La$_{24}$Li$_{18.67}$Ti$_{5.33}$O$_{56}$: a novel columnar intergrowth structure of perovskite and distorted, cation-excess zinc blende†

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The structure of the new phase, La$_{24}$Li$_{18.67}$Ti$_{5.33}$O$_{56}$, tetragonal, space group *P4/mbm*, *a* = 13.2443(13), *c* = 14.9258(20) Å, consists of alternating columns, rotated by 45° relative to each other, of perovskite-like structure, with Ti and Li in alternate octahedral sites, and twinned, distorted, zinc blende-like structure.

Distorted crystal structures commonly occur when one type of atom is too small for the sites available to it. The perovskite family, ABO$_3$, provides many examples of structural distortions involving either distorted octahedra, BO$_6$ if the B cation is slightly too small or tilted octahedra if the A cation is too small. In the latter case, the A cations and oxygen, collectively, form close packed, *cp*, layers but the A cation may be too small to occupy a site surrounded by 12 equidistant oxygens. Additional complications occur, in, for example, the tungsten bronzes, A$_{1-x}$BO$_3$, when vacancies are introduced into the A cation array.

We report here, the crystal structure of La$_{24}$Li$_{18.67}$Ti$_{5.33}$O$_{56}$ which represents a new kind of distorted, partially-collapsed, *cp* structure. The structure contains large packing atoms, La, and smaller atoms, Li and Ti, which can occupy either tetrahedral or octahedral sites, but the La:O ratio is 1:2.33 rather than 1:3 as in perovskite. Consequently, instead of a uniformly distorted structure, as in, *e.g.* GdFeO$_3$, the structure separates into infinite columns of relatively undistorted *cp* structure.

The new phase, La$_{24}$Li$_{18.67}$Ti$_{5.33}$O$_{56}$ was synthesised during an investigation of compound formation in the system La$_2$O$_3$–Li$_2$O–TiO$_2$; this system is of interest as it contains the perovskite-related phase La$_{1/2+x}$Li$_{1/2-3x}$TiO$_3$[1] which exhibits exceptionally high lithium ion conductivity, 1 × 10^{-3} Ω^{-1} cm^{-1} at room temperature. At the outset, the composition of the new phase was uncertain since volatilisation of Li$_2$O was significant under the conditions used, *viz.* 12–24 h at 900 °C in Au foil boats. Nevertheless, a sample which was essentially phase-pure by powder X-ray diffraction, (XRD), was obtained on reacting the mixture (7La$_2$O$_3$+10Li$_2$CO$_3$+3TiO$_2$); this had the same La:Ti ratio as deduced in the final formula, but an excess of Li. Its powder XRD pattern could not be indexed by trial-and-error methods but it was found by selected area electron diffraction, SAED, to be tetragonal, which then enabled the XRD pattern to be indexed on a primitive cell with *a* = 13.2443(13) and *c* = 14.9258(20) Å.

For the structure determination, a sub-cell with halved *c*, was used since all observed XRD lines as well as the neutron diffraction (ND) data could be satisfactorily indexed on a tetragonal cell with *a* = 13.2443(13) and *c* = 7.4629(10) Å, in the space group *P4/mbm* (no. 127); hence the structure contains a weak supercell that is observed only by SAED. It was not possible to solve the structure from either XRD or ND data alone. Using electron density maps obtained by applying 'Direct Methods' to the XRD data set, La positions were located

and this enabled an iterative solution and refinement of the structure to be carried out using combined XRD and ND data as input to the Rietveld programme GSAS.[2] After refinement of partial structure models at each stage, difference Fourier maps were constructed for both XRD and ND data and this gradually allowed the positions of more atoms to be identified, which were then inputted into the Rietveld refinement and the process repeated. This process was continued until a model corresponding to the stoichiometry 'La$_{24}$Ti$_6$O$_{48}$' was obtained, at which point the difference maps became relatively featureless. The remainder of the structure was determined using a combination of crystal chemical intuition, based on examination of coordination environments of the various atoms and their bond distances and bond valence analysis to indicate which oxygens were underbonded and whether Ti, Li sites contained Ti or Li alone or had mixed occupancy. A comparison of the goodness-of-fit parameter (χ^2) and *R* values of the partial structure La$_{24}$Ti$_6$O$_{48}$ with those of La$_{24}$Li$_{18.67}$Ti$_{5.33}$O$_{56}$ is given in Table 1, showing a clear improvement in the fit when the extra O site and Li sites are added. The observed, calculated and difference profiles of the XRD and ND data from the refinement of La$_{24}$Li$_{18.67}$Ti$_{5.33}$O$_{56}$ are provided as ESI†. Full details of the structure determination will be reported elsewhere together with a detailed description of the crystal structure.

