Acta Cryst. (1997). B53, 32–43

Octahedral Tilting in Perovskites. I. Geometrical Considerations

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(Received 17 April 1996; accepted 28 August 1996)

Abstract

The 23 Glazer tilt systems describing octahedral tilting in perovskites have been investigated. It is shown that in tilt systems $a^+a^+a^-$, $a^+b^+b^-$, $a^+a^+c^-$, $a^+b^+c^-$, $a^0b^+b^-$ and $a^0b^+c^-$ it is not possible to link together a three-dimensional network of perfectly rigid octahedra. In these tilt systems small distortions of the octahedra must occur. The magnitude of the distortions in the $a^+a^+a^-$ and $a^0b^+b^-$ tilt systems are estimated. A table of predicted space groups for ordered perovskites, $A_2MM'O_6$, for all 23 tilt systems is also given.

1. Introduction

The perovskite structure class encompasses a huge variety of compounds. Most of the metallic ions in the periodic table can be incorporated into the perovskite structure. Oxides and fluorides comprise the vast majority of perovskite compounds (Goodenough & Longo, 1970), but the perovskite structure is found for many combinations of cations and anions. Chlorides (Brynestad, Yakel & Smith, 1966; Horowitz, Amit, Makovsky, Ben Dor & Kalman, 1982), bromides (Knochenmuss, Reber, Rajasekharan & Güdel, 1986), hydrides (Messer, Eastman, Mers & Maeland, 1964), oxynitrides (Bacher *et al.*, 1988) and sulfides (Clearfield, 1963; Rodier & Laruelle, 1970; Noël, Padiou & Prigent, 1975) are all known with the perovskite structure. Since the perovskite structure can accommodate such a wide variety of ions, the physical properties of perovskite compounds are wonderfully diverse. Perovskite compounds with interesting dielectric, magnetic, electrical, optical and catalytic properties are all known and have been widely studied. Technological applications vary from the dielectric properties of $BaTiO_3$ (Shirane, Danner & Pepinski, 1957; Galasso, 1969), which make it an important material in the capacitor industry, to the superconductivity displayed by $Ba(Bi_{1-x}Pb_x)O_3$ (Sleight, Gillson & Bierstedt, 1975) and the perovskite-related high-temperature cuprate superconductors, to the fascinating magnetoresistive and magnetostrictive properties of $(La_{1-x}Ca_x)MnO_3$ (Hwang, Cheong, Radaelli, Marezio & Batlogg, 1995; Fontcuberta *et al.*, 1996). The technological importance of these compounds and many others has made the perovskite structure one of the most important structures in all material science.

The ideal perovskite structure has an AMX_3 stoichiometry and belongs to the cubic space group $Pm\bar{3}m$. The A cation is surrounded by 12 X anions in a dodecahedral environment, the M cation is octahedrally coordinated by six X ions, and the X anions are coordinated by two M cations and four A cations. There are at least two ways of visualizing the structure. The most common description of the perovskite structure is a three-dimensional cubic network of corner-sharing MX_6 octahedra. In this description the A cation sits in the center of a cube defined by eight corner-sharing octahedral units. An alternative way of visualizing the perovskite structure is to begin with a cubic close-packed array of X anions, then replace one out of every four X ions with an A cation in an ordered way to obtain a cubic close-packed AX_3 array. Finally, all the octahedral holes in the AX_3 lattice that do not border an A cation are filled with M cations (25% of the octahedral holes).

Even though there are a large number of simple perovskites, AMX_3, the number of possible compounds is greatly expanded when multiple ions are substituted for one or more of the original ions. In most cases this substitution occurs on the cation sites and leads to a large class of compounds known either as double or complex perovskites, $AA'MM'X_6$. When such substitutions are made the ions can occupy the original cation site of the simple structure in either a random or an ordered fashion. If an ordered arrangement is adopted the symmetry and, in many cases, the size of the unit cell are changed.

Although the ideal perovskite structure is cubic there are several structural deviations from the ideal cubic structure, both for simple and ordered perovskites. In fact, there are many more distorted perovskites than there are cubic perovskites. Even the mineral perovskite itself, $CaTiO_3$, is orthorhombic rather than cubic (Sasaki, Prewitt, Bass & Schulze, 1987). Cubic, tetragonal, orthorhombic, rhombohedral, monoclinic and triclinic perovskites are all known. These structural distortions are of interest not only from a crystallographer's point of view, but also because they can have important effects

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on the physical properties of perovskite compounds, particularly the electrical and magnetic properties. The influence small structural changes have on the magnetoresistance properties of manganese- and cobalt-based perovskites is an important example of this phenomenon (Hwang, Cheong, Radaelli, Marezio & Batlogg, 1995; Fontcuberta *et al.*, 1996; Briceño, Chang, Sun, Schultz & Xiang, 1995).

Distortions from the ideal perovskite structure can be attributed to one of three mechanisms: distortions of the octahedra, cation displacements within the octahedra and tilting of the octahedra. The first two distortion mechanisms are driven by electronic instabilities of the octahedral metal ion. The Jahn–Teller distortion in $KCuF_3$ (Okazaki & Suemune, 1961) is an example of an electronic instability that leads to octahedral distortions. The ferroelectric displacement of titanium in $BaTiO_3$ (Shirane, Danner & Pepinski, 1957) is an example of an electronic instability that leads to cation displacements. Although these distortion mechanisms are important in many compounds, they are not discussed further in this paper. The third and most common distortion mechanism, octahedral tilting, can be realized by tilting essentially rigid MO_6 octahedra while maintaining their corner-sharing connectivity. This type of distortion is typically observed when the A cation is too small for the cubic MO_3 corner-sharing octahedral network. In such cases it is the lowest energy distortion mode, because the A—O distances can be shortened while the first coordination sphere about the M cation remains unchanged. (In terms of the MO_3 lattice, only the soft M—O—M bond angle is disturbed.) Geometrical considerations associated with this distortion are the subject of this paper, while the interatomic forces that drive octahedral tilting distortions are the subject of the following paper.

Over the years many investigators have studied distortions in the perovskite structure. Thomas has devised a system for classifying perovskites based on the polyhedral volumes of the A and M cations, which is particularly useful when both cation displacements and octahedral tilting occur (Thomas, 1989, 1996; Thomas & Beitollahi, 1994). O'Keeffe & Hyde (1977) structurally described the three most common octahedral tilt systems; $a^+b^-b^-$, $a^-a^-a^-$ and $a^+a^+a^+$. Megaw & Darlington (1975) studied, in great detail, the effect of octahedral tilting and octahedral deformation in rhombohedral perovskites and Deblieck and coworkers classified possible tilting combinations in perovskite-like ABX_4 compounds (Deblieck, 1986; Deblieck, Van Tendeloo, Van Landuyt & Amelinckx, 1985). However, almost certainly the most influential work was published in 1972 by Glazer. This work contained an eloquent description of all possible simple octahedral tilting combinations (Glazer, 1972). An updated description, including a few minor corrections, can be found in the book '*Space Groups for Solid State Scientists*', by Burns & Glazer (1990). A similar but much less known approach was developed in Russia around the same time by Aleksandrov (1976). However, it is the notation developed by Glazer, to describe octahedral tilting distortions, that has become standard notation in the perovskite literature.

Somewhat surprisingly, a paper by Leinenweber & Parise (1995) claimed that tilt systems $a^+a^+c^-$ (#5) and $a^+a^+a^-$ (#7) do not produce structures belonging to space group *Pmmn* as predicted by Glazer. They contended that these two tilt systems actually result in structures belonging to space group $P4_2/nmc$ (Leinenweber & Parise, 1995). In addition to this discrepancy, the complications that arise when cation ordering and octahedral tilting occur simultaneously have not been addressed in a comprehensive manner. Both of these issues are discussed in detail in the sections that follow.

2. A brief review of Glazer notation

The notation developed by Glazer over 20 years ago to describe octahedral tilting distortions in perovskites has become the standard by which such distortions are described (Glazer, 1972). A familiarity with this notation is necessary to follow the discussion throughout this paper. As an aid to those unfamiliar with Glazer notation a brief review is presented below. Further explanation can be found in the original reference (Glazer, 1972).

Using Glazer notation a tilt system is described by specifying the rotations of the octahedra about each of the three Cartesian axes. The rotations about each axis are described by two parameters. The first of these parameters is a letter specifying the magnitude of the rotation about that axis, relative to the magnitude of the rotations about the other Cartesian axes. For example, in the $a^+a^+a^+$ system the rotation angle is the same about each of the three axes; whereas in the $a^+a^+c^+$ tilt system the rotation angle about the z axis is different from the rotation angle about the x and y axes. The second parameter is a superscript indicating whether the rotations in adjacent layers are in the same or opposite directions. A negative superscript indicates that the rotations of two neighboring octahedra, along the tilt axis, are in the opposite directions, while a positive superscript is used when they tilt in the same direction. A zero superscript is used when no rotations occur about an axis.

