0$ 8m, x,y,z $x \simeq 0, y \simeq 0, z \simeq \frac{1}{4}$
$I4/m$ (No. 87)	(0,0,0)	(0,0,c)	$a^0a^0c^-$	(1,1,0), $(\bar{1},1,0)$ ,(0,0,2)	(0,0,0)	4d, $0,\frac{1}{2}\frac{1}{4}$	2a, 0,0,0	2b, $0,0,\frac{1}{2}$	4e, 0,0,z $z \simeq \frac{1}{4}$ 8h, x,y,0 $x \simeq \frac{1}{4}, y \simeq \frac{1}{4}$
$C2/m$ (No. 12) $I2/m$	(0,0,0)	(0,b,b)	$a^0b^-b^-$ $a^0b^-b^-$	$(\bar{2},\bar{1},1)$ ,(0,1,1),(0,1, $\bar{1}$ ) (0,1, $\bar{1}$ ),(0,1,1),(2,0,0)	(0,0,0) (0,0,0)	4i, x,0,z $x \simeq \frac{1}{2}, z \simeq \frac{1}{4}$	2a, 0,0,0	2d, $0,0,\frac{1}{2}$	4i, x,0,z $x \simeq 0, z \simeq \frac{1}{4}$ 8j, x,y,z $x \simeq \frac{1}{4}, y \simeq \frac{1}{4}, z \simeq 0$
$R\bar{3}$ (No. 148)	(0,0,0)	(a,a,a)	$a^-a^-a^-$	$(\bar{1},1,0)$ ,(0, $\bar{1},1)$ ,(2,2,2)	(0,0,0)	6c, 0,0,z $z \simeq \frac{1}{4}$	3a, 0,0,0	3b, $0,0,\frac{1}{2}$	18f, x,y,z $x \simeq \frac{1}{3}, y \simeq \frac{1}{6}, z \simeq \frac{5}{12}$
$P\bar{1}$ (No. 2) $I\bar{1}$	(0,0,0)	(a,b,c)	$a^-b^-c^-$ $a^-b^-c^-$	(1,0,1),(1,1,0), $(\bar{1},1,0)$ (1,1,0), $(\bar{1},1,0)$ ,(0,0,2)	(0,0,0) (0,0,0)	4i, x,y,z $x \simeq 0, y \simeq \frac{1}{2}, z \simeq \frac{1}{4}$	2a, 0,0,0	2g, $0,0,\frac{1}{2}$	4i, x,y,z $x \simeq 0, y \simeq 0, z \simeq \frac{1}{4}$ 4i, x,y,z $x \simeq \frac{1}{4}, y \simeq \frac{1}{4}, z \simeq 0$ 4i, x,y,z $x \simeq \frac{1}{4}, y \simeq \frac{3}{4}, z \simeq 0$
$C2/c$ (No. 15)	(0,b,0)	(0,0,c)	$a^0b^+c^-$	$(\bar{2},0,0)$ ,(0,0,2),(0,2,0)	$(\frac{1}{2},0,\frac{1}{2})$	4e, $0,y,\frac{1}{4}$ $y \simeq 0$ 4e, $0,y,\frac{1}{4}$ $y \simeq \frac{1}{2}$	4c, $\frac{1}{4}\frac{1}{4},0$	4d, $\frac{1}{4}\frac{1}{4}\frac{1}{2}$	8f, x,y,z $x \simeq \frac{1}{4}, y \simeq 0, z \simeq 0$ 8f, x,y,z $x \simeq 0, y \simeq \frac{1}{4}, z \simeq 0$ 8f, x,y,z $x \simeq \frac{1}{4}, y \simeq \frac{1}{4}, z \simeq \frac{1}{4}$
$P2_1/c$ (No. 14) $P2_1/n$	(a,0,0)	(0,b,b)	$a^+b^-b^-$ $a^-a^-c^+$	(0,1, $\bar{1}$ ),(0,1,1),(2,1, $\bar{1}$ ) (1,1,0), $(\bar{1},1,0)$ ,(0,0,2)	(0,0,0) (0,0,0)	4e, x,y,z $x \simeq 0, y \simeq \frac{1}{2}, z \simeq \frac{1}{4}$	2a, 0,0,0	2b, $0,0,\frac{1}{2}$	4e, x,y,z $x \simeq 0, y \simeq 0, z \simeq \frac{1}{4}$ 4e, x,y,z $x \simeq \frac{1}{4}, y \simeq \frac{1}{4}, z \simeq 0$ 4e, x,y,z $x \simeq \frac{1}{4}, y \simeq \frac{3}{4}, z \simeq 0$
$P4_2/n$ (No. 86)	(a,a,0)	(0,0,c)	$a^+a^+c^-$	(2,0,0),(0,2,0),(0,0,2)	(1,0,0)	2a, $\frac{1}{4}\frac{1}{4}\frac{1}{4}$ 2b, $\frac{1}{4}\frac{1}{4}\frac{3}{4}$ 4e, $\frac{3}{4}\frac{1}{4}\frac{1}{4}$ $z \simeq \frac{1}{4}$	4c, 0,0,0	4d, $0,0,\frac{1}{2}$	8g, x,y,z $x \simeq \frac{1}{4}, y \simeq 0, z \simeq 0$ 8g, x,y,z $x \simeq 0, y \simeq \frac{1}{4}, z \simeq 0$ 8g, x,y,z $x \simeq 0, y \simeq 0, z \simeq \frac{1}{4}$

example,  $(a,b,c)$  and  $(a,a,a)$  span, respectively, three- and one-dimensional subspaces of the space of the order parameter associated with irrep  $M_3^+$ , and the former group can be obtained by an infinitesimal change from the latter, so  $Pnnn$  is a subgroup of  $Pn\bar{3}$ . By contrast,  $(a,a,a)$  cannot be obtained by infinitesimal changes from  $(0,a,a)$ , so there is no group-subgroup relationship between  $Pn\bar{3}$  and  $P4_2/nnm$ . Howard & Stokes (1998) described these procedures in greater detail. The group-subgroup relationships obtained are summarized in Fig. 1. The figure also indicates the phase transitions between group-subgroup pairs that are required by Landau theory (Landau & Lifshitz, 1980) to be first order. This information was obtained by a further use of *ISOTROPY*.

