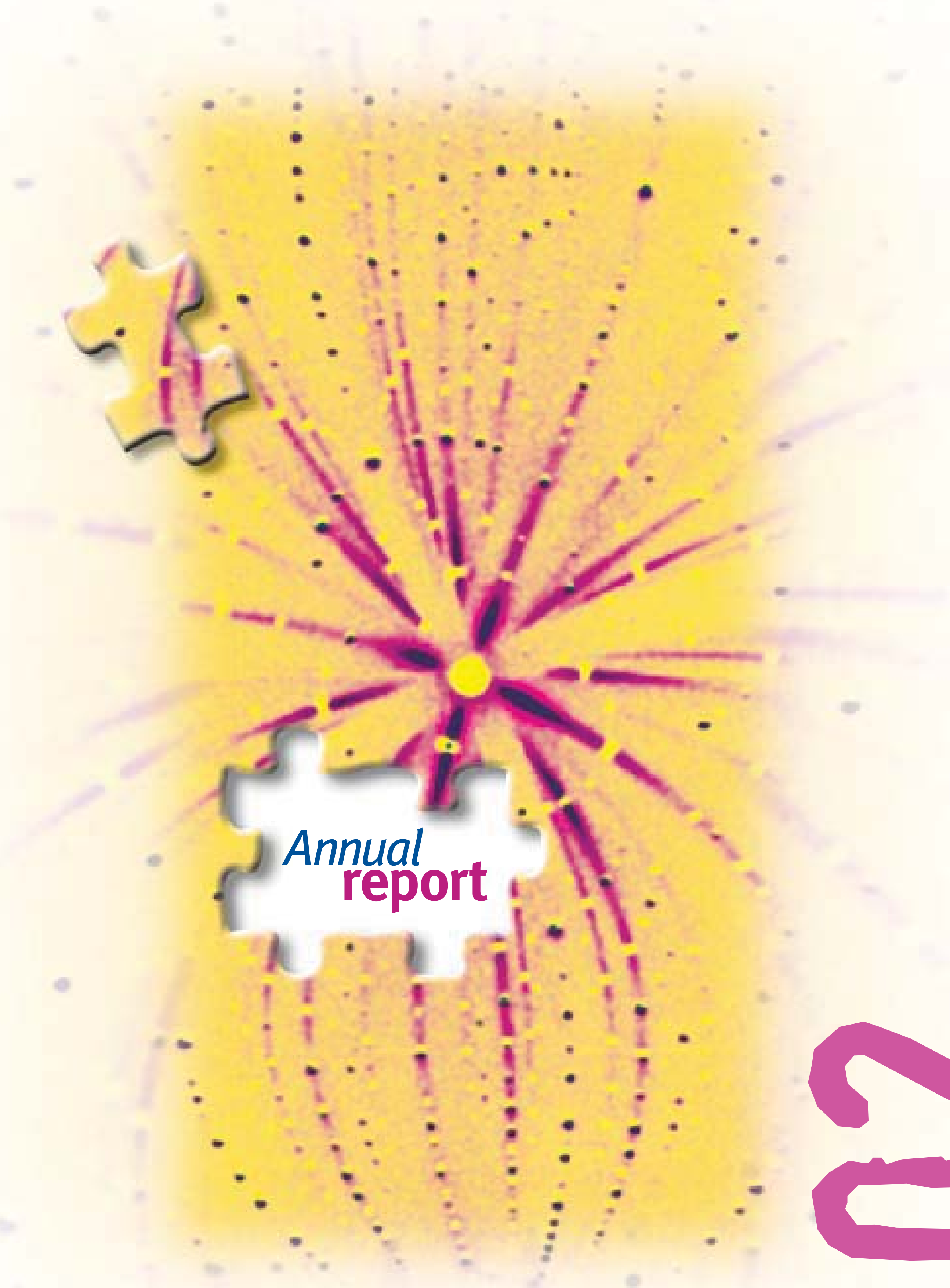

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Structural analysis *of Li-ion conducting perovskites $Li_{0.5-x}Na_xLa_{0.5}TiO_3$*

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In order to understand the influence of the crystal structure on Li-ion conductivity of $Li_{0.5-x}Na_xLa_{0.5}TiO_3$ perovskites, ND patterns of $Li_{0.5}La_{0.5}TiO_3$, $Li_{0.3}Na_{0.2}La_{0.5}TiO_3$ and $Na_{0.5}La_{0.5}TiO_3$ samples have been analysed. The Rietveld analysis of these patterns shows that Li ions are located at the centers of the faces of the primitive perovskite unit cell, and La and Na ions are distributed randomly at A sites of the perovskite. Therefore the number of vacant A sites increases with lithium content but decreases with La and Na content. The sharp decrease observed in dc-conductivity when the sodium content increases above x = 0.2, is interpreted in terms of a three-dimensional percolation limited diffusion of lithium ions. This result confirms the important role played by vacant A-sites on Li mobility.