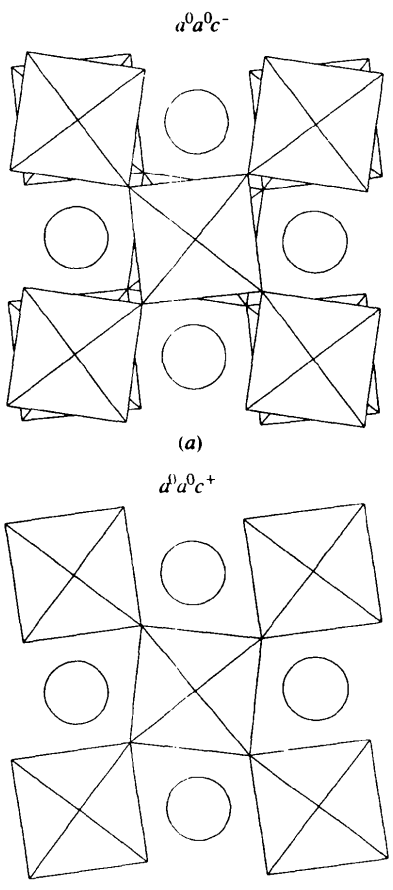
The clearest example of how Glazer notation describes tilted perovskite structures is a comparison of the two one-tilt systems, $a^0a^0c^+$ and $a^0a^0c^-$. The octahedra in both these tilt systems are rotated only about the fourfold axes parallel to the z axis. Fig. 1 shows a view looking down the z axis at eight octahedra in both tilt systems. It is clear in this figure that rotation of one octahedron forces four of the neighboring six octahedra to rotate in the opposite sense. This in turn causes all the octahedra in the (001) plane to be rotated with the same magnitude as the first octahedron. The final two neighboring octahedra, connected along the z

axis, are not coupled in the same way and can rotate independently. If these final two neighboring octahedra rotate in the same direction, as in Fig. 1(*b*), the $a^0a^0c^+$ tilt system results. If they rotate in the opposite direction, as in Fig. 1(*a*), the $a^0a^0c^-$ tilt system results. More complicated structures where independent tilting has to be considered in more than two layers is not described by Glazer notation.

3. Space-group descriptions of all 23 tilt systems

3.1. *Simulated structures and their comparison with Glazer's space-group assignments*

Although Glazer completely described the space group and symmetry associated with each tilting system it is far from trivial in many cases to turn that information into a model structure, complete with atomic positions. A complete description of the unit cell, where all the atomic positions are given, would be very useful in several situations. Such a model is needed to compare experimentally determined structures with ideal structures; as a starting point for Rietveld refinements; or to systematically study the differences in the ideal structures associated with each tilt system. With these applications in mind the *FORTRAN* program *POTATO* (Program Originated To Analyze Tilted Octahedra) was developed (Woodward, 1996). Given the Glazer symbol, the rotation angle about each of the Cartesian axes and the *M*—O bond distances as input, *POTATO* outputs a unit-cell description of the compound complete with atomic positions. The unit cell calculated by *POTATO* is always described as centrosymmetric triclinic ($P\bar{1}$) and doubled along all three axes. The true asymmetric unit is then found by examination of relationships between atomic positions or more conveniently with one of the automated routines now available [*e.g.* find symmetry within the *Insight*II package (Biosym Technologies, 1993)].* Using this approach the space group and



(*a*)

(*b*)

Fig. 1. A view looking down the *z* axis of two adjacent layers of octahedra for (*a*) the $a^0a^0c^-$ tilt system and (*b*) the $a^0a^0c^+$ tilt system. This view is a polyhedral representation of the crystal structure where each octahedron symbolizes a metal atom *M* surrounded by six O atoms. The metal atom is located in the center of the octahedron and an O atom is located at each corner. The round circles represent the *A* ions.

Table 1. *A comparison of the space groups predicted for each of the 23 simple tilt systems by Glazer (1972) with those generated by POTATO*

For tilt systems 4, 5, 6, 7, 17 and 18 the atomic positions calculated by *POTATO* always indicated slight distortions of the octahedra and,, therefore, no space group could be assigned as rigorously correct. This result is discussed in more detail in the text.

Tilt system number	Tilt system symbol	Space group (Glazer, 1972)	Space group (*POTATO*)
Three-tilt systems			
1	$a^+b^+c^+$	*Immm* (#71)	*Immm* (#71)
2	$a^+b^+b^+$	*Immm* (#71)	*Immm* (#71)
3	$a^+a^+a^+$	$Im\bar{3}$ (#204)	$Im\bar{3}$ (#204)
4	$a^+b^+c^-$	*Pmmn* (#59)	*Pmmn* (#59-2)
5	$a^+a^+c^-$	*Pmmn* (#50)	*Pmmn* (#59-2)
6	$a^+b^+b^-$	*Pmmn* (#59)	*Pmmn* (#59-2)
7	$a^+a^+a^-$	*Pmmn* (#59)	*Pmmn* (#59-2)
8	$a^+b^-c^-$	$A2_1/m11$ (#11)	$P2_1/m$ (#11-1)
9	$a^+a^-c^-$	$A2_1/m11$ (#11)	$P2_1/m$ (#11-1)
10	$a^+b^-b^-$	*Pmnb* (#62)	*Pnma* (#62)
11	$a^+a^-a^-$	*Pmnb* (#62)	*Pnma* (#62)
12	$a^-b^-c^-$	$F\bar{1}$ (#2)	$F\bar{1}$ (#2)
13	$a^-b^-b^-$	*I*2/*a* (#15)	*I*2/*a* (#15-3)
14	$a^-a^-a^-$	$R\bar{3}c$ (#167)	$R\bar{3}c$ (#167-2)
Two-tilt systems			
15	$a^0b^+c^+$	*Immm* (#71)	*Immm* (#71)
16	$a^0b^+b^+$	*I*4/*mmm* (#139)	*I*4/*mmm* (#139)
17	$a^0b^+c^-$	*Bmmb* (#63)	*Pmmn* (#59-2)
18	$a^0b^+b^-$	*Bmmb* (#63)	*Pmmn* (#59-2)
19	$a^0b^-c^-$	*F*2/*m*11 (#12)	*I*2/*m* (#12-3)
20	$a^0b^-b^-$	*Imcm* (#74)	*Imma* (#74)
One-tilt systems			
21	$a^0a^0c^+$	*C*4/*mmb* (#127)	*P*4/*mbm* (#127)
22	$a^0a^0c^-$	*F*4/*mmc* (#140)	*I*4/*mcm* (#140)
Zero-tilt systems			
23	$a^0a^0a^0$	$Pm\bar{3}m$ (#221)	$Pm\bar{3}m$ (#221)

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* Based on the results contained in this paper the current version of *POTATO* also gives the true space group and asymmetric unit for each tilt system.

Table 2. *Three different descriptions of the atomic positions of an $a^+a^+a^-$ tilted perovskite* ($a = 10°$)

The first two descriptions were generated in *POTATO*. In the first structure the distances were constrained to be constant (2.00 Å), while in the second structure the angles were constrained to remain 90°. The third description was generated using the O1, O2 and O3 positions common to all three descriptions and the symmetry generators associated with $P4_2/nmc$. All other oxygens in the unit cells can be generated from these 12 using the inversion centers on the *M* ions. The coordinates shown in bold are those where the second and third descriptions differ from the first description.

	Pmmn (*POTATO*, constant distance)			*Pmmn* (*POTATO*, 90° angles)			$P4_2/nmc$		
	x	*y*	*z*	*x*	*y*	*z*	*x*	*y*	*z*
O1	1/4	−0.0404	0.0482	1/4	−0.0404	0.0482	1/4	−0.0404	0.0482
O2	0.0482	1/4	−0.0404	0.0482	1/4	−0.0404	0.0482	1/4	−0.0404
O3	0.4518	1/4	−0.0404	0.4518	1/4	−0.0404	0.4518	1/4	−0.0404
O4	1/4	0.5404	0.0482	1/4	0.5404	0.0482	1/4	0.5404	0.0482
O5	−0.0404	0.0482	1/4	−0.0404	0.0482	**0.2513**	−0.0404	**0.0404**	1/4
O6	0.5404	0.0482	1/4	0.5404	0.0482	**0.2513**	0.5404	**0.0404**	1/4
O7	−0.0404	0.4518	1/4	−0.0404	0.4518	**0.2513**	−0.0404	**0.4596**	1/4
O8	0.5404	0.4518	1/4	0.5404	0.4518	**0.2513**	0.5404	**0.4596**	1/4
O9	1/4	0.0553	0.4703	1/4	**0.0394**	**0.4667**	1/4	**0.0482**	**0.4596**
O10	−0.0329	1/4	0.5535	**−0.0322**	1/4	**0.5542**	**−0.0404**	1/4	**0.5482**
O11	0.5329	1/4	0.5535	**0.5322**	1/4	**0.5542**	**0.5404**	1/4	**0.5482**
O12	1/4	0.4447	0.4703	1/4	**0.4606**	**0.4667**	1/4	**0.4518**	**0.4596**
	All distances 2.00 Å			1/3 of the distances 1.98 Å			1/3 of the distances 1.98 Å		
	1/3 of the angles 86.5°			All angles 90°			1/3 of the angles 88.4°		

asymmetric unit were calculated for each of the 23 Glazer tilt systems. The results of these calculations are compared with Glazer's findings in Table 1. The complete unit-cell descriptions for each tilt system are given in Appendix *B*.