### 3. Discussion

We first compare the results obtained here with those obtained in previous analyses of double perovskites, and then we use these results in a critical examination of reported structures of such compounds. Finally, the practical problem of distinguishing the various possible structures is discussed.

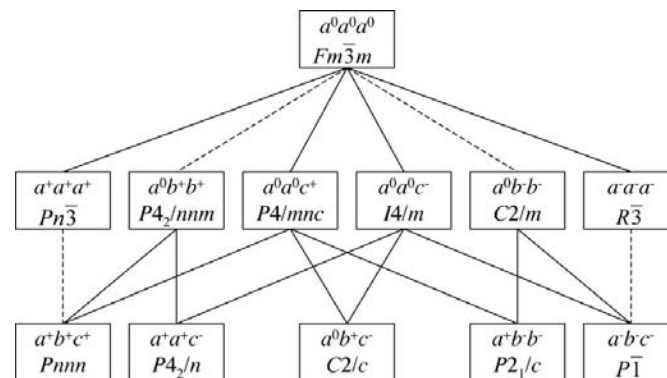
#### 3.1. Previous analyses of ordered double perovskite structures

Aleksandrov & Misjul (1981) analyzed the ordered double perovskites by similar group-theoretical methods. Their results, however, differ in certain details from those presented here. Aleksandrov & Misjul (1981) retain structures incorporating both in-phase and out-of-phase tilts around the same axis, while we removed such structures from our list; these structures were identified using the symbol  $\Delta = \varphi \pm \psi$ , and include structures in  $P4/m$  and  $P2/c$  which do not appear in our work. On the other hand, our structures in  $Pnnn$  (tilt system  $a^+b^+c^+$ ) and  $P\bar{1}$  (tilt system  $a^-b^-c^-$ ) do not appear in the earlier analysis. The results differ further as regards the nature of the possible phase transitions – Aleksandrov & Misjul (1981) find continuous transitions from  $Fm\bar{3}m$  ( $a^0a^0a^0$ ) to  $P4_2/nnm$  ( $a^0b^+b^+$ ) and  $C2/m$  ( $a^0b^-b^-$ ), whereas we find that these transitions are required to be first order. Despite these differences, it is perhaps unfortunate that the early work of Aleksandrov and his colleagues is not more widely recognized.

Woodward (1997a) examined the 23 tilt systems (in 17 different space groups) proposed by Glazer (1972, 1975) for simple  $ABX_3$  perovskites, and for each tilt system he considered which symmetry elements would be destroyed in the  $A_2BB'X_6$  double perovskite by the ordering of the  $B$  and  $B'$  cations into alternate octahedra. The structures of the double perovskites in the 23 tilt systems were found to conform to 13 different space groups, namely the 12 listed in Table 1 and  $P2/c$ . Subsequently, Howard & Stokes (1998) argued that different tilt systems described in the same space group were unobtainable in practice so that only the most general tilt system appearing in a given space group should be retained. Evidently, this reduces the number of tilt systems listed to the number of distinct space groups involved. Woodward's thirteenth space group,  $P2/c$ , which is also one of the space groups

listed by Aleksandrov & Misjul (1981), derives from Glazer's space group  $Pmmm$  (tilt system  $a^+b^+c^-$ ). The structure in this space group was omitted by Howard & Stokes (1998) on the grounds that it involved both positive and negative tilts around the same axis, and the corresponding structure in  $P2/c$  has been omitted from the present list. Woodward (1997a) included a useful compilation of cell edges (to be compared with the lattice vectors in Table 1) and atomic positions. Note that the atomic positions are readily available from the *ISOTROPY* computer program, and are recorded in Table 1. The values we obtained using *ISOTROPY* are in good agreement with the previous analysis by Woodward (1997a), although there were some minor inconsistencies in his work that are rectified in our Table 1. Woodward (1997a) did not include information on the group-subgroup relationships nor that on the natures of the phase transitions incorporated here in Fig. 1.

A recent comprehensive treatment of the symmetries of perovskite variants (Bock & Müller, 2002) includes a consideration of the structures of the  $A_2BB'X_6$  double perovskites. The results for the double perovskites are presented in Fig. 6 of Bock & Müller (2002). This figure shows 19 distinct space groups, whereas only 12 space groups are shown in our Table 1. The additional space groups may arise from distortions that are not considered in our work. Bock & Müller (2002) show, for example, space group  $I4/mmm$ , which can be derived by a simple tetragonal distortion from the cubic  $Fm\bar{3}m$ , but cannot be obtained through the rock-salt ordering or the octahedral tilting considered here. The tetragonal structure in  $I4/mmm$  might result from a cooperative Jahn-Teller elongation (or compression) of the  $BX_6$  and/or  $B'X_6$  octahedra, but we are not yet convinced that such a distortion occurs (see below). It is more puzzling that Bock & Müller (2002) do not show space groups  $P4_2/nnm$ ,  $Pnnn$ ,  $R\bar{3}$  and  $P4_2/n$ , which we found for structures with cation ordering and simple octahedral tilting.



