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addenda and errata

Structure for perovskites with layered ordering of *A*-site cations. Erratum

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The scheme of structures shown in Fig. 1 of the paper by Howard & Zhang (2004) is incomplete. Structures corresponding to different tilt systems, allowing but not requiring the layered ordering of *A*-site cations, were inadvertently omitted. The corrected version of this schematic is shown by Howard & Stokes (2004) as their Fig. 5. The additional structures can be shown to be unsuitable as candidate structures for the compounds considered by Howard & Zhang, so the arguments used by Howard & Zhang (2004) for structure identification remain unaffected.

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Structure for perovskites with layered ordering of *A*-site cations

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The structure of $La_{1/3}NbO_3$ is that of a perovskite with La^{3+} cations ordered into alternate layers of perovskite *A*-sites. This is the description of a tetragonal structure and yet the room-temperature structure shows an orthorhombic distortion. The structure of $La_{2/3}TiO_3$ shows similar features. It has been recognized only very recently that the orthorhombic distortion in both these compounds is due to octahedral tilting. It seems clear from the literature that $Ce_{2/3}TiO_3$, $Pr_{2/3}TiO_3$, $Nd_{2/3}TiO_3$ and $Ce_{1/3}NbO_3$ adopt the same structure. Structures of other perovskites, such as $Ln_{2/3}TiO_3$, $Ln_{1/3}NbO_3$ and $Ln_{1/3}TaO_3$ (Ln = lanthanoid), when orthorhombically distorted, may be similar.

Certain *A*-site deficient perovskites, such as $La_{1/3}NbO_3$, are of interest because the vacancies at the *A*-sites facilitate the electrochemical insertion of Li^+ ions and the subsequent movement of Li^+ ions through the lattice. These materials have potential as anode materials for high energy-density lithium-ion batteries (Scrosati, 1995). In a recently published study Nakayama *et al.* (2003) sought to use extended X-ray absorption fine structure (EXAFS) to elucidate structural changes associated with increasing concentration of inserted Li^+ ions. In reviewing this work, it became apparent to us that the structure of $La_{1/3}NbO_3$ itself might not be well understood.

The structure of $La_{1/3}NbO_3$ is known to be of the perovskite type, with the La^{3+} ions located in *A*-sites, in (but not filling) every second layer. The other layers of *A*-sites remain vacant. According to this description the *c*-axis is doubled, yet the symmetry remains tetragonal. However, a small orthorhombic distortion is observed. This is the description first given by Iyer & Smith (1967), who showed the lattice dimensions[1] as $a = 3.911 \pm 0.005$, $b = 3.917 \pm 0.005$, $c = 7.908 \pm 0.002$ Å, yet refined the structure as tetragonal in space group *P*4/*mmm*. Referred to the edge of the cubic perovskite aristotype, both the orthorhombic cell reported and the tetragonal cell used in the refinement would be considered as 1 × 1 × 2 cells.

The situation regarding the structure of $La_{1/3}NbO_3$ is reminiscent of the situation pertaining to, until very recently, the closely related compound $La_{2/3}TiO_3$. The best established feature of the structure of $La_{2/3}TiO_3$ was *A*-site cation ordering, such that almost all the vacancies were located in alternate layers, with few if any vacancies in the other layers. High-resolution X-ray diffraction studies (Yoshioka & Kikkawa, 1998; Yashima *et al.*, 2000; Ali *et al.*, 2002; Yashima *et al.*, 2002) had shown that the symmetry was orthorhombic, apparently on a 1 × 1 × 2 cell. The material becomes tetragonal at elevated temperature (~633 K), in space group *P*4/*mmm*, on a 1 × 1 × 2 cell, and the space group of the orthorhombic structure was given as *Pmmm*, also on a 1 × 1 × 2 cell. There was, however, nothing in the structural model to suggest why orthorhombic distortion should occur.

There now appears to be a consensus as to the correct model for the structure[2] of $La_{2/3}TiO_3$ (Inaguma *et al.*, 2002; Yashima *et al.*, 2003; Howard & Zhang, 2003).

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[1] Although the cell might be tetragonal on the basis of the errors quoted, Iyer & Smith (1967) report resolved peak splitting in the Guinier pattern as establishing the lower symmetry.

