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On the Location of Li^+ Cations in the Fast Li-Cation Conductor $La_{0.5}Li_{0.5}TiO_3$ Perovskite[**]

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Interest in solids which conduct lithium ions has increased considerably in recent years because of the potential application of such solids in rechargeable lithium batteries. The ionic conductivity of $La_{2/3-s/3}Li_sTiO_3$ perovskites is one of the highest reported values in crystalline lithium cation conductors[1, 2] ($\sigma \approx 10^{-3}\ \Omega^{-1}\mathrm{cm}^{-1}$ at $T = 300$ K), which makes these compounds good candidates for use as solid electrolytes in lithium batteries. The conductivities in the Pr and Nd perovskites are two and three orders of magnitude lower than for their La analogues.[2]

The perovskite structure (general formula ABO_3) can be regarded as a three-dimensional framework made up of vertex-sharing BO_6 octahedra with a large A cation in each of the 12-coordinated cavities of the framework. In the solid solution $La_{2/3-s/3}Li_sTiO_3$ ($0 \leq s \leq 0.5$) Li atoms were thought to replace La atoms at the A sites, which would lead to a progressive reduction of vacancies at these positions. However, the location of the Li atoms in the crystal structures of this family had not previously been possible from X-ray diffraction (XRD) data.

If the radius of the A cation is too small, the void is reduced in size by tilting of the BO_6 octahedra. The effect of tilting, when widely extended, is a predominant feature in the determination of the overall space-group symmetry of a particular perovskite. The precise structure determination of these oxides by XRD is particularly difficult because the superlattice reflections associated with the tilting of the TiO_6 octahedra arise from the oxygen atoms, which are weak scatterers when compared with La and Ti. Hence, neutron powder diffraction (NPD) measurements are more suitable for these investigations.

Following previous work,[3–5] we report a neutron powder diffraction study of the perovskite with the highest Li-substitution level, $La_{0.5}Li_{0.5}TiO_3$, in which we have, for the first time, located the Li^+ cations within the structure and have established the tilting scheme of the TiO_6 octahedra. Moreover, our data demonstrate that the solid solution mentioned does extend up to values of $s = 0.5$, a figure which had been controversial up to this time.

The powder sample of $La_{0.5}Li_{0.5}TiO_3$ exhibited excellent crystallinity, as shown by the sharpness of the XRD reflections (Figure 1 a). The XRD pattern could be indexed in a cubic unit cell with $a = 3.8714(5)$ Å, characteristic of a perovskite structure. Nevertheless, the NPD pattern (Figure 1 b) clearly showed the presence of superstructure reflections which could not be indexed in the simple cubic unit cell; these reflections arise from the tilting of the TiO_6 octahedra. Therefore, it was necessary to consider a larger unit cell. The reflections of the NPD diagram of $La_{0.5}Li_{0.5}TiO_3$ were indexed in an hexagonal unit cell with the systematic absences suggesting the space group $R\bar{3}c$ (no. 167). This rhombohedral space group corresponds to one of Glazer's octahedral tilt schemes for perovskite related structures,[6] which is adopted by a wide number of perovskites when the tilting angle of the octahedra remains small (for instance, $LaAlO_3$, $LaCuO_3$,or $LaNiO_3$).

A first Rietveld refinement was performed on a structural model in which Li atoms were not included; the starting parameters used were those of $LaNiO_3$[7] in the hexagonal setting of the space group $R\bar{3}c$ ($Z = 6$) with La placed at 6a (0,0,1/4), Ti at 6b (0,0,0), and oxygen at 18e (x,0,1/4) positions; the single x parameter was to be determined during the refinement. Unit cell parameters were $a = 5.4711(4)$, $c = 13.404(1)$ Å. The refinement of the La occupancy factor (over 6a positions) led to the expected value of 0.5 atoms per formula unit. This result seemed to exclude the possiblility that the Li cations are located at A sites of the perovskite, randomly distributed over the 6a positions together with La. This situation would have led to a significantly lower La occupancy factor, since the scattering length of Li is negative (see the Experimental Section). After the Rietveld refinement of this structural model, an R_{Bragg} factor of 0.074 was