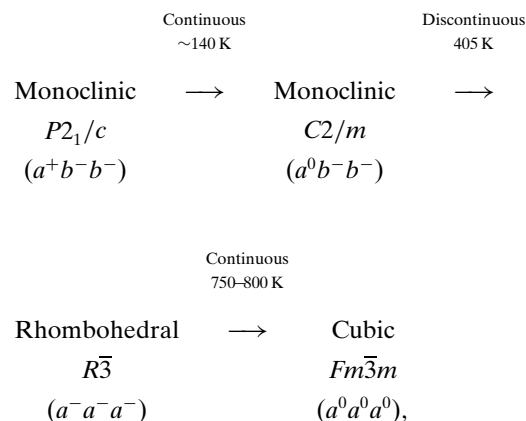
**Figure 1**  
A schematic diagram indicating the group-subgroup relationships among the 12 space groups appearing in Table 1. A dashed line joining a group to its subgroup indicates that the corresponding phase transition is required by Landau theory to be first order.

### 3.2. Review of known structures

In their review of more than 160 double perovskite oxides exhibiting rock-salt ordering on the *B* site,<sup>3</sup> Anderson *et al.* (1993) noted that the most commonly occurring structures were those in space groups  $Fm\bar{3}m$  (tilt system  $a^0a^0a^0$ ) and  $P2_1/n$  (the non-standard setting of  $P2_1/c$ ;  $a^+b^-b^-$ ). These authors do give examples of double perovskites showing other tilt patterns, in  $I2/m$  (the non-standard setting of  $C2/m$ ;  $a^0b^-b^-$ ) and in  $R\bar{3}$  ( $a^-a^-a^-$ ), while both tetragonal ( $Sr_2NiWO_6$  in  $I4/m$ ;  $a^0a^0c^-$ ) and triclinic ( $Ba_2LaRuO_6$  in  $P\bar{1}$ ) structures can be found in earlier literature (Koehl, 1973; Battle *et al.*, 1983). Given that tilt system  $a^+b^-b^-$  occurs in about half of all the simple  $ABX_3$  perovskites, it may not be surprising that it should be encountered frequently in the double perovskites, but it is surprising that so few of the other structures are found. Anderson *et al.* (1993) declared that many compounds reported in the literature as orthorhombic on a cell with approximate dimensions (relative to the edge of the simple parent) of  $2^{1/2} \times 2^{1/2} \times 2$  should properly be regarded as monoclinic in space group  $P2_1/n$ . We concur with the argument that there is no valid orthorhombic structure for an ordered double perovskite on a  $2^{1/2} \times 2^{1/2} \times 2$  cell (there is only one orthorhombic space group, *i.e.*  $Pnmm$ , in our Table 1, and that is on a  $2 \times 2 \times 2$  cell), but we think it likely that at least some of these structures might be tetragonal in space groups  $P4/mnc$  ( $a^0a^0c^+$ ) or  $I4/m$  ( $a^0a^0c^-$ ), both of which are on  $2^{1/2} \times 2^{1/2} \times 2$  cells. Indeed, an examination of lattice parameters presented for apparently orthorhombic compounds by Anderson *et al.* (1993) in their Table III reveals compounds such as  $Sr_2LuRuO_6$  (shows  $a = 5.7400 \text{ \AA}$ ,  $b = 5.7375 \text{ \AA}$ ,  $c = 8.1118 \text{ \AA}$  and  $\beta = 90.16^\circ$ ), which could be tetragonal rather than monoclinic.<sup>4</sup> In early work on  $Sr_2FeMoO_6$  (Galasso *et al.*, 1966), the structure was described as tetragonal, but the space group was not determined at that time. Certainly, there have been reports of tetragonal structures in double perovskites since Anderson *et al.* (1993) published their review.

A particularly interesting early study, which was overlooked in the Anderson *et al.* (1993) review, was that by Cox & Sleight (1976, 1979) on  $BaBiO_3$ . This compound is, in effect, the ordered double perovskite  $Ba_2Bi^{3+}Bi^{5+}O_6$ , by virtue of the charge ordering of the Bi ions. Cox & Sleight (1976, 1979) reported the structure to be monoclinic in  $I2/m$  ( $C2/m$ ) at room temperature and to show a first-order transition to rhombohedral in  $R\bar{3}$  at  $\sim 405 \text{ K}$  and a continuous transition to cubic (but still a double perovskite) at  $\sim 750\text{--}800 \text{ K}$ . More recently, Pei *et al.* (1990) extended the study to low temperatures, and reported an apparently continuous transition at  $\sim 140 \text{ K}$  to a primitive monoclinic structure on the same cell. From inspection of Fig. 1 and Table 1, we suggest that the

low-temperature structure is that in  $P2_1/n$  ( $P2_1/c$ ), since that structure can be obtained from  $I2/m$  ( $C2/m$ ) by a continuous phase transition. Thus, we suggest that the sequence of transitions in  $Ba_2Bi^{3+}Bi^{5+}O_6$  can be summarized as



which is consistent with the scheme of Fig. 1.

Woodward (1997c) examined a number of ordered double perovskites and reassigned a number of double perovskites (for example,  $Sr_2ScTaO_6$  and  $Sr_2InTaO_6$ ) from cubic in  $Fm\bar{3}m$  to monoclinic in  $P2_1/n$  on the basis of weak superlattice reflections violating the face-centering condition. His work also suggests that structures in  $I4/m$  (tilt system  $a^0a^0c^-$ ) are more common among double perovskites than is generally appreciated. He reported one compound,  $Sr_2YTaO_6$ , as being triclinic, with tilt system  $a^+b^-c^-$ , whereas we excluded this system on the grounds that it cannot be obtained through simple tilts. This compound clearly merits closer inspection.