One curiosity of this analysis was that for tilt systems $a^+b^+c^-$ (#4), $a^+a^+c^-$ (#5), $a^+b^+b^-$ (#6), $a^+a^+a^-$ (#7), $a^0b^+c^-$ (#17) and $a^0b^+b^-$ (#18) slight distortions of the octahedra were always necessary in order to retain the connectivity of the octahedra. Interestingly, the two tilt systems, $a^+a^+c^-$ (#5) and $a^+a^+a^-$ (#7), that Leinenweber & Parise (1995) claimed were incorrectly assigned by Glazer are among this group. At first this seemed to be a shortcoming of the algorithms used in *POTATO*. However, despite several modifications to *POTATO* this anomaly persisted. This led to the realization that the octahedral distortions were not caused by an error in *POTATO*, but rather are an inherent geometric property of these six tilt systems.* Proof of this claim is given in Appendix *B* and demonstrated in Appendix *C* by calculating the metal–oxygen vectors that define octahedra in the $a^+a^+a^-$ tilt system.

3.2. *Space-group assignments for tilt systems 4, 5, 6, 7, 17 and 18*

With the exception of the above-mentioned tilt systems, *POTATO* was able to generate perfectly linked networks of rigid octahedra for all tilt systems. Furthermore, for these tilt systems the space groups and lattice constants predicted by Glazer were found to agree exactly with the unit-cell descriptions generated by *POTATO*. With regard to those tilt systems where distortions of the octahedra must occur it becomes impossible to uniquely define a space group. The problem arises because the symmetry of the unit cell depends on the way in which the octahedra are distorted. Table 2 compares the atomic positions, bond distances and angles for a hypothetical compound belonging to the $a^+a^+a^-$ tilt system. The first two structures have symmetry described by space group *Pmmn*, as suggested by Glazer (Glazer, 1972; Burns & Glazer 1990). The difference between the two structures is that in the first structure all the bond distances have remained rigid, while in the second structure all the bond angles have been constrained to be 90°. The third structure has symmetry corresponding to space group $P4_2/nmc$, as suggested by Leinenweber & Parise (1995). It is evident from this table that the atomic positions are quite similar in all three structures. In Table 3 the results of a similar calculation for the $a^0b^+b^-$ tilt system are shown. Here the description in *Pmmn* as output from *POTATO* is very close to a unit cell having *Bmmb* symmetry, as predicted by Glazer. In this tilt system the octahedral distortions are very small. Although it is not possible to rigorously assign a space group for these tilt systems, it seems reasonable to assume that actual compounds will crystallize in the more symmetric of the two available space groups. Based on that assumption the $a^+a^+b^-$ and $a^+a^+a^-$ tilt systems are assigned to $P4_2/nmc$ and the $a^0b^+c^-$ and $a^0b^+b^-$ tilt systems assigned to *Bmmb* (standard setting *Cmcm*). The $a^+b^+c^-$ and $a^+b^+b^-$ tilt systems cannot be tetragonal, because the *a* and *b* lattice constants are different and so they remain orthorhombic, *Pmmn*, as originally suggested by Glazer (1972). Therefore, in essence none of the assignments in Glazer's work (Burns & Glazer, 1990) are incorrect.

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* O'Keeffe & Hyde (1977) had suggested that octahedral distortions must occur in some tilt systems, but did not identify which tilt systems.

Table 3. *Three different descriptions of the atomic positions of an $a^0b^+b^-$ tilted perovskite ($a = 10°$)*

The first two descriptions were generated in *POTATO*. In the first structure the distances were constrained to be constant (2.00 Å), while in the second structure the angles were constrained to remain at 90°. The third description was generated using the O1, O2 and O3 positions common to all three descriptions and the symmetry generators associated with *Bmmb* (nonstandard setting of space group #63, *Cmcm*). All other oxygens in the unit cells can be generated from these 12 using the inversion centers on the *M* ions. The coordinates shown in bold face type are those where the second and third description differ from the first description. The *Bmmb* coordinates have been shifted by (−1/4, −1/4, 0) for comparison with the *Pmmn* coordinates.

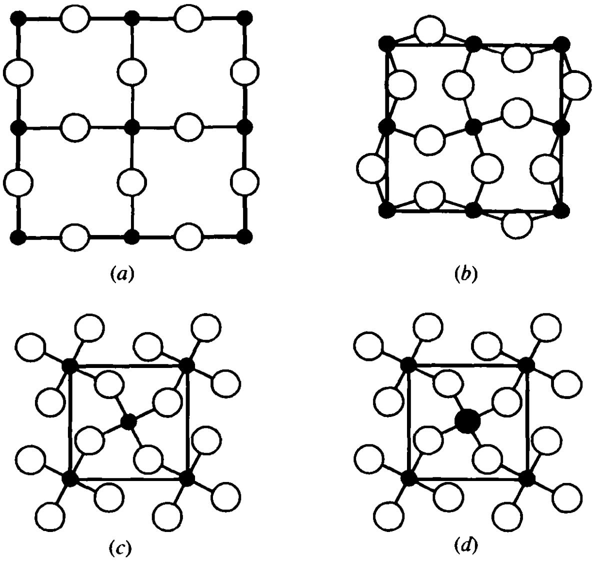
	Pmmn			*Pmmn*			*Bmmb*		
	(*POTATO*, constant distance)			(*POTATO*, 90° angles)					
	x	*y*	*z*	*x*	*y*	*z*	*x*	*y*	*z*
O1	1/4	−0.0438	0.0438	1/4	−0.0438	0.0438	1/4	−0.0438	0.0438
O2	0.0445	1/4	0.0038	0.0445	1/4	0.0038	0.0445	1/4	0.0038
O3	0.4555	1/4	0.0038	0.4555	1/4	0.0038	0.4555	1/4	0.0038
O4	1/4	0.5438	0.0438	1/4	0.5438	0.0438	1/4	0.5438	0.0438
O5	−0.0445	0.0038	1/4	−0.0445	0.0038	1/4	−0.0445	0.0038	1/4
O6	0.5445	0.0038	1/4	0.5445	0.0038	1/4	0.5445	0.0038	1/4
O7	−0.0445	0.4962	1/4	−0.0445	0.4962	1/4	−0.0445	0.4962	1/4
O8	0.5445	0.4962	1/4	0.5445	0.4962	1/4	0.5445	0.4962	1/4
O9	1/4	0.0451	0.4576	1/4	**0.0438**	0.4576	1/4	**0.0438**	**0.4562**
O10	−0.0431	1/4	0.5113	−0.0431	1/4	0.5113	**−0.0445**	1/4	**0.5038**
O11	0.5431	1/4	0.5113	0.5431	1/4	0.5113	**0.5445**	1/4	**0.5038**
O12	1/4	0.4549	0.4576	1/4	**0.4562**	0.4576	1/4	**0.4562**	**0.4562**
	All distances 2.000 Å			1/3 of the distances 1.998 Å			All distances 2.000 Å		
	1/6 of the angles 90.3°			All angles 90°			1/3 of the angles 90.9°		

However, for tilt systems $a^+a^+b^-$ (#5) and $a^+a^+a^-$ (#7) the space group $P4_2/nmc$ suggested by Leinenweber & Parise (1995) is equally justified and may be favored due to its higher symmetry.

4. Combined effect of cation ordering and octahedral tilting

In the cubic perovskite structure 1:1 ordering of the *M*-site cations requires the unit cell to be doubled along all three crystallographic directions, in order to maintain translational symmetry. The lattice also changes from simple cubic (space group $Pm\bar{3}m$) to face-centered cubic (space group $Fm\bar{3}m$). Octahedral tilting can also cause a doubling of the unit cell and often accompanies cation ordering. Therefore, it is instructive to consider the combined effects of cation ordering and octahedral tilting.