During the final stages of refinement, the composition of the new phase was determined from site occupancy factors. The absolute Li,Ti contents are slightly uncertain since some sites contained mixed Li,Ti occupancy; it was assumed that overall, these sites were full, but it is also possible that they contain some vacancies, compensated by a higher Ti/Li ratio.

The structure contains layers perpendicular to *c* (not shown) of La and O atoms that are alternately planar and buckled. The layers at *z* = ¼ and 0, ½, shown in projection in Fig. 1 and Fig. 2 are not *cp* in this orientation: for them to be *cp*, each packing atom (La, O) should be surrounded by a hexagonal ring of six other packing atoms. It is, however, possible, if we consider for a moment La and O to be equivalent, to identify fragments of *cubic close packed, ccp*, unit cells, *e.g.* four La(1) atoms around O(8) at both corner and face centre positions, Fig. 1, giving rise to the 'domino-five' arrangement of a *ccp* cell face; in addition, parallel to *c*, the 'domino-fives' alternate with square arrangements of O(7), Fig. 2, which represent side face centres of the *ccp* unit cells. Centred at corner and face centre positions,

Table 1 Comparison of χ^2 and R values[a]

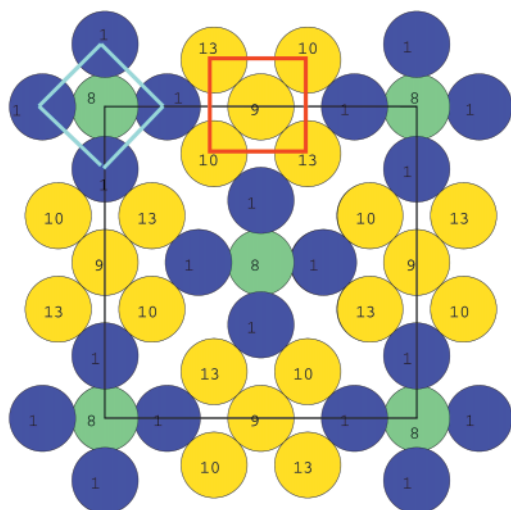|	La$_{24}$Ti$_6$O$_{48}$	La$_{24}$Li$_{18\ 2/3}$Ti$_{5\ 1/3}$O$_{56}$
χ^2	16.31	5.393
wR_p (ND)	6.28	3.43
R_p (ND)	11.61	6.39
wR_p (XRD)	6.83	6.46
R_p (XRD)	4.91	4.73
wR_p (overall)	6.30	3.62
R_p (overall)	5.44	4.86

[a] % Value.

Fig. 1 *ab* Section at $z = 0.25$, with idealised La–O and O–O bond lengths: La(1): purple; O(9), O(10), O(13): yellow; O(8): green. The zinc blende-related columns are yellow, with the subcell outlined in red; the perovskite columns are green/purple with the subcell outlined in blue.
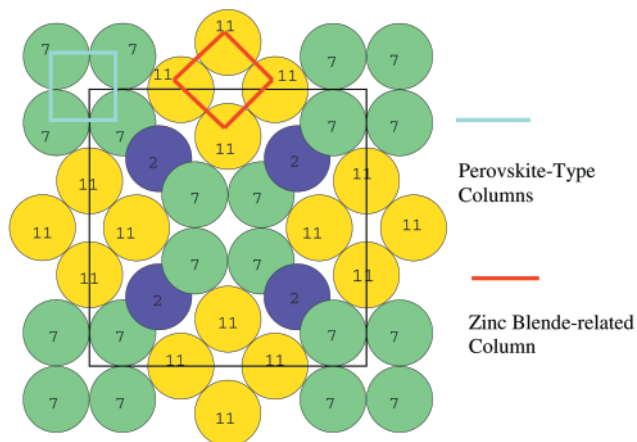