[2] It is difficult to prepare $La_{1/3}TiO_3$ in pure form. For this reason, these structure solutions depend on preparations involving a modest amount of *A*- or *B*-site substitution.

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In our study, of $\mathrm{La}_{0.6}\mathrm{Sr}_{0.1}\mathrm{TiO}_3$ (Howard & Zhang, 2003), we first accepted the observation of layered ordering of the *A*-site cations, then suggested that the orthorhombic distortion might be due to a tilting of the TiO_6 octahedra. Next, a group theoretical approach, such as in previous work (Howard & Stokes, 1998; Stokes *et al.*, 2002; Howard *et al.*, 2003) was used to enumerate the possible structures. The layered ordering of cations (or vacancies) on the perovskite *A*-site was recognized as transforming according to the irreducible representation X_3^- ($\mathbf{k} = 0,0,\frac{1}{2}$) of the aristotype space group $Pm\bar{3}m$. The octahedral tilting was represented through the irreducible representations (irreps) R_4^+ ($\mathbf{k} = \frac{1}{2},\frac{1}{2},\frac{1}{2}$) corresponding to modes with out-of-phase tilting of octahedra in successive layers and M_3^+ ($\mathbf{k} = \frac{1}{2},\frac{1}{2},0$) associated with in-phase octahedral tilting. The different possible structures were enumerated using the computer program *ISOTROPY*,[3] with results as summarized in Fig. 1. For each structure, that figure shows the space group, the tilt system using Glazer's notation[4] (Glazer, 1972, 1975) and the approximate dimensions of the unit cell in terms of the cell edge of the $Pm\bar{3}m$ aristotype. *ISOTROPY* also suggests the approximate atomic coordinates in the new unit cell. Given that the room-temperature structure could be derived from the high-temperature tetragonal structure by a continuous phase transition, and also that it was orthorhombic, the only candidate structures were those in *Cmmm* (tilt system $a^-b^0c^0$) and *Pmma* ($a^-a^-c^0$). Since an orthorhombic structure on a $2^{1/2} \times 2 \times 2^{1/2}$ cell could not account for the peak splitting observed in the synchrotron X-ray studies, *Pmma* was eliminated, leaving the *Cmmm* ($a^-b^0c^0$) structure as the only possibility. In our synchrotron-based X-ray diffraction study we sought and found weak reflections indicative of cell doubling along all the main axes (contrast the 2 × 2 × 2 cell for *Cmmm* with the 1 × 1 × 2 cell previously suggested) and attributed these reflections to the effects of octahedral tilting. Structural refinement was completed and the structure finally obtained is represented in Fig. 2(*a*). It was concluded that the TiO_6 octahedra tilt about the *x*-axis by *ca* 4.7°.