To illustrate the combined effect of cation ordering and octahedral tilting consider the tetragonally distorted $a^0a^0c^-$ tilt system. Upon tilting the structure distorts from cubic to face-centered tetragonal, space group $F4/mmc$. This is a nonstandard setting and the unit cell must be redefined in order describe the structure in terms of the standard space-group setting, $I4/mcm$. The new unit cell is body-centered and the relationship between the lattice constants in the face-centered cell and the new cell is $a_I = a_F/2^{1/2}$ and $c_I = c_F$. Introducing cation order lowers the symmetry once again to $I4/m$. The relationship between the *a* and *b* axes in the simple cubic cell, the face-centered tetragonal cell and the body-centered tetragonal cell is illustrated in Fig. 2. The introduction of cation ordering will always result in a loss of symmetry, either space-group symmetry elements or translational symmetry. The symmetry of the ordered unit cell must be lower than the disordered or simple unit cell, because the octahedral cation sites are no longer equivalent. This destroys any symmetry operations that relate neighboring octahedral sites. In this example, half


(*a*) (*b*)

(*c*) (*d*)

Fig. 2. The relationship between the *a* and *b* axes in (*a*) the simple cubic perovskite cell before an octahedral tilting distortion, (*b*) the face-centered tetragonal cell after an octahedral tilting distortion, (*c*) the body-centered tetragonal cell and (*d*) the ordered body-centered tetragonal cell. Mirror planes parallel to the *c* axis cut through the O atoms and relate the corner *M* ions (0,0,0) with the *M* ion at the center of the *ab* face ($\frac{1}{2}$,$\frac{1}{2}$,0) in the unit cell shown in (*c*). Ordering of different cations on the *M* site destroys those mirror planes (as well as all the glide planes), as shown in (*d*).

Table 4. *Space groups for all possible simple tilt systems both with and without 1:1 cation ordering*

Tilt system number	Tilt system symbol	Space group (no ordering)	Space group (1:1 ordering)
Three-tilt systems			
1	$a^+b^+c^+$	$Immm$ (#71)	$Pnnn$ (#48)
2	$a^+b^+b^+$	$Immm$ (#71)	$Pnnn$ (#48)
3	$a^+a^+a^+$	$Im\bar{3}$ (#204)	$Pn\bar{3}$ (#201)
4	$a^+b^+c^-$	$Pmmn$ (#59-2)	$P2/c$ (#13)
5	$a^+a^+c^-$	$P4_2/nmc$ (#137-2)	$P4_2/n$ (#86)
6	$a^+b^+b^-$	$Pmmn$ (#59-2)	$P2/c$ (#13)
7	$a^+a^+a^-$	$P4_2/nmc$ (#137-2)	$P4_2/n$ (#86)
8	$a^+b^-c^-$	$P2_1/m$ (#11-1)	$P\bar{1}$ (#2)
9	$a^+a^-c^-$	$P2_1/m$ (#11-1)	$P\bar{1}$ (#2)
10	$a^+b^-b^-$	$Pnma$ (#62)	$P2_1/n$ (#14-2)
11	$a^+a^-a^-$	$Pnma$ (#62)	$P2_1/n$ (#14-2)
12	$a^-b^-c^-$	$F\bar{1}$ (#2)	$F\bar{1}$ (#2)
13	$a^-b^-b^-$	$I2/a$ (#15-3)	$F\bar{1}$ (#2)
14	$a^-a^-a^-$	$R\bar{3}c$ (#167-2)	$R\bar{3}$ (#148-2)
Two-tilt systems			
15	$a^0b^+c^+$	$Immm$ (#71)	$Pnnn$ (#48)
16	$a^0b^+b^+$	$I4/mmm$ (#139)	$P4_2/nnm$ (#134)
17	$a^0b^+c^-$	$Cmcm$ (#63)	$C2/c$ (#15$\bar{1}$)
18	$a^0b^+b^-$	$Cmcm$ (#63)	$C2/c$ (#15$\bar{1}$)
19	$a^0b^-c^-$	$I2/m$ (#12$\bar{3}$)	$I\bar{1}$ (#2)
20	$a^0b^-b^-$	$Imma$ (#74)	$I2/m$ (#12$\bar{3}$)
One-tilt systems			
21	$a^0a^0c^+$	$P4/mbm$ (#127)	$P4/mnc$ (#128)
22	a^0a^0c	$I4/mcm$ (#140)	14/m (#87)
Zero-tilt systems			
23	$a^0a^0a^0$	$Pm\bar{3}m$ (#221)	$Fm\bar{3}m$ (#225)

of the symmetry elements are destroyed, including the mirror plane perpendicular to the fourfold axis and c glide planes parallel to the fourfold axis, lowering the symmetry of the ordered $a^0a^0c^-$ from $I4/mcm$ to $I4/m$.

In a similar manner the space groups for ordered perovskites in all 23 of the simple tilt systems can be determined. This analysis was performed using *International Tables for X-ray Crystallography* (1983, Vol. A) and double-checked using *POTATO* with an ordered arrangement of cations. The results are given in Table 4 along with the final space-group assignments for simple tilt systems. For each tilt system the space group describing the ordered perovskite is a maximal nonisomorphic subgroup of the space group describing the simple perovskite and, of course, all the ordered perovskite space groups are subgroups of $Fm\bar{3}m$. Unlike Glazer's work with the tilt systems of simple perovskites, there is no precedent in the literature with which to compare the results of Table 4. However, Leinenweber (1996) has derived a similar table of predicted space groups for ordered perovskites, using a completely different approach, similar to the method used originally by Glazer, and his results are in complete agreement with the results of Table 4.

POTATO is also able to generate unit-cell descriptions for ordered perovskites $A_2MM'O_6$, where the M'—O distance differs from the M—O distance. When the two bond distances are nonequivalent and structures are generated for each of the 23 tilt systems, distorted octahedra result for several of the tilt systems, including tilt systems 4–7 and 17–18. This is not unexpected because they are the same tilt systems where, as shown by geometrical arguments made earlier, the octahedra are forced to distort for simple perovskites. In addition, tilt systems 8–11 now also show slight distortions in their octahedra as the M—O and M'—O bond distances become increasingly different. It is uncertain at this time whether this is a geometrical limitation of these tilt systems when the M—O and M—O bond distances differ. More work is necessary to conclusively prove this point.

5. Conclusions

With the aid of *POTATO* the 23 tilt systems originally described by Glazer have been investigated. It has been shown that in the tilt systems $a^+a^+a^-$, $a^+b^+b^-$, $a^+a^+c^-$, $a^+b^+c^-$, $a^0b^+b^-$ and $a^0b^+c^-$ it is not possible to link together a three-dimensional network of perfectly rigid octahedra. In these tilt systems small distortions of the octahedra must occur to preserve connectivity of the octahedra. The distortions are smaller in the $a^0b^+c^-$ and $a^0b^+b^-$ tilt systems than they are in the other four tilt systems. These distortions can have important consequences, particularly on the crystallography. For example, in tilt systems $a^+a^+c^-$ (#5) and $a^+a^+a^-$ (#7) it appears as though $P4_2/nmc$ is a more reasonable space-group assignment than $Pmmn$, based on its higher symmetry. Finally, a table of predicted space groups for compounds that display both cation ordering and octahedral tilting has been derived.

I would like to thank Dr Arthur Sleight for his support and many helpful suggestions throughout this project. I would also like to thank Dr John Evans for a careful and critical reading of the manuscript and countless discussions over the entire period of this work.

APPENDIX *A*

Standard unit-cell descriptions of distorted perovskites

A practical difficulty of working with distorted perovskites is the widespread use of nonstandard cell settings. These types of descriptions are useful when comparing two different structures, but can be confusing when many different compounds and space groups are examined. Transforming to a standard setting, which is necessary when using many software packages, can sometimes be confusing, time consuming and lead to possible errors. Adding to the confusion is the fact that among the space groups corresponding to the different tilt systems there are several different choices of origin and unit-cell size. In the course of this analysis, using

Table 5. *Atomic positions and unit-cell descriptions for all the space groups generated by simple tilting of the MO_6 octahedra*

The number immediately below the space group name is the space group number in *International Tables for X-ray Crystallography* (1983, Vol. A). All the space-group descriptions are standard settings. The other number in the first column signifies the tilt systems corresponding to each space group.