Fig. 2 *ab* Section at $z = 0$, with Idealised La–O and O–O bond lengths. La(2): purple; O(11): yellow; O(7): green. Column colours as in Fig. 1. Section at $z = \frac{1}{2}$ (not shown) is very similar, but with La(3) instead of La(2), O(5) instead of O(11) and O(6) instead of O(7).

therefore, columns of mixed La,O *ccp* cells run parallel to *c*. These have the perovskite structure, not only as regards the La, O distribution but also the octahedral positions at, *e.g.* 000 and $00\frac{1}{2}$, which are occupied, alternately, by Ti and Li.

A second set of *ccp* columns is centred on the edge-centre positions, *i.e.* in Fig. 1 oxygens O(10), O(13), around O(9) at $0\frac{1}{2}\frac{11}{24}$ and $\frac{1}{2}0\frac{1}{24}$, with oxygens O(11) at $z = 0$, Fig. 2, and O(5) at $z = \frac{1}{2}$ (not shown). These columns are somewhat distorted from the idealised, square symmetry. An *ab* projection of one such
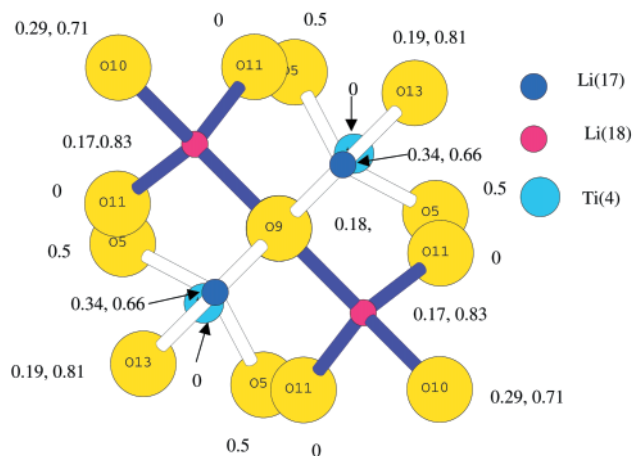

Fig. 3 Distorted zinc blende-related columns with Ti octahedrally coordinated in the basal plane.

column is shown in Fig. 3; Li occupies one set of tetrahedral sites to give a zinc blende arrangement, but, a twin plane exists at each unit cell face (*i.e.* $z = 0, \frac{1}{2}$) and the pattern of tetrahedral site occupancy parallel to *c* is –empty–empty–occupied–occupied–… rather than …empty–occupied –... as in zinc blende. Additionally, these distorted *ccp* cells contain Ti in sites at $z = 0$; in an undistorted structure, these sites would be two-coordinate, but because of the distortions, are octahedral, (oxygens O(11) at $z = 0$, O(13) at $z = 0.19, 0.81$ and O(9) at $z = 0.18, 0.82$).

To complete the structure, it is necessary to see how the columns of perovskite-like and cation-excess, zinc blende-like structure are connected. From Figs. 1 and 2, it can be seen that adjacent columns are rotated by 45° about *c*, relative to each other. In the sections at $z = 0$ and $z = \frac{1}{2}$ (not shown), extra La(2) and La(3) atoms are located between the two types of column, whereas at $z = \frac{1}{4}, \frac{3}{4}$, all La, O atoms belong to one or other of the two column types.

The coordination numbers of the packing atoms vary, depending on their location, from a maximum of 12 for O(8) in the centres of the perovskite columns. Overall, the structure is not a continuous *cp* structure but nevertheless, the average volume of an La, O packing atom, 16.3 Å³, is close to the lower limit found for ideal *cp* structures. Thus, within the two types of column, the packing arrangement of La, O approximates to *cp* but between the columns the structure cannot be idealised to *cp*.

Notes and references

1 A. D. Robertson, S. Garcia-Martin, A. Coats and A. R. West, *J Mater. Chem.*, 1995, **9**, 1405.
1 A. C. Larson and R. B. van Dreele, Los Alamos Laboratory Report No La-Ur-86-748, 1998.