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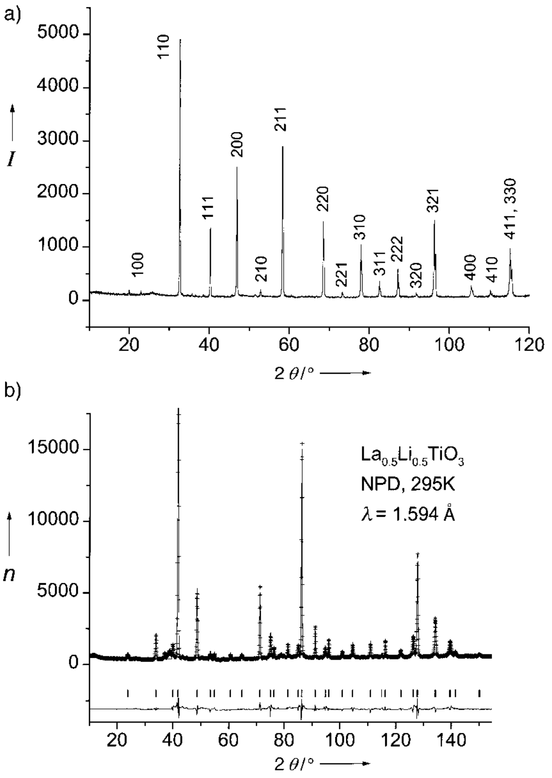

Figure 1. a) XRD diagram for $La_{0.5}Li_{0.5}TiO_3$, indexed according to a simple cubic unit cell (subcell of the true structure); b) calculated (full line) and observed (horizontal marks) neutron powder diffraction profiles at 295 K, refined in the rhombohedral $R\bar{3}c$ space group. The difference profile is shown underneath.

reached, including anisotropic refinement of the oxygen thermal motion.

The small discrepancies between the observed and calculated intensities provided information on the remaining scattering density which was not considered in the starting model. A Fourier synthesis, performed over the difference between observed and calculated structural factors, yielded information on the location of the "missing" atoms. A difference Fourier map at this step showed us the unambiguous location of Li atoms at 18d (1/2,0,0) positions. As shown in Figure 2, peaks of negative density ($\rho \approx -1.1$ fm Å^{-3}) are located in the $z = 0$ Fourier section at (1/2,0,0) and equivalent positions. After the introduction of Li into the structural model, the R_{Bragg} factor dropped to 0.048. The refined occupancy factor was in excellent agreement with the expected Li content of 0.5 atoms per formula unit. The quality of the fit of NPD data after the final refinement is illustrated in Figure 1b. The final atomic coordinates and thermal factors are included in Table 1.[8] A simplified view of the crystal structure is shown in Figure 3.

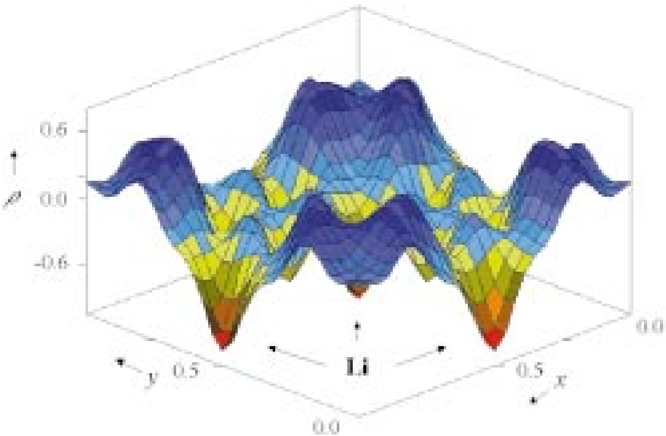

Figure 2. Difference Fourier map for $z = 0$ showing the location of Li atoms at (1/2,0,0) and equivalent positions. The vertical axis corresponds to the scattering density ρ (in fm Å^{-3}), which is negative at the Li positions.