Space group	Unit-cell size	Cation positions	Anion positions	Comments
Immm (A-71) Tilt systems 1, 2 and 15	$a \simeq 2a_p$ $b \simeq 2a_p$ $c \simeq 2a_p$	*A* cation $(2a)$ $0, 0, 0$ $(2b)$ $0, \frac{1}{2}, \frac{1}{2}$ $(2c)$ $\frac{1}{2}, \frac{1}{2}, 0$ $(2d)$ $\frac{1}{2}, 0, \frac{1}{2}$ *M* cation $(8k)$ $\frac{1}{4}, \frac{1}{4}, \frac{1}{4}$	$(8l)$ $0, y, z$ $y \simeq \frac{1}{4}, z \simeq \frac{1}{4}$ $(8m)$ $x, 0, z$ $x \simeq \frac{1}{4}, z \simeq \frac{1}{4}$ $(8n)$ $x, y, 0$ $x \simeq \frac{1}{4}, y \simeq \frac{1}{4}$	Shift by $\frac{1}{4}, \frac{1}{4}, \frac{1}{4}$
Im$\bar{3}$ (A-204) Tilt system 3	$a \simeq 2a_p$ $b \simeq 2a_p$ $c \simeq 2a_p$	*A* cation $(2a)$ $0, 0, 0$ $(6b)$ $0, \frac{1}{2}, \frac{1}{2}$ *M* cation $(8c)$ $\frac{1}{4}, \frac{1}{4}, \frac{1}{4}$	$(24g)$ $0, y, z$ $y \simeq \frac{1}{4}, \simeq \frac{1}{4}$	Shift by $\frac{1}{4}, \frac{1}{4}, \frac{1}{4}$
Pmmn (A-59-2) Tilt systems 4 and 6	$a \simeq 2a_p$ $b \simeq 2a_p$ $c \simeq 2a_p$	*A* cation $(2a)$ $\frac{1}{4}, \frac{1}{4}, z$ $z \simeq \frac{1}{4}$ $(2a)$ $\frac{1}{4}, \frac{1}{4}, z$ $z \simeq \frac{3}{4}$ $(2b)$ $\frac{1}{4}, \frac{3}{4}, z$ $z \simeq \frac{1}{4}$ $(2b)$ $\frac{1}{4}, \frac{3}{4}, z$ $z \simeq \frac{3}{4}$ *M* cation $(4c)$ $0, 0, 0$ $(4d)$ $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$	$(4e)$ $\frac{1}{4}, y, z$ $y \simeq 0, z \simeq 0$ $(4e)$ $\frac{1}{4}, y, z$ $y \simeq 0, z \simeq \frac{1}{2}$ $(4f)$ $x, \frac{1}{4}, z$ $y \simeq 0, z \simeq 0$ $(4f)$ $x, \frac{1}{4}, z$ $y \simeq 0, z \simeq \frac{1}{2}$ $(8g)$ x, y, z $x \simeq 0, y \simeq 0, z \simeq \frac{1}{4}$	No origin shift Out-of-phase tilting about the *c* axis
$P4_2/nmc$ (A-137-2) Tilt systems 5 and 7	$a \simeq 2a_p$ $b \simeq 2a_p$ $c \simeq 2a_p$	*A* cation $(2a)$ $\frac{3}{4}, \frac{1}{4}, \frac{3}{4}$ $(2b)$ $\frac{3}{4}, \frac{1}{4}, \frac{1}{4}$ $(4d)$ $\frac{1}{4}, \frac{1}{4}, z$ $z \simeq \frac{1}{4}$ *M* cation $(8e)$ $0, 0, 0$	$(8g)$ $\frac{1}{4}, y, z$ $y \simeq 0, z \simeq 0$ $(8g)$ $\frac{1}{4}, y, z$ $y \simeq \frac{1}{2}, z \simeq \frac{1}{2}$ $(8f)$ $x, -x, \frac{1}{4}$ $x \simeq \frac{1}{2}$	No origin shift Out-of-phase tilting about the *c* axis.
$P2_1/m$ (A-11-1) Tilt systems 8 and 9	$a \simeq 2^{1/2}a_p$ $b \simeq 2a_p$ $c \simeq 2^{1/2}a_p$ $\beta \neq 90°$	*A* cation $(2e)$ $x, \frac{1}{4}, z$ $x \simeq 0, z \simeq 0$ $(2e)$ $x, \frac{1}{4}, z$ $x \simeq \frac{1}{2}, z \simeq \frac{1}{2}$ *M* cation $(2b)$ $\frac{1}{2}, 0, 0$ $(2c)$ $0, 0, \frac{1}{2}$	$(2e)$ $x, \frac{1}{4}, z$ $x \simeq 0, z \simeq \frac{1}{2}$ $(2e)$ $x, \frac{1}{4}, z$ $x \simeq \frac{1}{2}, z \simeq 0$ $(4f)$ x, y, z $x \simeq \frac{1}{4}, y \simeq 0, z \simeq \frac{1}{4}$ $(4f)$ x, y, z $x \simeq \frac{1}{4}, y \simeq 0, z \simeq \frac{3}{4}$	Shift by $0, 0, \frac{1}{2}$ In-phase tilting about the *b* axis
Pnma (A-62) Tilt systems 10 and 11	$a \simeq 2^{1/2}a_p$ $b \simeq 2a_p$ $c \simeq 2^{1/2}a_p$ $\beta \neq 90°$	*A* cation $(4c)$ $x, \frac{1}{4}, z$ $x \simeq 0, z \simeq 0$ *M* cation $(4b)$ $\frac{1}{2}, 0, 0$	$(4c)$ $x, \frac{1}{4}, z$ $x \simeq 0, z \simeq \frac{1}{2}$ $(8d)$ x, y, z $x \simeq \frac{1}{4}, y \simeq 0, z \simeq \frac{1}{4}$	Shift by $0, 0, \frac{1}{2}$ In-phase tilting about the *b* axis
$F\bar{1}$ (A-2) Tilt system 12	$a \simeq 2a_p$ $b \simeq 2a_p$ $c \simeq 2a_p$ $\alpha \neq \beta \neq \gamma \neq 90°$	*A* cation $(8i)$* x, y, z $x \simeq \frac{1}{4}, y \simeq \frac{1}{4}, z \simeq \frac{1}{4}$ *M* cation $(4a)$ $0, 0, 0$ $(4b)$ $0, 0, \frac{1}{2}$	$(8i)$ x, y, z $x \simeq \frac{1}{4}, y \simeq 0, z \simeq 0$ $(8i)$ x, y, z $z \simeq 0, y \simeq \frac{1}{4}, z \simeq 0$ $(8i)$ x, y, z $x \simeq 0, y \simeq 0, z \simeq \frac{1}{4}$	No origin shift The standard setting is $P\bar{1}$, add face-centered generators for $F\bar{1}$
$I2/a$ (A-15-3) Tilt system 13	$a \simeq 2a_p$ $b \simeq 2^{1/2}a_p$ $c \simeq 2^{1/2}a_p$ $\beta \neq 90°$	*A* cation $(4e)$ $\frac{1}{4}, y, 0$ $y \simeq 0$ *M* cation $(4b)$ $0, \frac{1}{2}, 0$	$(4e)$ $\frac{1}{4}, y, 0$ $y \simeq \frac{1}{2}$ $(8f)$ x, y, z $x \simeq 0, y \simeq \frac{1}{4}, z \simeq \frac{1}{4}$	Shift by $0, \frac{1}{2}, 0$
$R\bar{3}c$ (A-167-2) Tilt system 14	$a \simeq 2^{1/2}a_p$ $b \simeq 2^{1/2}a_p$ $c \simeq 2^{1/2}a_p$ $\alpha \neq \beta \neq \gamma \simeq 60°$	*A* cation $(2a)$ $\frac{1}{4}, \frac{1}{4}, \frac{1}{4}$ *M* cation $(2b)$ $0, 0, 0$	$(6e)$ $x, \frac{1}{2} - x, \frac{1}{4}$ $x \simeq \frac{3}{4}$	No origin shift Rhombohedral cell

Table 5 (*cont.*)

Space group	Unit-cell size	Cation positions	Anion positions	Comments
$I4/mmm$ (A-139) Tilt system 16	$a \simeq 2a_p$ $b \simeq 2a_p$ $c \simeq 2a_p$	A cation (2*a*) $0, 0, 0$ (2*b*) $0, 0, \frac{1}{2}$ (4*c*) $\frac{1}{2}, 0, 0$ M cation (8*f*) $\frac{1}{4}, \frac{1}{4}, \frac{1}{4}$	(8*h*) $x, x, 0 \quad x \simeq \frac{1}{4}$ (16*n*) $0, y, z \quad y \simeq \frac{1}{4}, z \simeq \frac{1}{4}$	Shift by $-\frac{1}{4}, \frac{1}{4}, \frac{1}{4}$ No tilting about the c axis
$Cmcm$ (A-63) Tilt systems 17 and 18	$a \simeq 2a_p$ $b \simeq 2a_p$ $c \simeq 2a_p$	A cation (4*c*) $0, y, \frac{1}{4} \quad y \simeq 0$ (4*c*) $0, y, \frac{1}{4} \quad y \simeq \frac{1}{2}$ M cation (8*d*) $\frac{1}{4}, \frac{1}{4}, 0$	(8*e*) $x, 0, 0 \quad x \simeq \frac{1}{4}$ (8*f*) $0, y, z \quad y \simeq \frac{1}{4}, z \simeq 0$ (8*g*) $x, y, \frac{1}{4} \quad x \simeq \frac{1}{4}, y \simeq \frac{1}{4}$	Shift by $\frac{1}{4}, -\frac{1}{4}, 0$ In-phase tilting about the c axis
$I2/m$ (A-12-3) Tilt system 19	$a \simeq 2^{1/2}a_p$ $b \simeq 2a_p$ $c \simeq 2^{1/2}a_p$ $\beta \neq 90°$	A cation (4*i*) $x, 0, z \quad x \simeq \frac{1}{4}, z \simeq \frac{3}{4}$ M cation (4*e*) $\frac{1}{4}, \frac{1}{4}, \frac{1}{4}$	(4*i*) $x, 0, z \quad x \simeq \frac{1}{4}, z \simeq \frac{1}{4}$ (4*g*) $0, y, 0 \quad y \simeq \frac{1}{4}$ (4*h*) $\frac{1}{2}, y, 0 \quad y \simeq \frac{1}{4}$	Shift by $\frac{1}{4}, \frac{1}{4}, \frac{1}{4}$ No tilting about the b axis
$Imma$ (A-74) Tilt system 20	$a \simeq 2a_p$ $b \simeq 2^{1/2}a_p$ $c \simeq 2^{1/2}a_p$	A cation (4*e*) $0, \frac{1}{4}, z \quad z \simeq \frac{3}{4}$ M cation (4*b*) $\frac{1}{4}, \frac{1}{4}, \frac{1}{4}$	(4*e*) $0, \frac{1}{4}, z \quad z \simeq \frac{1}{4}$ (8*g*) $x, 0, 0 \quad x \simeq \frac{1}{4}$	Shift by $\frac{1}{4}, \frac{1}{4}, \frac{1}{4}$ No tilting about the a axis
$P4/mbm$ (A-127) Tilt system 21	$a \simeq 2^{1/2}a_p$ $b \simeq 2^{1/2}a_p$ $c \simeq a_p$	A cation (2*c*) $0, \frac{1}{2}, \frac{1}{2}$ M cation (2*a*) $0, 0, 0$	(2*b*) $0, 0, \frac{1}{2}$ (4*g*) $x, x + \frac{1}{2}, 0 \quad x \simeq \frac{1}{4}$	No origin shift In-phase tilting about the c axis
$I4/mcm$ (A-140) Tilt system 22	$a \simeq 2^{1/2}a_p$ $b \simeq 2^{1/2}a_p$ $c \simeq 2a_p$	A cation (4*b*) $0, \frac{1}{2}, \frac{1}{4}$ M cation (4*c*) $0, 0, 0$	(4*a*) $0, 0, \frac{1}{4}$ (8*h*) $x, x + \frac{1}{2}, 0 \quad x \simeq \frac{1}{4}$	No origin shift Out-of-phase tilting about the c axis
$Pm\bar{3}m$ (A-221) Tilt system 23	$a = b = c = a_p$	A cation (1*b*) $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$ M cation (1*a*) $0, 0, 0$	(3*d*) $\frac{1}{2}, 0, 0$	No origin shift