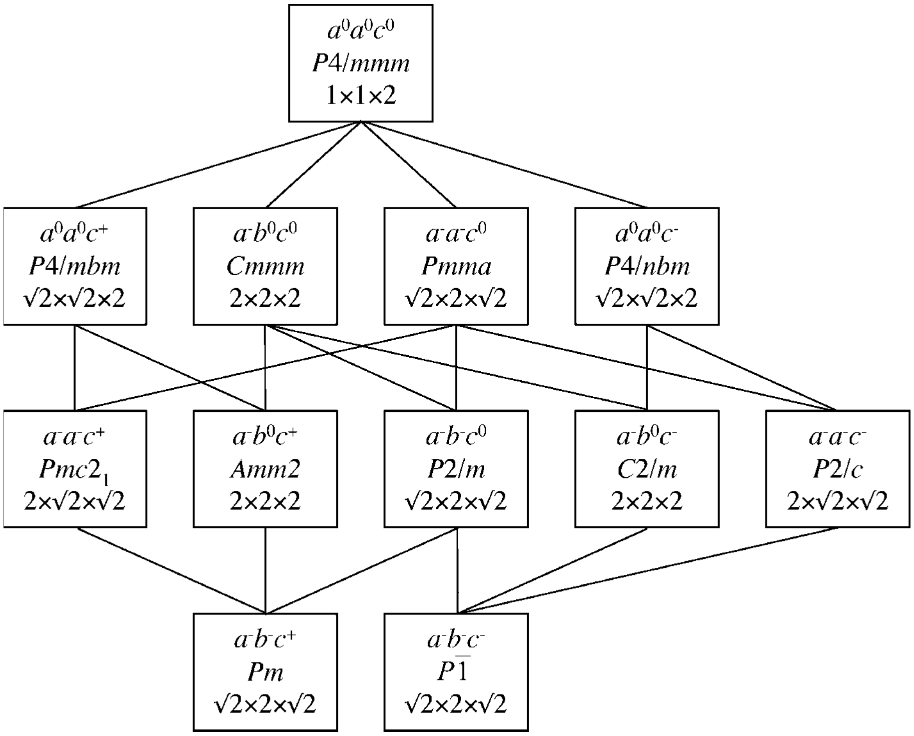

Figure 1
A schematic diagram showing the different possible structures generated by the layered ordering of cations on the perovskite *A* site, followed by the corner-linked tilting of the BX_6 octahedra. The entries indicate the tilt system, using Glazer's notation, the space group and the approximate cell dimensions in terms of the cell edge of the $Pm\bar{3}m$ aristotype. The lines indicate group–subgroup relationships among the different structures – the corresponding phase transitions are allowed to be continuous. This figure has been reproduced from Howard & Zhang, *J. Phys. Condens. Matter*, ©IOP Publishing Ltd, 2003.

The tilting of the TiO_6 octahedra in $\mathrm{La}_{2/3}\mathrm{TiO}_3$ implies only a small shift in oxygen positions and because the X-ray diffraction is dominated by heavier elements, the corresponding weak superlattice reflections had been previously overlooked. In effect, we found these reflections because we were looking for them and were using an X-ray diffractometer with excellent performance as regards signal-to-noise. These reflections are relatively stronger in neutron diffraction and it was their observation in neutron patterns that led other workers (Inaguma *et al.*, 2002; Yashima *et al.*, 2003) to the same structural solution.

There is every reason to suppose that the structure of $\mathrm{La}_{1/3}\mathrm{NbO}_3$ will be closely similar to that of $\mathrm{La}_{2/3}\mathrm{TiO}_3$. The occupancies of the *A*-sites by La^+ ions in $\mathrm{La}_{2/3}\mathrm{TiO}_3$ in successive layers are, ideally, 100% and 33%, and vacancies present to the level of 0% and 67%. In $\mathrm{La}_{1/3}\mathrm{NbO}_3$ these numbers for cations and vacancies are interchanged. If the orthorhombic distortion is attributed again to octahedral tilting, the group theoretical analysis carries through unchanged. Once again, the structure in *Cmmm* is left as the only real possibility. To confirm this structure, it would be necessary to find the superlattice reflections showing that the cell was not of dimensions 1 × 1 × 2, but of dimensions 2 × 2 × 2. Evidently, these reflections were not observed in the initial X-ray studies (Iyer & Smith, 1967). These reflections were seen in electron diffraction patterns (Carrillo *et al.*, 2000), from which the structure was determined as orthorhombic in *Cmmm* on a 2 × 2 × 2 cell.[5] They were also seen in a recent neutron study (Dilanian *et al.*, 2000), where refinement led to a structure for $\mathrm{La}_{1/3}\mathrm{NbO}_3$ that is essentially identical with the structure of $\mathrm{La}_{2/3}\mathrm{TiO}_3$ (Fig. 2). Based on the coordinates recorded by Dilanian *et al.* (2000), the tilt angle in $\mathrm{La}_{1/3}\mathrm{NbO}_3$ is estimated at ~4.7°, the same as in $\mathrm{La}_{2/3}\mathrm{TiO}_3$.