Flerov *et al.* (1998) published another extensive review on ordered double perovskites, with a focus on halides rather than the oxides of the Anderson *et al.* (1993) review. Flerov *et al.* (1998) report on structures in  $I4/m$  (*e.g.* low-temperature structures of  $Cs_2NaLnCl_6$ ,  $Ln = Bi, La, Pr$  and  $Y$ ), a space group that appears on our list. However, we are led to question the report that the structure of  $Rb_2NaTnCl_6$  is tetragonal in  $P4/nbm$ , since this space group does not appear in our analysis. Flerov *et al.* (1998) also reviewed experimental evidence on phase transitions. There have been reports of phase transitions from monoclinic  $P2_1/n$  to  $Fm\bar{3}m$  in cryolite  $Na_3AlF_6$ , from  $I4/m$  to  $Fm\bar{3}m$  in the  $Cs_2NaLnCl_6$  compounds mentioned above, from  $P2_1/n$  to  $Fm\bar{3}m$  via  $P4/mnc$  for  $Cs_2LiCr(CN)_6$ , and from  $P2_1/n$  to  $Fm\bar{3}m$  via two intermediate structures in  $Cs_2RbDyF_6$ . Except for the reportedly direct transition from  $P2_1/n$  to  $Fm\bar{3}m$  (from our figure, we believe one or more intermediates should be involved<sup>5</sup>), we regard these transition pathways as plausible. In the case of  $Cs_2LiCr(CN)_6$ , the space group of the tetragonal intermediate was inferred from optical studies (Ryan & Swanson, 1976).

Mitchell (2002) includes another review of the ordered double perovskites in his recently published book. Although

<sup>3</sup> The review by Anderson *et al.* (1993) also presents one double perovskite,  $La_2CuSnO_6$ , said to exhibit a layered ordering of the *B*-site cations in combination with octahedral tilting. The space group is given as  $P2_1/m$  on a  $2 \times 2 \times 2$  cell. Using *ISOTROPY*, we found that the irrep associated with this cation ordering is  $X_1^+$ , and that the structures arising from  $X_1^+$  and just  $M_3^+$  and/or  $R_1^+$  octahedral tilting do not include a structure in  $P2_1/m$ .

<sup>4</sup> Anderson *et al.* (1993) already suggest that the monoclinic distortion might not be well established. Here we question whether the differences between  $a$ ,  $b$  and  $c/2^{1/2}$  are sufficient to establish an orthorhombic distortion.

<sup>5</sup> Note added in proof: Zhou & Kennedy (2003) recently carried out a high-resolution synchrotron X-ray diffraction study of  $Na_3AlF_6$  to examine just this point. In fact, the transition from  $P2_1/n$  to  $Fm\bar{3}m$  was found to be first order, and no intermediate phases were involved.

the  $Fm\bar{3}m$  and  $P2_1/n$  structures are still favored, other structures, including the  $I4/m$  tetragonal ( $a^0a^0c^-$ ) and  $P\bar{1}$  triclinic ( $a^-b^-c^-$ ), are recognized. Mitchell (2002) reviews the 'few data' available on phase transitions in the rock-salt ordered compounds. The data he reviews seem to us to be inconsistent, and the reported transitions generally do not correspond to the transition pathways expected from Fig. 1. We see from that figure that transitions between the  $Fm\bar{3}m$  cubic and the monoclinic  $P2_1/n$  structure would proceed (if continuous) via the intermediate tetragonal structure in  $P4/mnc$  ( $a^0a^0c^+$ ). Given that so many of the double perovskites are reported to adopt these cubic and monoclinic structures, it is surprising that there has been no report to date of the direct observation of the intermediate tetragonal structure in  $P4/mnc$ .<sup>6</sup> Mitchell (2002) also includes a discussion of tetragonal structures in space group  $I4/mmm$ , such as might result from a cooperative Jahn–Teller distortion of the  $BX_6$  and/or  $B'X_6$  octahedra without tilting. Note that space group  $I4/mmm$  (no tilting) shows the same reflection conditions as  $I4/m$  ( $a^0a^0c^-$ ), and the two are thus difficult to distinguish experimentally.<sup>7</sup> This problem is reflected in the literature on  $Ba_2CuWO_6$ , which is claimed by Reinen & Weitzel (1976) to be a Jahn–Teller tetragonal structure in  $I4/mmm$  and by Bokhimi (1992) to be a structure in  $I4/m$  involving out-of-phase octahedral tilting. A similar problem has been encountered in rhombohedral double perovskites in distinguishing between space groups  $R\bar{3}m$  (no tilting) and  $R\bar{3}$  ( $a^-a^-a^-$ ). Fu *et al.* (1997) reported  $Ba_2BiSbO_6$  to be in  $R\bar{3}m$ , on the basis of single-crystal X-ray data, but later reinvestigated this compound using neutron diffraction and concluded that the correct space group was  $R\bar{3}$  (Fu, 2000). Primo-Martin & Jansen (2001) reported  $Sr_2CoSbO_6$  to be in  $R\bar{3}$  on the basis of monochromatic X-ray diffraction data. The rhombohedral distortion in these compounds is probably the result of octahedral tilting, in which case the true space-group symmetry is  $R\bar{3}$ .

Two recently prepared ordered double perovskites, namely  $CaCu_3Sb_2Ga_2O_{12}$  and  $CaCu_3Ta_2Ga_2O_{12}$ , which adopt  $Pn\bar{3}$  symmetry (tilt system  $a^+a^+a^+$ ; Byeon *et al.*, 2003), represent another structure conforming to our analysis.