Table 6. *Atomic positions and unit-cell descriptions for all the space groups generated by tilting of the octahedra in combination with 1:1 cation ordering*

The number immediately below the space group name is the space-group number in *International Tables for X-ray Crystallography* (1983, Vol. A). All the space-group descriptions are standard settings. The other number in the first column signifies the tilt systems corresponding to each space group. Note that the ordered tilt system #20 and simple tilt system #19 both are assigned to space group $I2/m$, but the choice of origin and atomic positions are different for the two structures.

Space group	Unit-cell size	Cation positions	Anion positions	Comments
$Pnnn$ (A-48-1) Tilt systems 1, 2 and 15	$a \simeq 2a_p$ $b \simeq 2a_p$ $c \simeq 2a_p$	A cation (2*a*) $0, 0, 0$ (2*b*) $0, \frac{1}{2}, \frac{1}{2}$ (2*c*) $\frac{1}{2}, \frac{1}{2}, 0$ (2*d*) $\frac{1}{2}, 0, \frac{1}{2}$ M and M' cations (4*e*) $\frac{1}{4}, \frac{1}{4}, \frac{1}{4} \quad (M)$ (4*f*) $\frac{3}{4}, \frac{3}{4}, \frac{3}{4} \quad (M')$	(8*m*) x, y, z $x \simeq 0, y \simeq \frac{1}{4}, z \simeq \frac{1}{4}$ (8*m*) x, y, z $x \simeq \frac{1}{4}, y \simeq 0, z = \frac{1}{4}$ (8*m*) x, y, z $x \simeq \frac{1}{4}, y \simeq \frac{1}{4}, z \simeq 0$	Shift by $\frac{1}{4}, \frac{1}{4}, \frac{1}{4}$
$Pn\bar{3}$ (A-201-1)	$a \simeq 2a_p$ $b \simeq 2a_p$ $c \simeq 2a_p$	A cation (2*a*) $0, 0, 0$ (6*d*) $0, \frac{1}{2}, \frac{1}{2}$	(24*h*) x, y, z $x \simeq 0, y \simeq \frac{1}{4}, z \simeq \frac{1}{4}$	Shift by $\frac{1}{4}, \frac{1}{4}, \frac{1}{4}$

Table 6 (*cont.*)