Interest in ionic conducting solids has increased in recent years because of their potential application as solid electrolytes in batteries, fuel cells and other electrochemical devices. $Li_yLa_{2/3-y/3}TiO_3$ perovskites, with 0<y<0.5, are among the best Li-ion conductors, showing a dc conductivity of 10^{-3} S/cm at room temperature. Since the discovery of their outstanding electrical properties, several groups have investigated structural features of these perovskites; however, the conditions that enhance Li mobility have not been completely identified.

	x = 0	x = 0.2	x = 0.5
a (Å)	5.4712 (3)	5.4799 (1)	5.4868 (1)
c (Å)	13.4046 (7)	13.4230 (7)	13.4239 (5)
V (Å³)	347.49 (3)	349.08 (2)	349.999 (2)
R_p	5.18	5.86	5.29
R_{wp}	7.23	7.89	7.19
R_B	3.93	3.62	2.88
R_F	3.75	2.98	2.55
X^2	7.67	3.36	2.66
La occ	0.504 (10)	0.498 (10)	0.501 (11)
B_{iso}	0.10 (3)	0.25 (6)	0.68 (7)
3∗(Li occ)	0.495 (40)	0.210 (30)	—
B_{iso}	10.1 (9)	9.2 (9)	—
Na occ	—	0.177 (20)	0.480 (20)
B_{iso}	—	0.25 (6)	0.68 (8)
Ti B_{iso}	1.08 (12)	0.51 (7)	0.48 (7)
O x	0.5317 (5)	0.5397 (3)	0.5396 (3)
B_{iso}	1.75 (8)	1.29 (9)	1.02 (8)
Ti-O	1.942 (2)	1.949 (2)	1.951 (2)
$(M-O)_{av.}$	2.739 (2)	2.744 (1)	2.744 (2)
$(Li-O)_{av.}$	1.939 (9)	1.943 (8)	—
$(O-O)_{l.}$	4.121 (5)	4.190 (5)	4.192 (5)
$(O-O)_{s.}$	3.632 (5)	3.584 (5)	3.588 (5)
Ti-O-Ti	169.8 (4)	167.3 (3)	167.4 (4)

Table 1: Structural information deduced from refinement of ND patterns of $Li_{0.5-x}Na_xLa_{0.5}TiO_3$ samples. Thermal factors of La and Na cations were constrained to vary together during refinement

A previous study of perovskites $Li_yLa_{2/3-y/3}TiO_3$ showed that, depending on Li content, the symmetry of samples can be orthorhombic (0.04<y<0.20) or tetragonal (0.20<x<0.5) [1]. In this series, the distribution of La and vacant A sites becomes progressively ordered in alternating planes along the c-axis when the Li content decreases [2,3]. When samples are quenched from 1350ºC into liquid nitrogen, the structure becomes rhombohedral with unit cell parameters √2 a, √2 a, 3√2 a [4]. In the former materials, two-dimensional displacements are favoured. However, in the latter compounds a three-dimensional behaviour is detected.

In the $Li_yLa_{2/3-y/3}TiO_3$ series, the conductivity value increases slightly with the lithium content, passing through a small maximum at y = 0.33. In the $Li_{0.5-x}Na_xLa_{0.5}TiO_3$ series, a sharp decrease in dc-conductivity was observed when the sodium content increased above x = 0.2, which has been interpreted in terms of a three-dimensional percolation limited diffusion of lithium ions [5,6].

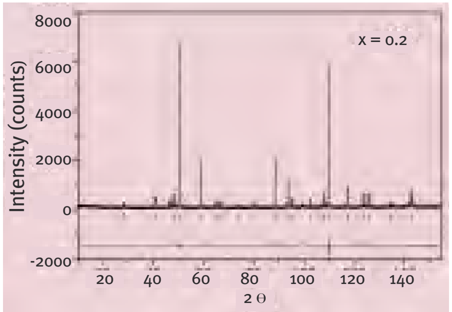

Figure 1: Rietveld refinement of the ND pattern of the $Li_{0.3}Na_{0.2}La_{0.5}TiO_3$ sample, recorded at 298K, assuming the R-3c space group. Bars correspond to Bragg peak positions. The difference profile is shown underneath.

In order to analyse the influence of two alkaline cations (Li, Na) on conductivity of $Li_{0.5-x}Na_xLa_{0.5}TiO_3$ perovskites, NPD patterns of $Li_{0.5}La_{0.5}TiO_3$, $Li_{0.3}Na_{0.2}La_{0.5}TiO_3$ and $Na_{0.5}La_{0.5}TiO_3$ samples were recorded at increasing temperatures (300-700 K) with the D1A diffractometer (λ = 1.913 Å). In all cases a rhombohedral *R-3c* symmetry was found, and the unit-cell parameters remained essentially unchanged along the series. RB and Rwp factors obtained in the Rietveld analysis were always below 3.9% and 7.9% (see figure 1 and table 1).

The structural analysis of these samples showed that Li ions are located at the centers of the faces of the primitive perovskite unit cell, whereas La and Na ions are distributed at random at the A sites of the perovskite (figure 2). Location of lithium at the face-centers of the perovskite unit-cell implies that the amount of vacant A-sites involved in conductivity is considerably higher than that deduced from the structural formula. This fact explains high values of dc-conductivity measured in Li-rich perovskites.