The structures of  $Sr_2FeMoO_6$  and closely related compounds have been frequently reinvestigated since it was reported (Kobayashi *et al.*, 1998) that this compound displays a magnetoresistive effect at room temperature. It has been confirmed that  $Sr_2FeMoO_6$  is tetragonal at room temperature, and the  $I4/m$  space group has been suggested (Chmaissem *et al.*, 2000), in accordance with our entry for tilt system  $a^0a^0c^-$ . Chmaissem *et al.* (2000) noted an apparently continuous phase transition from tetragonal to cubic in  $Fm\bar{3}m$  at  $\sim 420$  K. The structure in the  $I4/m$  phase exhibits ferrimagnetic order. The

space group was chosen after the authors used *ISOTROPY* to confirm the validity of the  $I4/m$  structure and to check (*cf.* our Fig. 1) that there could be a continuous transition from this structure to the cubic one. The structure of the same compound has been described (*e.g.* Tomioka *et al.*, 2000) in space group  $I4/mmm$ , which does not appear in Table 1. We have already noted the difficulty of distinguishing this space group from  $I4/m$ . Although we agree that it is generally good practice to describe a structure in the highest available symmetry, we believe the result is not correct in this case. Space group  $I4/mmm$  does permit a tetragonal distortion of the structure but will not permit the octahedral tilting that we believe is responsible for the distortion in this case. Tilting of the octahedron about the  $z$  axis (tilt system  $a^0a^0c^-$ ) would place the  $8h$  O atom at  $\frac{1}{4} - u, \frac{1}{4} + u, 0$  ( $u$  being small), which is possible in  $I4/m$ , in which the  $8h$  site is at  $x,y,0$ , but not possible in  $I4/mmm$ , since there the  $8h$  site is restricted to  $x,x,0$ . In a neutron diffraction study of a number of related compounds (Ritter *et al.*, 2000), the structure of  $Sr_2FeMoO_6$  was described as tetragonal (tilt system  $a^0a^0c^-$ ), in space group  $P4_2/m$ . This description is clearly not correct. Note that Ritter *et al.* (2000) suggest some possibly continuous transition from structures in monoclinic  $P2_1/n$  through tetragonal structures to cubic structures in  $Fm\bar{3}m$ . If such a sequence is confirmed then it may be concluded, by reference to Fig. 1, that the space group for the intermediate tetragonal structure is  $P4/mnc$ .

Structures of double perovskites continue to be reported as monoclinic in space group  $P2_1/n$ . This description may be correct in many cases, but we believe some of the structures reported in this symmetry in fact have higher symmetry. The double perovskite  $Ba_2PrRuO_6$ , which is of interest because of its unusual magnetic properties at low temperatures, is reported to be monoclinic in  $P2_1/n$  (*e.g.* Izumiyama *et al.*, 2001). Izumiyama *et al.* (2001) give the lattice parameters at 150 K as  $a = 6.0063$  Å,  $b = 5.9863$  Å,  $c = 8.4677$  Å and  $\beta = 90.04^\circ$ , and show a useful extract from the neutron diffraction pattern recorded at that temperature. This diffraction pattern provides no real evidence of peak splitting or broadening to suggest that the symmetry is lower than tetragonal and, accordingly, we have indexed the peaks on a  $2^{1/2} \times 2^{1/2} \times 2$  tetragonal cell (the same indexing as on the  $2^{1/2} \times 2^{1/2} \times 2$  monoclinic cell). The space group could be  $I4/m$ , except that one weak peak at  $\sim 47.5^\circ$ , which is indexed as 212, breaks the  $I$ -centering condition. In these circumstances, we believe it possible that the pattern could be well fitted with a structure in space group  $P4/mnc$  that corresponds to tilt system  $a^0a^0c^+$ . In other words, we believe that this may be one example of a higher-symmetry structure described as monoclinic. In addition, we report that, in a recent high-resolution synchrotron X-ray study of Ir-rich compositions in the closely related  $Ba_2PrRu_{1-x}Ir_xO_6$  system (Kennedy *et al.*, 2003), the metric was found to be tetragonal not monoclinic, but weak reflections breaking the  $I$ -centering conditions were observed. The pattern was well fitted by assuming a tetragonal structure in space group  $P4/mnc$ . A neutron powder diffraction study as a function of temperature, on one of these samples, confirmed this structure as the appropriate choice.

<sup>6</sup> It is interesting to note that Boysen & Hewat (1978) have observed double perovskite structures, including this intermediate tetragonal, in  $K_2SnCl_6$ . Though  $K_2SnCl_6$  is not strictly a double perovskite, it can be viewed as one, in which however the  $B'$  cation sites are vacant.

<sup>7</sup> Note also that space group  $I4/m$  can accommodate Jahn–Teller distortion along with the octahedral tilting. Since the Jahn–Teller distortion destroys the threefold symmetry of the octahedron, this distortion cannot be accommodated in any space group containing a threefold axis (Lufaso & Woodward, 2003).

By way of a summary on double perovskites, we list in Table 2, where possible, two examples of each of the 12 structural variants we have described.

### 3.3. Remarks on structure determination

Fig. 1 shows 12 distinct structures produced by rock-salt cation ordering combined with octahedral tilting. The experimental data are usually powder diffraction patterns, and the problems of proving cation ordering and then distinguishing among these different structures can be severe.