Table 1. Atomic coordinates and isotropic thermal factors (B_{iso}) for $La_{0.5}Li_{0.5}TiO_3$ after the final NPD refinement.

Atom	Site	x	y	z	f_{occ}	B_{iso}[Å^2]
La	6a	0	0	0.25	0.504(9)	0.17(10)
Li	18d	0.5	0	0	0.162(3)	6.7(10)
Ti	6b	0	0	0	1.0	1.17(12)
O_1	18e	0.5321(6)	0	0.25	1.0	1.75(8)[a]

[a] Anisotropic thermal factors: $\beta_{11} = 0.024(2)$, $\beta_{22} = 0.008(3)$, $\beta_{33} = 0.0026(5)$, $\beta_{12} = 0.004(3)$, $\beta_{13} = -0.0019(5)$, $\beta_{23} = -0.0037(5)$.

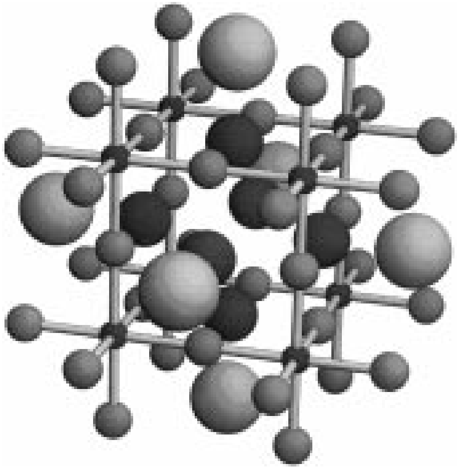

Figure 3. Elementary pseudo-cubic unit cell for $La_{0.5}Li_{0.5}TiO_3$ perovskite, which shows the relative location of Li (dark large spheres) and La (light large spheres) atoms. La positions are half-occupied; Li positions are one-sixth occupied.

The structure of $La_{0.5}Li_{0.5}TiO_3$ is constituted by a network of TiO_6 octahedra slightly tilted along the pseudocubic rhombohedral axes ($a^-a^-a^-$ in Glazer's nomenclature[6]) in order to optimize La–O distances. The Ti-O-Ti angle, which describes the tilting of the octahedra, is close to 170°. The bond lengths are all reasonable;[8] the TiO_6 octahedra are almost perfectly regular (Ti–O 1.943(1) Å), and La is 12-fold coordinated to oxygen atoms with La–O bond lengths in the range 2.911–2.559 Å. La positions are half-occupied, leaving 0.5 vacancies per formula unit, distributed at random in the structure. The Li^+ cations are fourfold coordinated to oxygen atoms, in square-planar configuration. This environment for Li is different to the tetrahedral-like coordination found by Skakle et al.[9] in the Pr and Nd analogues, which show a much lower conductivity. In $La_{0.5}Li_{0.5}TiO_3$, the Li cations are placed at the middle of windows formed by four TiO_6 octahedra, with Li–O bond lengths of 1.81 and 2.07 Å.

The simplified structure illustrated in Figure 3 corresponds to the ABO_3 cubic perovskite structure ($Z = 1$), where Ti atoms occupy the corners of a cube, oxygen atoms are at the middle of the edges, and La ions (or La vacancies) are the geometrical center of the cube. The position occupied by Li corresponds to the center of every face. Since there are 0.5 Li atoms per formula unit (i.e., per pseudo-cubic unit cell), the occupancy factor of Li is only ⅙.

The observed oxygen thermal factors are surprisingly high; $B_{\mathrm{iso}}(\mathrm{O})$ takes a value of 1.75(8) Å^2. This large value accounts for disorder introduced by Li distribution, leading to small shifts of those O atoms directly linked to Li, which introduces an overall smearing of the O nuclear density. In fact, the oxygen thermal factor is rather anisotropic, described by very flattened ellipsoids. The short axis of the ellipsoid is along the highly covalent Ti–O–Ti bonds.