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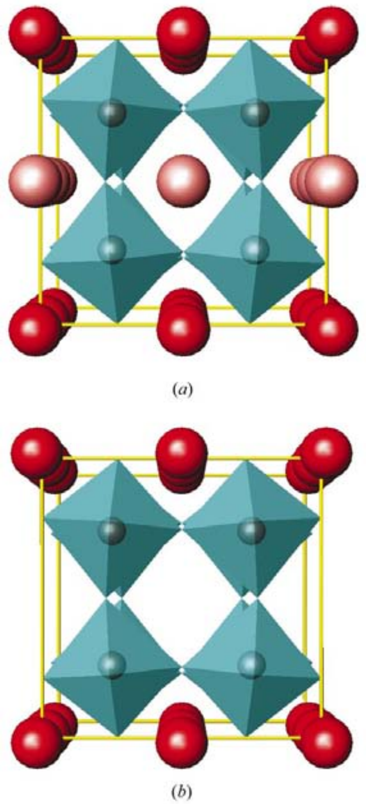
[3] *ISOTROPY* is a software package developed by Stokes and Hatch at Brigham Young University. *ISOTROPY* is available at www.physics.byu.edu/~stokesh/isotropy.html.

[4] The symbol $a^{\#}b^{\#}c^{\#}$ is used to indicate no tilting, in-phase tilting, out-of-phase tilting around the ⟨001⟩ axes of the parent perovskite by showing the superscript # as 0, +, −, respectively.

[5] The electron diffraction determination of the space group as *Cmmm* should be reliable. However, in the structure proposed by Carrillo *et al.* (2000), and refined from laboratory X-ray data, we do not consider that a correct choice of atomic (Wyckoff) positions has been made.


(a)

(b)

Figure 2
Representation of the room-temperature orthorhombic structures of (*a*) $La_{2/3}TiO_3$, reproduced from Howard & Zhang (2003), and (*b*) $La_{1/3}NbO_3$, based on the coordinates reported by Dilanian *et al.* (2000). The TiO_6 or NbO_6 units are shown as octahedra, with the Ti^{4+} and Nb^{5+} ions being visible within them. The darker and lighter spheres in (*a*) represent fully (100%) and partly (33%) occupied layers, and the spheres in (*b*) represent the partly (67%) occupied layers, of La^{3+} ions. The out-of-phase octahedral tilting around the *x*-axis (coming out of the paper) is readily seen. The figures were prepared using *ATOMS* (Dowty, 1999).

A survey of the literature has uncovered certain related perovskites which we believe adopt the same structure. Yoshii (2000*a*,*b*) has reported that $Ce_{2/3}TiO_3$, $Pr_{2/3}TiO_3$ and $Nd_{2/3}TiO_3$ are isostructural with $La_{2/3}TiO_3$, but used the earlier description of that structure: orthorhombic in *Pmmm* on a 1 × 1 × 2 cell. We expect these compounds are indeed isostructural with $La_{2/3}TiO_3$ and as such we would describe them now in *Cmmm* on a 2 × 2 × 2 cell. A neutron study of $Ce_{1/3}NbO_3$ (Bridges *et al.*, 2000) led to a description of the structure as monoclinic, in the space group *P*2/*m*, on a $2^{1/2} \times 2 \times 2^{1/2}$ cell. This is in fact the structure with tilt system $a^-b^-c^0$, which appears in our Fig. 1, but it has lower symmetry than the structure we have described here. However, we calculate that the primitive net on the *ac* plane defined by $a = 5.5267$, $c = 5.5245$ Å and $\beta = 90.294°$ can be represented as a centred net with dimensions $a = 7.8344$, $b = 7.7943$ Å, $\beta = 89.98°$, which we take to be a centred rectangular net. The structure can therefore be described on a C-centred orthorhombic cell, with $a = 7.8344$, $b = 7.7943$, $c = 7.8824$ Å. Expressing atomic coordinates in terms of this C-centred orthorhombic cell, we find that the structure can indeed be described in the higher (*Cmmm*) symmetry, with tilting around the *x*-axis only ($a^-b^0c^0$). The tilt angle here is ~6.5°. In the original study of niobates and tantalates by Iyer & Smith (1967), compounds $R_{1/3}NbO_3$, *R* = Pr, Nd, and $R_{1/3}TaO_3$, *R* = Pr, Nd, Sm, also appeared orthorhombic in Guinier patterns, yet were all refined as perovskites in the tetragonal space group *P*4/*mmm*, on a 1 × 1 × 2 cell. Further studies may reveal that these compounds also adopt the $La_{1/3}NbO_3$ structure described in this note.

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