Our general practice in studies of simple perovskites (Howard *et al.*, 2000, 2002) has been to start by indexing reflections or groups of reflections on a double-edge unit cell. On this indexing, the even–even–even reflections represent the fundamental reflections of the ideal cubic aristotype  $ABX_3$  in space group  $Pm\bar{3}m$ . In-phase octahedral tilting ( $M$ -point) produces superlattice reflections with even–odd–odd indices, and out-of-phase tilting ( $R$ -point) produces superlattice reflections with odd–odd–odd indices.<sup>8</sup> The simultaneous occurrence of  $M$ -point and  $R$ -point distortions will produce some (weaker)  $X$ -point reflections, which are indexed as even–even–odd. Many of our studies have been carried out using neutron diffraction, since this is relatively more sensitive to O- and F-atom positions.

In the case of the ordered double perovskites, the rock-salt cation ordering is associated with the  $R$ -point, so its contribution also appears at the odd–odd–odd reflections. In the X-ray case, given sufficient contrast between the X-ray scattering powers of cations  $B$  and  $B'$ , the contribution of cation ordering is expected to obscure any contribution from  $R$ -point octahedral tilting, thus making the out-of-phase (–) octahedral tilting difficult to ascertain. On the other hand, the observation of strong odd–odd–odd superlattice reflections in the X-ray pattern can be taken as a firm indication of cation ordering. If the only tilting is out-of-phase (–), there are no reflections diagnostic of tilting that are distinct from the cation-ordering reflections. In this case, a combination of X-ray diffraction, which is generally more sensitive to the cation ordering, and neutron diffraction, which is sensitive to octahedral tilting, provides the best means to establish and quantify the tilts.

The coupling of  $R$ -point cation ordering with  $M$ -point (+) octahedral tilting may produce significant intensities at the even–even–odd  $X$ -point reflections. Thus, the observation in the X-ray pattern of reasonable intensities at these points [see, for example, the peak labelled 111 (indexing on the doubled cell as 201) in the pattern from  $Nd_2MgTiO_6$  shown by Anderson *et al.* (1993) in their Fig. 11a] establishes both cation ordering and  $M$ -point (+) octahedral tilting. However, Glazer (1975) suggests, and our own detailed calculations confirm, that the coupling of the cation ordering with the  $M$ -point (+) tilting depends on  $A$ -cation displacements, while reference to Table 1 shows that, in all the structures involving  $M$ -point (+)

<sup>8</sup> A more detailed analysis of tilting in simple perovskites (Glazer, 1975) shows that when the odd indices are equal the even–odd–odd and odd–odd–odd reflections will be very weak or absent.

**Table 2**

Representative examples of perovskites for each of the structures formed by octahedral tilting and 1:1 rock-salt ordering of the octahedral cations.

Unless otherwise noted, structure determinations refer to room temperature and pressure.

Space group	Tilts	Examples	References
$Fm\bar{3}m$ (No. 225)	$a^0a^0a^0$	$Ba_2MnWO_6$	Azad <i>et al.</i> (2001)
		$Rb_2KScF_6$	Faget <i>et al.</i> (1996)
$P4/mnc$ (No. 128)	$a^0a^0c^+$	$Ba_2PrRu_{1-x}Ir_xO_6$	Kennedy <i>et al.</i> (2003)
$P4_2/nmm$ (No. 134)	$a^0b^+b^+$	No reported examples	
$Pn\bar{3}$ (No. 201)	$a^+a^+a^+$	$CaCu_3Ga_2Sb_2O_{12}$	Byeon <i>et al.</i> (2003)
		$CaCu_3Ga_2Ta_2O_{12}$	Byeon <i>et al.</i> (2003)
$Pnnn$ (No. 48)	$a^+b^+c^+$	No reported examples	
$I4/m$ (No. 87)	$a^0a^0c^-$	$Sr_2FeMoO_6$	Chmaissem <i>et al.</i> (2000)
		$Sr_2CrTaO_6$	Woodward (1997c)
$I2/m$ (No. 12)	$a^0b^-b^-$	$Ba_2Bi^{3+}Bi^{5+}O_6$	Cox & Sleight (1979)
		$Ba_2PrBiO_6$	Harrison <i>et al.</i> (1995)
$R\bar{3}$ (No. 148)	$a^-a^-a^-$	$Ba_2YbBiO_6$	Harrison <i>et al.</i> (1995)
		$Ba_2Bi^{3+}Bi^{5+}O_6$ (305–900 K)	Cox & Sleight (1979)
$I\bar{1}$ (No. 2)	$a^-b^-c^-$	$Ba_2LaRuO_6$	Battle <i>et al.</i> (1983)
		$Ba_2La(Ru_{0.5}Sb_{0.5})O_6$	Almaer <i>et al.</i> (1993)
$C2/c$ (No. 15)	$a^0b^+c^-$	No reported examples	
$P2_1/n$ (No. 14)	$a^-a^-c^+$	$La_2LiSbO_6$	Lopez <i>et al.</i> (1992)
		$Sr_2NdBiO_6$	Lenz & Müller-Buschbaum (1990)
$P4_2/n$ (No. 86)	$a^+a^+c^-$	No reported examples	

but not  $R$ -point (–) tilts, the  $A$ -cation positions are fixed. Thus, the observation of significant X-ray intensities at the  $X$ -points implies, in fact, cation ordering along with both  $M$ -point (+) and  $R$ -point (–) octahedral tilting. Reflections indicating  $M$ -point (+) tilting (alone or in combination with  $R$ -point tilting) can be sought directly in X-ray or neutron diffraction patterns, and the peaks from  $Ba_2PrRuO_6$  and  $Ba_2PrRu_{1-x}Ir_xO_6$ , which were described above as breaking the  $I$ -centering condition, are just such peaks.<sup>9</sup>

<sup>9</sup> The results from our analysis can be summarized as follows. (i) Reasonable intensities in the X-ray patterns at the  $X$ -points indicate both in-phase (+) and out-of-phase (–) tilts, in addition to the cation ordering. (ii) Observable intensities at the  $M$ -points but not at the  $X$ -points indicate in-phase (+) tilts only. (iii) The absence of intensity at both the  $M$ - or the  $X$ -points suggests an absence of tilting or out-of-phase (–) tilting only.