Space group	Unit-cell size	Cation positions	Anion positions	Comments
Tilt system 3		M and M' cations $(4b)\ \frac{1}{4},\frac{1}{4},\frac{1}{4}\quad (M)$ $(4c)\ \frac{3}{4},\frac{3}{4},\frac{3}{4}\quad (M')$		
$P2/c$ (A-13-5) Tilt systems 4 and 6	$a \simeq 2a_p$ $b \simeq 2a_p$ $c \simeq 2a_p$ $\gamma \neq 90°$	A cation $(2e)\ \frac{1}{4},\frac{1}{4},z\quad z \simeq \frac{1}{4}$ $(2e)\ \frac{1}{4},\frac{1}{4},z\quad z \simeq \frac{3}{4}$ $(2f)\ \frac{1}{4},\frac{3}{4},z\quad z \simeq \frac{1}{4}$ $(2f)\ \frac{1}{4},\frac{3}{4},z\quad z \simeq \frac{3}{4}$ M and M' cations $(2a)\ 0,0,0\quad (M)$ $(2b)\ \frac{1}{2},0,\frac{1}{2}\quad (M)$ $(2c)\ 0,0,\frac{1}{2}\quad (M')$ $(2d)\ \frac{1}{2},0,0\quad (M')$	$6x(4g)\ x,y,z$ $x \simeq \frac{1}{4}, y \simeq 0, z \simeq 0$ $x \simeq 0, y \simeq \frac{1}{4}, z \simeq 0$ $x \simeq 0, y \simeq 0, z \simeq \frac{1}{4}$ $x = 0, y \simeq \frac{1}{4}, z \simeq \frac{1}{2}$ $x \simeq \frac{1}{2}, y \simeq 0, z \simeq \frac{1}{4}$ $x \simeq \frac{1}{4}, y \simeq 0, z \simeq \frac{1}{2}$	No origin shift Out-of-phase tilting about the c axis
$P4_2/n$ (A-86) Tilt systems 5 and 7	$a \simeq 2a_p$ $b \simeq 2a_p$ $c \simeq 2a_p$	A cation $(2a)\ \frac{1}{4},\frac{1}{4},\frac{1}{4}$ $(2b)\ \frac{1}{4},\frac{1}{4},\frac{3}{4}$ $(4e)\ \frac{3}{4},\frac{1}{4},z\quad z \simeq \frac{1}{4}$ M and M' $(4c)\ 0,0,0\quad (M)$ $(4d)\ \frac{1}{2},\frac{1}{2},\frac{1}{2}\quad (M')$	$(8g)\ x,y,z$ $x \simeq \frac{1}{4}, y \simeq 0, z \simeq 0$ $(8g)\ x,y,z$ $x \simeq \frac{1}{4}, y \simeq 0, z \simeq \frac{1}{2}$ $(8g)\ x,y,z.$ $x \simeq 0, y \simeq 0, z \simeq \frac{1}{4}$	No origin shift Out-of-phase tilting about the c axis
$P2_1/n$ (A-14-2) Tilt systems 10 and 11	$a \simeq 2^{1/2}a_p$ $b \simeq 2^{1/2}a_p$ $c \simeq 2a_p$ $\beta \neq 90°$	A cation $(4e)\ x,y,z$ $x \simeq 0, y \simeq 0, z \simeq \frac{1}{4}$ M and M' cations $(4c)\ 0,\frac{1}{2},0\quad (M)$ $(4d)\ \frac{1}{2},0,0\quad (M')$	$(4e)\ x,y,z$ $x \simeq \frac{1}{4}, y \simeq \frac{1}{4}, z \simeq 0$ $(4e)\ x,y,z$ $x \simeq \frac{1}{4}, y \simeq \frac{1}{4}, z \simeq \frac{1}{2}$ $(4e)\ x,y,z$ $x \simeq \frac{1}{2}, y \simeq 0, z \simeq \frac{1}{4}$	Shift by $0,\frac{1}{2},0$ In-phase tilting about the b axis
$P\bar{1}$ (A-2) Tilt systems 8 and 9 $F\bar{1}$ (A-2) Tilt systems 1, 2 and 13 $I\bar{1}$ (A-2) Tilt system 19	$P\bar{1}$ and $F\bar{1}$ $a \simeq 2a_p$ $b \simeq 2a_p$ $c \simeq 2a_p$ $\alpha \neq \beta \neq \gamma \neq 90°$ $I\bar{1}$ $a \simeq 2^{1/2}a_p$ $b \simeq 2a_p$ $c \simeq 2^{1/2}a_p$ $\beta \neq 90°$	A cation $(2i)\ x,y,z$ $x \simeq \frac{1}{4}, y \simeq \frac{1}{4}, z \simeq \frac{1}{4}$ $(2i)\ x,y,z$ $x \simeq \frac{3}{4}, y \simeq \frac{1}{4}, z \simeq \frac{1}{4}$ $(2i)\ x,y,z$ $x \simeq \frac{1}{4}, y \simeq \frac{3}{4}, z \simeq \frac{1}{4}$ $(2i)\ x,y,z$ $x \simeq \frac{1}{4}, y \simeq \frac{1}{4}, z \simeq \frac{3}{4}$ M cation $(1a)+(1e)+(1f)+(1g)$ M' cation $(1b)+(1c)+(1d)+(1h)$	$12x(2i)\ x,y,z$ $x \simeq \frac{1}{4}, y \simeq 0, z \simeq 0$ $x \simeq 0, y \simeq \frac{1}{4}, z \simeq 0$ $x \simeq 0, y \simeq 0, z \simeq \frac{1}{4}$ $x \simeq \frac{1}{4}, y \simeq \frac{1}{2}, z \simeq 0$ $x \simeq \frac{1}{4}, y \simeq 0, x \simeq \frac{1}{2}$ $x \simeq 0, y \simeq \frac{1}{4}, z \simeq \frac{1}{2}$ $x \simeq \frac{1}{2}, y \simeq \frac{1}{4}, z \simeq 0$ $x \simeq 0, y \simeq \frac{1}{2}, z \simeq \frac{1}{4}$ $x \simeq \frac{1}{2}, y \simeq 0, z \simeq \frac{1}{4}$ $x \simeq \frac{1}{4}, y \simeq \frac{1}{2}, z \simeq \frac{1}{2}$ $x \simeq \frac{1}{2}, y \simeq \frac{1}{4}, z \simeq \frac{1}{2}$ $x \simeq \frac{1}{2}, y \simeq \frac{1}{2}, z \simeq \frac{1}{4}$	No origin shift The standard setting is $P\bar{1}$ For $F\bar{1}$ use face-centered generators in addition For $I\bar{1}$ use body-centered generators in addition
$R\bar{3}$ (A-148-2) Tilt system 14	$a \simeq 2^{1/2}a_p$ $b \simeq 2^{1/2}a_p$ $c \simeq 2^{1/2}a_p$ $\alpha \simeq \beta \neq \gamma \simeq 60°$	A cation $(2c)\ x,x,x\quad x \simeq \frac{1}{4}$ M and M' cations $(1a)\ 0,0,0\quad (M)$ $(1b)\ \frac{1}{2},\frac{1}{2},\frac{1}{2}\quad (M')$	$(6f)\ x,y,z$ $x \simeq \frac{3}{4}, y \simeq \frac{3}{4}, z \simeq \frac{1}{4}$	No origin shift Rhombohedral cell
$P4_2/nnm$ (A-134-1) Tilt system 16	$a \simeq 2a_p$ $b \simeq 2a_p$ $c \simeq 2a_p$	A cation $(2a)\ 0,0,0$ $(2b)\ 0,0,\frac{1}{2}$ $(4c)\ \frac{1}{2},0,0$ M and M' cations $(4e)\ \frac{1}{4},\frac{1}{4},\frac{1}{4}\quad (M)$ $(4f)\ \frac{3}{4},\frac{3}{4},\frac{3}{4}\quad (M')$	$(8m)\ x,x,z$ $x \simeq \frac{1}{4}, z \simeq 0$ $(16n)\ x,y,z$ $x \simeq \frac{1}{4}, y \simeq \frac{1}{2}, z \simeq \frac{3}{4}$	Shift by $-\frac{1}{4},\frac{1}{4},\frac{1}{4}$ No tilting about the c axis
$C2/c$ (A-15-1) Tilt systems 17 and 18	$a \simeq 2a_p$ $b \simeq 2a_p$ $c \simeq 2a_p$ $\beta \neq 90°$	A cation $(4e)\ 0,y,\frac{1}{4}\quad y \simeq 0$ $(4e)\ 0,y,\frac{1}{4}\quad y \simeq \frac{1}{2}$ M and M' cations $(4c)\ \frac{1}{4}.\frac{1}{4},0\quad (M)$ $(4d)\ \frac{1}{4},\frac{1}{4},\frac{1}{2}\quad (M')$	$(8f)\ x,y,z$ $x \simeq \frac{1}{4}, y \simeq 0, z \simeq 0$ $(8f)\ x,y,z$ $x \simeq 0, y \simeq \frac{1}{4}, z \simeq 0$ $(8f)\ x,y,z$ $x \simeq \frac{1}{4}, y \simeq \frac{1}{4}, z \simeq \frac{1}{4}$	Shift by $\frac{1}{4},-\frac{1}{4},0$ In-phase tilting about the c axis

Table 6 (*cont.*)

Space group	Unit-cell size	Cation positions	Anion positions	Comments
$I2/m$ (A-12-3) Tilt system 20	$a \simeq 2^{1/2}a_p$ $b = 2^{1/2}a_p$ $c \simeq 2a_p$ $\beta \neq 90°$	A cation (4i) $x, 0, z$ $x \simeq \frac{1}{2}, z \simeq \frac{1}{4}$ M and M' cations (2a) $0, 0, 0$ (M) (2d) $\frac{1}{2}, \frac{1}{2}, 0$ (M')	(4i) $x, 0, z$ $x \simeq 0, z \simeq \frac{1}{4}$ (8j) $x, y, z,$ $x \simeq \frac{1}{4}, y \simeq \frac{1}{4}, z \simeq 0$	No origin shift No tilting about the c axis
$P4/mnc$ (A-128) Tilt system 21	$a \simeq 2^{1/2}a_p$ $b \simeq 2^{1/2}a_p$ $c \simeq 2a_p$	A cation (2c) $0, \frac{1}{2}, \frac{1}{4}$ M and M' cations (2a) $0, 0, 0$ (M) (2b) $0, 0, \frac{1}{2}$ (M')	(4e) $0, 0, z$ $z \simeq \frac{1}{4}$ (8h) $x, y, 0$ $x \simeq \frac{1}{4}, y \simeq \frac{1}{4}$	No origin shift In-phase tilting about the c axis
$I4/m$ (A-87) Tilt system 22	$a \simeq 2^{1/2}a_p$ $b \simeq 2^{1.2}a_p$ $c \simeq 2a_p$	A cation (4b) $0, \frac{1}{2}, \frac{1}{4}$ M and M' cations (2a) $0, 0, 0$ (M) (2b) $0, 0, \frac{1}{2}$ (M')	(4e) $0, 0, z$ $z \simeq \frac{1}{4}$ (8h) $x, y, 0$ $x \simeq \frac{1}{4}, y \simeq \frac{1}{4}$	No origin shift Out-of-phase tilting about the c axis
$Fm\bar{3}m$ (A-225) Tilt system 23	$a = b = c = 2a_p$	A cation (8c) $\frac{1}{4}, \frac{1}{4}, \frac{1}{4}$ M and M' cations (4a) $0, 0, 0$ (M) (4b) $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$ (M')	(24e) $x, 0, 0$ $x \simeq \frac{1}{4}$	No origin shift

POTATO, the standard space-group description of each tilt system was determined. These descriptions are given in Table 5 for simple perovskites and in Table 6 for ordered perovskites. One note of caution: both the $a^0b^-c^-$ (#19) tilt system among simple perovskites (Table 5) and the $a^0b^-b^-$ (#20) tilt system for ordered perovskites (Table 6) belong to the $I2/m$ space group, but the atomic positions are different for the two tilt systems. Hopefully, this information will be of practical assistance to others working with distorted perovskite structures.

APPENDIX *B*
Vector proof of distorted octahedra in tilt systems 4, 5, 6, 7, 17 and 18

In Glazer's original paper he points out that a mirror plane exists perpendicular to any axis about which there is either no tilting or in-phase tilting (Glazer, 1972). These mirror planes are located halfway between the octahedra they separate (for example, at $x = \frac{1}{4}$ and $x = \frac{3}{4}$ in the doubled unit cell). With this in mind consider any of the ++– or 0+– tilt systems mentioned above. All these tilt systems have mirror planes located perpendicular to the x and y axes. As a consequence of having two mutually perpendicular mirror planes these tilt systems must have orthogonal axes. Now consider the octahedron centered at the origin and the octahedron located directly above it along the c axis. The orientation of each octahedron can be uniquely described by three metal–oxygen vectors pointing approximately down the x, y and z axes. For the octahedron at the origin these vectors will be denoted by

$$\mathbf{V}_{1x} = A1\mathbf{x} + B1\mathbf{y} + C1\mathbf{z},$$
$$\mathbf{V}_{1y} = A2\mathbf{x} + B2\mathbf{y} + C2\mathbf{x},$$
$$\mathbf{V}_{1z} = A3\mathbf{x} + B3\mathbf{y} + C3\mathbf{z}.$$

While for the second octahedron under consideration the metal–oxygen vectors describing the tilting of this octahedra can be defined as

$$\mathbf{V}_{2x} = a1\mathbf{x} + b1\mathbf{y} + c1\mathbf{z},$$
$$\mathbf{V}_{2y} = a2\mathbf{x} + b2\mathbf{y} + c2\mathbf{z},$$
$$\mathbf{V}_{2z} = a3\mathbf{x} + b3\mathbf{y} + c3\mathbf{z}.$$

The relationship between these six vectors is shown in Fig. 3. The other three M—O vectors associated with each octahedron can be generated using the inversion center at the origin of the octahedron and provide no additional information about the orientation of the octahedra.