The octahedral tilting ($a^-a^-a^-$ in Glazer's notation) produced Ti-O-Ti angles near 167º and an oblique distortion of unit cell faces that impeded Na ions from passing through the square windows that connect contiguous A sites of the perovskite. Thermal factors deduced for Li are considerably higher than those deduced for Na, indicating that the mobility of Li^+ ions is much more important than that of Na^+ ions (see table 1). In three analysed cases, octahedral tilting decreased when temperature increased.

Taking into account the fact that Na atoms preferentially occupy A-sites, we have considered a percolation model in which A sites associated with Li ions are vacant and participate in ionic diffusion, but La^{3+} and Na^+ ions occupy A sites blocking conduction pathways of the perovskite. In this model, the vacancy distribution is random and the dc conductivity is given by the expression $\sigma_{dc}=K(n-np)^2$, where n is the number of vacant A-sites and np is the percolation threshold for a three-dimensional cubic network ($n_p \approx 0.31$). In agreement with these predictions, the ion conductivity decreases drastically near the percolation threshold (see figure 3a).

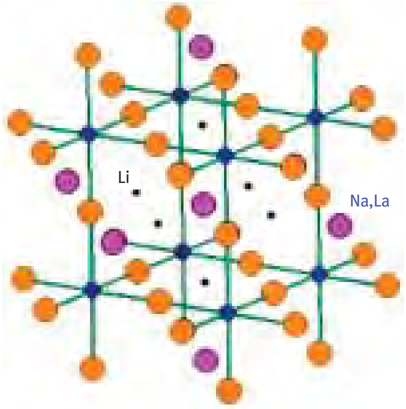

Figure 2: Elementary pseudocubic unit-cell of perovskites, indicating Li and Na locations.

Based on these structural results, the number of vacant A-sites should correspond to the sum of nominal vacancies plus Li content. From this fact, the number of vacancies that participate in lithium diffusion should be calculated as the sum of nominal vacancies plus the Li content, $n = [\mathrm{Li}]+$Ü . Substitution of Li by Na ions reduces the number of vacant sites n. When the number of vacancies decreases below the percolation threshold, $n_p = 0.31$, the conductivity of $Li_{0.5-x}Na_xLa_{0.5}TiO_3$ perovskites decreases by six orders of magnitude, from 10^{-3} to 10^{-10} S/cm [5]. In the case of the $Li_yLa_{2/3-y/3}TiO_3$ series, where $n>0.31$, this situation is not reached. These considerations are illustrated in figure 3a, where we have plotted room temperature dc-conductivity data for both the $Li_yLa_{2/3-y/3}TiO_3$ and the $Li_{0.5-x}Na_xLa_{0.5}TiO_3$ series as a function of n. The results obtained confirm the important role played by the number of vacant A-sites on the Li conductivity of these perovskites. Above the percolation threshold, the number of conducting paths is important; however, below the percolation threshold only local motions are possible (see figure 3b).

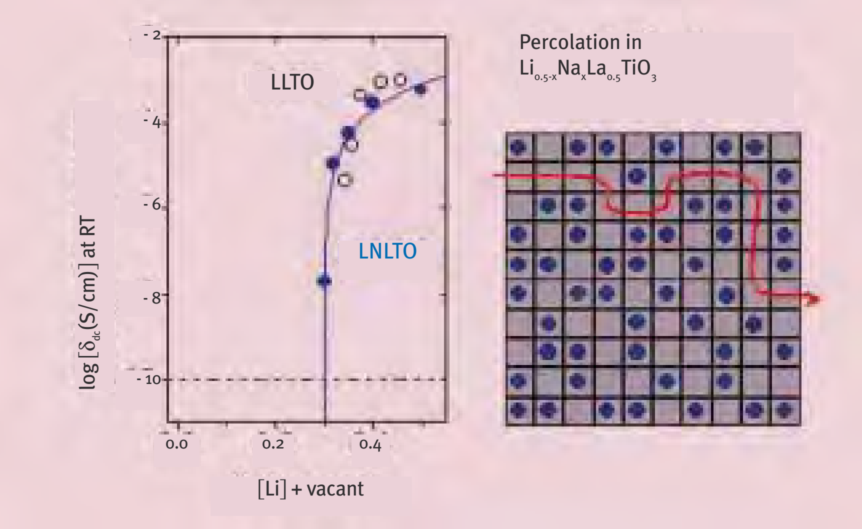

Figure 3: a) Room temperature dc conductivity of $Li_{0.5-x}Na_xLa_{0.5}TiO_3$ (blue circles) and $Li_yLa_{2/3-y/3}TiO_3$ (open circles) versus lithium plus vacant A-sites. RT dc-conductivity values are $<10^{-10}$ S/cm (our experimental resolution) for samples with n<0.3 b) Schematic illustration of lithium diffusion paths near the percolation threshold.

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