The number of structures to be considered will be reduced following the analysis of tilts just described. To follow the example of  $\text{Ba}_2\text{PrRu}_{1-x}\text{Ir}_x\text{O}_6$ , the identification of the  $M$ -point reflection means that the tilt system must involve in-phase (+) tilts. Therefore, the number of possible structures is reduced to seven. In many cases, the possible structures can be further restricted by examining the metric,<sup>10</sup> and, in the example being considered, this appears to be tetragonal on a  $2^{1/2} \times 2^{1/2} \times 2$  unit cell. Examination of the entries in Table 1 shows that only one tetragonal structure involves in-phase (+) tilting on a  $2^{1/2} \times 2^{1/2} \times 2$  unit cell, this being the structure in space group  $P4/mnc$  (tilt system  $a^0a^0c^+$ ). Of course, once a space group and structural model are selected, the patterns should be examined against the metric and extinction conditions for the selected structure and, whenever possible, fitting of (preferably neutron) diffraction patterns by the Rietveld method should be carried out.

Crystal chemical arguments can also be useful in many instances. For example, by Pauling's rule of parsimony (Pauling, 1929) it could reasonably be argued that, for the ordered double perovskite with a single  $A$ -site cation,  $A_2BB'X_6$ , structures providing just one crystallographically distinct  $A$ -site (see Table 1) would be favored. Additional evidence about the structures might be obtained from an examination of the temperature-induced phase transitions by high-resolution diffraction at fine intervals of temperature. As can be seen from Fig. 1, the observation of two structures linked by a continuous phase transition limits the structural possibilities. We have employed this method to good effect in structural studies of the single perovskites such as  $\text{SrZrO}_3$  (Howard *et al.*, 2000) and  $\text{WO}_3$  (Howard *et al.*, 2002).

#### 4. Summary

Group-theoretical methods implemented using the computer program *ISOTROPY* have been used to enumerate the double perovskite structures produced by a rock-salt pattern of  $B$ -site cation ordering combined with octahedral tilting. The group-subgroup relationships have been derived and these are displayed in Fig. 1, which also indicates whether the corresponding phase transitions are allowed to be continuous. A review of the literature suggested that a number of the structures that have been claimed to be monoclinic in space group  $P2_1/n$  may in fact have higher symmetry, most probably tetragonal. Equally, it is likely that some of the compounds reported to be cubic in  $Fm\bar{3}m$  have lower symmetry. A number of incorrect or inappropriate structures were found. It is hoped that the group-theory results presented in this paper (Table 1 and Fig. 1) may prove an aid to the determination or review of the structures of double perovskites. The search for

<sup>10</sup> Note that the symmetry can be lower than the metric would indicate. For example,  $\text{Ca}_{0.5}\text{Sr}_{0.5}\text{TiO}_3$  at room temperature (Howard *et al.*, 2001), and  $\text{SrZrO}_3$  at elevated temperature (Howard *et al.*, 2000) are both confirmed to be orthorhombic (space groups  $Pnma$  and  $Imma$ , respectively), even though at the highest available resolution they appear metrically tetragonal. The orthorhombic space group was determined by electron microdiffraction in the first case and by an analysis of the phase transitions in the second.

and study of expected temperature-induced transitions, for example, from the monoclinic  $P2_1/n$  structure through perhaps tetragonal intermediates to cubic  $Fm\bar{3}m$ , would seem to be worthwhile. Previous experience (*e.g.* Howard *et al.*, 2002) suggests that the use of group theory, in conjunction with high-resolution neutron or X-ray diffraction measurements as a function of temperature, is a particularly effective means to address the structures of these materials.