We suggest a mechanism for Li diffusion across the solid, in which the unoccupied five-sixths of 18d positions and half of the 6a positions (the remaining half being occupied by La atoms) constitute the path for Li hopping. The Li cations reside at 18d positions (where they have been located by diffraction methods), but the conduction mechanism appears to involve A vacancies, which Li^+ ions can hop into, avoiding those perovskite subcells that contain La cations. This model can be used to explain the dependence of Li conductivity (σ_{dc}) on Li content seen by Kawai and Kuwano,[10] and Inaguma et al.[11] They observed that the maximum conductivity in $La_{2/3-s/3}Li_sTiO_3$ is detected at high Li contents ($s \approx 0.35$). This observation could not be interpreted on the basis of a random distribution of Li, La and A vacancies in the A sites of a perovskite, as a strong decrease in σ_{dc} would be predicted for $s \approx 0.5$. However, the huge σ_{dc} for high Li contents can be explained by assuming the existence of a high number of vacant sites (the unoccupied 18d and 6a positions) which participate in the Li motion. The unusual coordination of Li, in the center of the oxygen windows determined by four TiO_6 octahedra, and the existence of a partially unoccupied cation sublattice for Li motion, explains the ion mobility and, therefore, the ionic conductivity and outstanding electrical properties of these promising Li-conducting materials.

Experimental Section

In order to reduce the absorption cross-section of the sample in the neutron experiment, a ^{7}Li-enriched $La_{0.5}Li_{0.5}TiO_3$ sample (4 g) was prepared in polycrystalline form by heating a stoichiometric mixture of high-purity Li_2CO_3, La_2O_3, and TiO_2 reagents at 1200 °C. The powder obtained from the reaction was pelletized and fired at 1350 °C in air for 12 h and then quenched to room temperature. The metal molar ratio was determined by inductively coupled plasma spectroscopy (ICP) using a JY-70 PLUS spectrometer.

The XRD patterns were collected at 295 K with $Cu_{K\alpha}$ radiation in a Philips PW1050/25 diffractometer, by step-scanning from 10 to 120° in 2Θ, in increments of 0.02° and with a counting time of 5 s for each step. The NPD diagram of $La_{0.5}Li_{0.5}TiO_3$ was collected at 295 K in the high-resolution D2B diffractometer at ILL-Grenoble. A wavelength of 1.594 Å was selected from a Ge monochromator. The counting time was 4 h, using 4 g of sample contained in a vanadium can. The first 28 peaks of the NPD diagram of $La_{0.5}Li_{0.5}TiO_3$ were unambiguously indexed with the TREOR4 program[12] in an hexagonal unit cell (de Wolff figure of merit $M_{20} = 16$).

For the neutron profile refinements (FULLPROF program),[13] a pseudo-Voigt function was chosen to generate the line shape of the diffraction peaks. The coherent scattering lengths for La, Li, Ti, and O were 8.24, −1.90, −3.438, and 5.803 fm. The Li atoms were located by Fourier synthesis, using the FOURIER and GFOURIER programs.[14] In the final refinement run, the following parameters were refined: background coefficients, zero-point, half-width, and pseudo-Voigt parameters for the peak shape; scale factor and positional parameter for O; occupancy factors for La and Li; thermal isotropic factors for La, Li, and Ti, and anisotropic factors for O; and unit-cell parameters. Crystallographic data for $La_{0.5}Li_{0.5}TiO_3$: *R*-3*c*, hexagonal setting, $a = 5.4711(4)$, $c = 13.404(1)$ Å, $V = 347.44(5)$ Å^3, $\rho_{\mathrm{calcd}} = 4.84$ g cm^{-3}, $Z = 6$, $R_{\mathrm{wp}} = 0.086$, $R_{\mathrm{p}} = 0.061$, $R_{\mathrm{exp}} = 0.019$, $R_{\mathrm{Bragg}} = 0.048$, measurement range $10 \leq 2\Theta \leq 155°$, 3190 data points, 84 observed reflections, 23 parameters refined. Further details of the crystal structure investigations can be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: (+49) 7247-808-666; e-mail: crysdata@fiz-karlsruhe.de), on quoting the depository number CSD-411039.

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