The inversion center that must be present at the origin of each octahedron restricts the M-cation positions to lie on the unit-cell axes. The metal centers of these two octahedra will be located at (0,0,0) and (0,0,$\frac{1}{2}$). Couple this with the fact that the axes are orthogonal and it is clear that in order for the two octahedra to be linked together and the second metal cation to be located directly above the first metal cation on the z axis the following relations must hold

$$a3 = A3,$$
$$b3 = B3,$$

and in order to keep all the M—O vectors the same length (necessary to maintain perfect octahedra), the third component of vector $\mathbf{V}_{2z}$ is also uniquely determined as

$$c3 = -C3.$$

Therefore, in any of the ++− or 0+− tilt systems an arbitrary tilt of the octahedron at the origin fixes the vector $\mathbf{V}_{2z}$.

The vectors $\mathbf{V}_{2x}$ and $\mathbf{V}_{2y}$ are also subject to several constraints. To begin with, the oxygen ions at the end of both these vectors must lie on the mirror planes discussed previously. This requirement also holds true for the octahedron at the origin so that

$$a1 = A1 = \frac{1}{2}\mathbf{a},$$
$$b2 = B2 = \frac{1}{2}\mathbf{b},$$

where **a** and **b** are the lattice constants along the x and y axes, respectively. Now the only unknown components remaining are $b1$, $c1$, $a2$ and $c2$. In other words, once the tilting of the first octahedron has been specified, five of the nine coefficients describing the orientation of the second octahedron are determined. However, in order to keep the second octahedron perfectly rigid the following equations must be satisfied

$$D^2 = a1^2 + b1^2 + c1^2, \quad (1)$$
$$D^2 = a2^2 + b2^2 + c2^2, \quad (2)$$
$$0 = (a1)(a2) + (b1)(b2) + (c1)(c2) \quad (3)$$
$$0 = (a1)(a3) + (b1)(b3) + (c1)(c3) \quad (4)$$
$$0 = (a2)(a3) + (b2)(b3) + (c2)(c3). \quad (5)$$

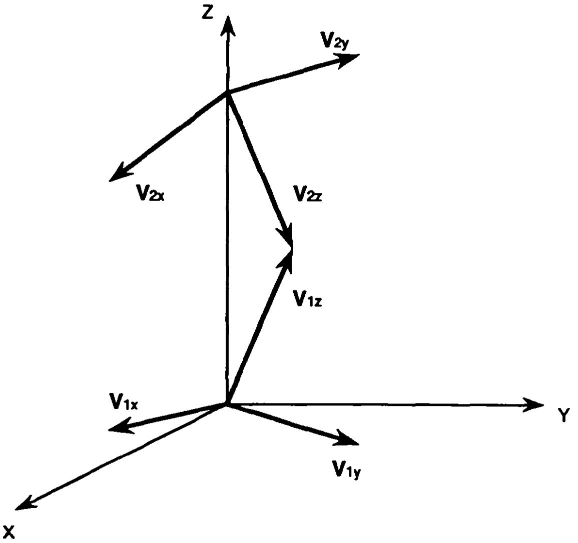


Fig. 3. The metal–oxygen vectors discussed in the text for two octahedra linked along the z axis of an $a^+a^+a^-$ tilted perovskite.

The first two equations must be satisfied in order to keep all the M—O distances constant (where D is the M—O bond distance) and the last three equations must be satisfied to keep all the O–M—O bond angles 90°. This leaves only four unknowns available to satisfy five linearly independent equations. In general, this will not be possible and one of the equations above will not be satisfied. The physical consequence of this is that either one of the bond angles or bond distances must distort from its ideal value in a perfect octahedron. To test this assertion calculations were carried out to ensure that for an arbitrary tilt of the first octahedron, it was not possible to simultaneously satisfy (1)–(5) for the second octahedron. The calculation of $\mathbf{V}_{2x}$, $\mathbf{V}_{2y}$ and $\mathbf{V}_{2z}$ for tilt system $a^+a^+a^-$ is given in Appendix C, as an example.

APPENDIX *C*

Calculation of metal oxygen vectors in the $a^+a^+a^-$ tilt system

Consider the $a^+a^+a^-$ tilt system with three 10° clockwise tilts and a metal–oxygen distance of 2.00 Å. Performing 10° tilts about each of the three Cartesian axes results in the origin octahedron having an orientation described by the following vectors

$$\mathbf{V}_{1x} = 1.9397\mathbf{x} - 0.3132\mathbf{y} + 0.3736\mathbf{z},$$
$$\mathbf{V}_{1y} = 0.3736\mathbf{x} + 1.9397\mathbf{y} - 0.3132\mathbf{z},$$
$$\mathbf{V}_{1z} = 0.3133\mathbf{x} + 0.3736\mathbf{y} + 1.9397\mathbf{z},$$

where the coefficients represent distances in Å between the metal ion at the origin and the three oxygen ions defining the octahedral orientation. Imposing the restrictions placed on the second octahedron by the mirror planes and the orthogonal axes gives the following values for the M—O vectors of the second octahedron

$$\mathbf{V}_{2x} = 1.9397\mathbf{x} + b1\mathbf{y} + c1\mathbf{z},$$
$$\mathbf{V}_{2y} = a2\mathbf{x} + 1.9397\mathbf{y} - c2\mathbf{z},$$
$$\mathbf{V}_{2z} = 0.3133\mathbf{x} + 0.3736\mathbf{y} - 1.9397\mathbf{z}.$$

By combining (2) and (4) above the vector $\mathbf{V}_{2x}$ can be found so that it is perpendicular to $\mathbf{V}_{2z}$ and of length 2.00 Å. When this calculation is carried out a quadratic equation in $c2$ is obtained. Since the equation is a quadratic there are two solutions

$$\mathbf{V}_{2x} = 1.9397\mathbf{x} + 0.4299\mathbf{y} - 0.2305\mathbf{z}$$
$$\mathbf{V}_{2x} = 1.9397\mathbf{x} - 0.3131\mathbf{y} - 0.3736\mathbf{z}.$$

Both of these vectors are 2.00Å long and perpendicular to $\mathbf{V}_{2z}$, but the second vector corresponds to in-phase tilting about the z axis, while the first vector is correct for out-of-phase tilting about the z axis. All the tilt systems considered here have out-of-phase tilting about the z axis, so the first of the two vectors above will be taken as $\mathbf{V}_{2x}$ and the second vector discarded. The final vector $\mathbf{V}_{2y}$ must be perpendicular to both $\mathbf{V}_{2x}$ and $\mathbf{V}_{2z}$. A vector mutually perpendicular to these two vectors can be generated by taking the cross product $\mathbf{V}_{2x} \times \mathbf{V}_{2z}$. The magnitude of this vector is now scaled so that its y component is 1.9397, giving the vector

$$\mathbf{V}_{2y} = -0.3783\mathbf{x} + 1.9397\mathbf{y} + 0.4347\mathbf{z}.$$

Combining the above calculations the orientation of the second octahedron can be described by the following set of three vectors

$$\mathbf{V}_{2x} = 1.9397\mathbf{x} + 0.4299\mathbf{y} - 0.2305\mathbf{z},$$
$$\mathbf{V}_{2y} = -0.3783\mathbf{x} + 1.9397\mathbf{y} + 0.4347\mathbf{z},$$
$$\mathbf{V}_{2z} = 0.3133\mathbf{x} + 0.3736\mathbf{y} - 1.9397\mathbf{z}.$$

The way in which these vectors were calculated guarantees they will satisfy (1) and (3)–(5), but no constraint has been placed on the length of vector $\mathbf{V}_{2y}$. Calculating the length of $\mathbf{V}_{2y}$ gives a value of 2.024 Å, slightly longer than all the other *M*—O vectors. This result can be extended to all the ++− and 0+− tilt systems. Therefore, we see that it is mathematically impossible to achieve linked octahedra in these tilt systems without distortions of the octahedra. The magnitude of these distortions will depend on the size of the tilt angles and the length of the *M*—O bonds.

Note that when calculating the $\mathbf{V}_{2x}$ vector two solutions were found, the second vector was discarded because it corresponded to in-phase tilting about all three axes. However, if the calculations are carried through with this vector the final orientation of the second octahedra satisfies all five equations. This is in agreement with the fact that *POTATO* is able to generate structures possessing perfectly rigid octahedra in the +++ and 0++ tilt classes.

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