The authors thank Professor Harold Stokes for checking the table and figure, and for his encouragement of this work. CJH and BJK are investigating perovskites with the support of a grant from the Australian Research Council. PMW acknowledges the National Science Foundation, grant number DMR-0094271, for financial support. This work developed from discussions of the structure of  $\text{Ba}_2\text{PrRu}_{1-x}\text{Ir}_x\text{O}_6$  during a visit to the Australian National Beamline Facility in Tsukuba, Japan. Travel 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. & Misjul, S. V. (1981). *Sov. Phys. Crystallogr.* **26**, 612–618.
- Almaer, S. A., Battle, P. D., Lightfoot, P., Mellen, R. S. & Powell, A. V. (1993). *J. Solid State Chem.* **102**, 375–381.
- Anderson, M. T., Greenwood, K. B., Taylor, G. A. & Poepfelmeir, K. R. (1993). *Prog. Solid State Chem.* **22**, 197–233.
- Azad, A. K., Ivanov, S. A., Eriksson, S. G., Eriksen, J., Rundlof, H., Mathieu, R. & Svedlindh, P. (2001). *Mater. Res. Bull.* **36**, 2215–2228.
- Battle, P. D., Goodenough, J. B. & Price, R. (1983). *J. Solid State Chem.* **46**, 234–244.
- Bock, O. & Müller, U. (2002). *Acta Cryst.* **B58**, 594–606.
- Bokhimi (1992). *Powder Diffr.* **7**, 228–230.
- Boysen, H. & Hewat, A. W. (1978). *Acta Cryst.* **B34**, 1412–1418.
- Byeon, S.-H., Lufaso, M. W., Parise, J. B., Woodward, P. M. & Hansen, T. (2003). *Chem. Mater.* Accepted for publication.
- Chmaissem, O., Kruk, R., Dabrowski, B., Brown, D. E., Xiong, X., Kolesnik, S., Jorgensen, J. D. & Kimball, C. W. (2000). *Phys. Rev. B*, **62**, 14197–14206.
- Cox, D. E. & Sleight, A. W. (1976). *Solid State Commun.* **19**, 969–973.
- Cox, D. E. & Sleight, A. W. (1979). *Acta Cryst.* **B35**, 1–10.
- Faget, H., Granec, J., Tressaud, A., Rodriguez, V., Roisnel, T., Flerov, I. N. & Gorev, M. V. (1996). *Eur. J. Solid State Inorg. Chem.* **33**, 893–905.
- Flerov, I. N., Gorev, M. V., Aleksandrov, K. S., Tressaud, A., Granec, J. & Couzi, M. (1998). *Mater. Sci. Eng. R*, **24**, 81–151.
- Fu, W. T. (2000). *Solid State Commun.* **116**, 461–464.
- Fu, W. T., de Gelder, R. & de Graaff, R. A. G. (1997). *Mater. Res. Bull.* **32**, 657–662.
- Galasso, F. S., Douglas, F. C. & Kasper, R. J. (1966). *J. Chem. Phys.* **44**, 1672–1674.
- Glazer, A. M. (1972). *Acta Cryst.* **B28**, 3384–3392.
- Glazer, A. M. (1975). *Acta Cryst.* **A31**, 756–762.
- Harrison, W. T. A., Reis, K. P., Liu, L., Jacobson, A. J., Schneemeyer, L. F. & Waszczak, J. V. (1995). *Chem. Mater.* **7**, 2161–2167.
- 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; erratum (2002). **B58**, 565.



- Howard, C. J., Withers, R. L. & Kennedy, B. J. (2001). *J. Solid State Chem.* **160**, 8–12.
- Izumiyama, Y., Doi, Y., Wakeshima, M., Hinatsu, Y., Shimojo, Y. & Morii, Y. (2001). *J. Phys. Condens. Matter*, **13**, 1303–1313.
- Kennedy, B. J., Li, L., Hunter, B. A. & Howard, C. J. (2003). In preparation.
- Kobayashi, K.-I., Kimura, T., Sawada, H., Terakura, K. & Tokura, Y. (1998). *Nature (London)*, **395**, 677–680.
- Koehl, P. (1973). *Z. Anorg. Allg. Chem.* **401**, 121–131.
- Kuwata, J., Uchino, K. & Nomura, S. (1981). *Ferroelectrics*, **37**, 592–582.
- Landau, L. D. & Lifshitz, E. M. (1980). *Statistical Physics*, 3rd ed., ch. XIV. New York: Pergamon Press.
- Lenz, A. & Müller-Buschbaum, H. (1990). *J. Less Common Met.* **161**, 141–146.
- Lopez, M. L., Veiga, M. L., Rodriguez-Carvajal, J., Fernandez, F., Jerez, A. & Pico, C. (1992). *Mater. Res. Bull.* **27**, 647–654.
- Lufaso, M. W. & Woodward, P. M. (2003). In preparation.
- Megaw, H. D. (1973). In *Crystal Structures – A Working Approach*. Philadelphia: W. B. Saunders.
- Miller, S. C. & Love, W. F. (1967). In *Tables of Irreducible Representations of Space Groups and Corepresentations of Magnetic Space Groups*. Boulder: Pruett.
- Mitchell, R. H. (2002). *Perovskites – Modern and Ancient*, ch. 4. Thunder Bay, Ontario: Almaz Press.
- Park, S.-E. & Shrout, T. R. (1997). *J. Appl. Phys.* **82**, 1804–1811.
- Pauling, L. (1929). *J. Am. Chem. Soc.* **51**, 1010–1026.
- Pei, S., Jorgensen, J. D., Dabrowski, B., Hinks, D. G., Richards, D. R., Mitchell, A. W., Newsam, J. M., Sinha, S. K., Vaknin, D. & Jacobson, A. J. (1990). *Phys. Rev. B*, **41**, 4126–4141.
- Primo-Martin, V. & Jansen, M. (2001). *J. Solid State Chem.* **157**, 76–85.
- Reinen, D. & Weitzel, H. (1976). *Z. Anorg. Allg. Chem.* **424**, 31–38.
- Ritter, C., Ibarra, M. R., Morellon, L., Blasco, J., Garcia, J. & De Teresa, J. M. (2000). *J. Phys. Condens. Matter*, **12**, 8295–8308.
- Ryan, R. R. & Swanson, B. I. (1976). *Phys. Rev. B*, **13**, 5320–5329.
- Stokes, H. T. & Hatch, D. M. (1984). *Phys. Rev. B*, **30**, 4962–4967; erratum (1985). **31**, 4700.
- Stokes, H. T., Kisi, E. H., Hatch, D. M. & Howard, C. J. (2002). *Acta Cryst.* **B58**, 934–938.
- Tomioka, Y., Okuda, T., Okimoto, Y., Kumai, R., Kobayashi, K.-I. & Tokura, Y. (2000). *Phys. Rev. B*, **61**, 422–427.
- Woodward, P. M. (1997a). *Acta Cryst.* **B53**, 32–43.
- Woodward, P. M. (1997b). *Acta Cryst.* **B53**, 44–66.
- Woodward, P. M. (1997c). PhD thesis, Oregon State University, USA.
- Woodward, P. M. & Karen, P. (2003). *Inorg. Chem.* **42**, 1121–1129.
- Zhou, Q. & Kennedy, B. J. (2003). *J. Solid State Chem.* Submitted.