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Microstructural Study of $La_{0.5}Li_{0.5}TiO_3$

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A microstructural study of the perovskite $La_{0.5}Li_{0.5}TiO_3$ is presented. A new, tetragonal cell, $a = 2^{1/2}a_p$ and $c = 2a_p$, is proposed on the basis of the cubic perovskite subcell ($a_p \sim 3.8$ Å). By transmission electron microscopy a microdomain twinned structure has been observed. The twinning corresponds to the three possible orientations of the doubled c-axis. Besides these twinned domains, other domains have also been detected where fringe spacings corresponding to $2a_p \times 2a_p$ are present. This seems to indicate the alternation of lanthanum and lithium along the [001] direction.

INTRODUCTION

Ionic conducting solid materials have received considerable attention in the last few years due to their potential utility in several solid state devices: electrochemical sensors, secondary (rechargeable) batteries, electrochromic displays, etc.

Recently, very high ionic conductivity has been reported for $La_{0.5}Li_{0.5}TiO_3$, a perovskite based compound (1). The mechanism and the origin of its interesting transport properties are not yet known. The starting point for an understanding of the phenomenon would be an exact determination of the atomic arrangement in this material. This is still under discussion since its discovery in 1953 (2), when a simple cubic perovskite was claimed. Later work suggested an orthorhombic perovskite (3), while other authors (4, 5) have indexed the X-ray diffraction pattern based on a tetragonal tungsten bronze structure. On the other hand, Inaguma *et al.* (1) have successfully compared experimental with simulated powder X-ray diffraction patterns for this material, $La_{0.5}Li_{0.5}TiO_3$, assuming that La^{3+} and Li^+ are perfectly ordered in a double perovskite cell along the c-axis ($a_p \times a_p \times 2a_p$), where a_p corresponds to the ideal cubic perovskite cell parameter. In an attempt to arrive at a better understanding of this solid, we have performed a structural study by a combination of XRD, ED, and HREM techniques.

EXPERIMENTAL

$Li_{0.5}La_{0.5}TiO_3$ was synthesized from stoichiometric amounts of La_2O_3, Li_2CO_3, and TiO_2 of high purity. Lanthanum oxide was heated to 800°C in air for 6 hr and subsequently stored in a CO_2- and H_2O-free atmosphere. The reagents were ground and slowly heated to 800°C to avoid loss of the alkaline compound. They were then kept at this temperature for 4 hr and heated again to 1150°C for 12 hr. The calcined powder was then pressed into pellets and fired in air at 1350°C for 6 hr.

The molar ratio of the metals was determined by inductive coupled plasma (ICP) spectroscopy using a JY-70 Plus instrument.

X-ray diffraction experiments were performed on a Siemens D-5000 automatic diffractometer equipped with a graphite monochromator and Cu$K\alpha$ radiation. Structural refinements have been done by the Rietveld method (6) using the Fullproff program (7).

Samples for transmission electron microscopy were crushed in an agate mortar and ground in n-butyl alcohol; drops of the obtained suspension were deposited on a carbon coated copper grid. Electron diffraction was carried out on a JEOL 2000 FX microscope working at 200 kV. High resolution electron microscopy was performed on a JEOL 4000 EX instrument operating at 400 kV.

Magnetic susceptibility measurements in the temperature range 77–300 K were made using an automatic magnetometer DMS-500 under a variable magnetic field. The minimum magnetic field was 14 kG.

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RESULTS AND DISCUSSION

(a) General Structural Aspects

ICP chemical analysis showed that the molar ratio of cations corresponds to the formula $Li_{0.48(2)}La_{0.54(2)}TiO_y$. We have estimated the oxygen content by balancing the electroneutrality of the solid. The only cation with several possible oxidation states is Ti (Ti^{3+}, Ti^{4+}). The presence of such cations was investigated by measuring the magnetic susceptibility. Since we have observed a nonmagnetic behavior, the presence of $Ti^{3+}(d^1)$ can be rejected. From this result, and taking the chemical analysis into consideration, we can say that the oxygen content, y, is very close to the oxygen stoichiometry of the perovskite-type structure.

The analysis of our X-ray diffraction data revealed that neither the simple cubic perovskite cell (2) ($a_p \sim 3.8$ Å) nor the cell proposed by Inaguma *et al.* (1) ($a_p \times a_p \times 2a_p$) is appropriate to describe the structure of the oxide. Indexing of the X-ray diffraction pattern, shown in Fig. 1, can be done, however, using a double primitive cell with dimensions $2a_p \times 2a_p \times 2a_p$ in S.G. $P\bar{4}3m$; nevertheless two reflections (indicated in Fig. 1 as (*)) cannot be assigned to the presence of any known lithium, lanthanum, and/or titanium oxide. In considering the double cell we have taken into account a possible ordering between lanthanum and lithium ions along the three crystallographic cubic perovskite axes. However, even without this ordering being taken into account, the pattern can also be indexed using a smaller cell, but one with lower symmetry than the double-cubic cell. This new cell, $2^{1/2}a_p \times 2^{1/2}a_p \times 2a_p$ corresponds to the sometimes called "diagonal perovskites." It can easily be related to the perovskite type-structure by considering the diagonals of the cubic perovskite cell base as the new a and b parameters and doubling the third direction with respect to a_p. The best fit for the tetragonal cell corresponds to S.G. $P4mm$. However, due to the width of the peaks, probably related to a rather disordered microstructure (see below), the refinement of the XRD pattern profile by the Rietveld method ($R_p = 15.9$, $R_{wp} = 21.7$, $R_B = 8.27$, G.O.F. = 10.8) did not clear out the structural ambiguity.

To obtain detailed information about the structure, we have performed an electron diffraction study. Two diffraction patterns are shown in Fig. 2 (subindex p refers to the basic cubic perovskite cell, $a_p \sim 3.8$ Å). The extra reflections $(h/2\ 0\ 0)_p$, $(0\ 0\ l/2)_p$ and $(h/2\ 0\ l/2)_p$ that can be seen in Fig. 2a point to a doubling of both cell parameters, a and c. The doubling of the third parameter, b, can also be proposed based on Fig. 2b, where extra spots have to be indexed as $(h/2\ k/2\ l/2)_p$. Although, from this interpretation, the cubic cell $2a_p \times 2a_p \times 2a_p$, rather than the diagonal cell $2^{1/2}a_p \times 2^{1/2}a_p \times 2a_p$, appears to better

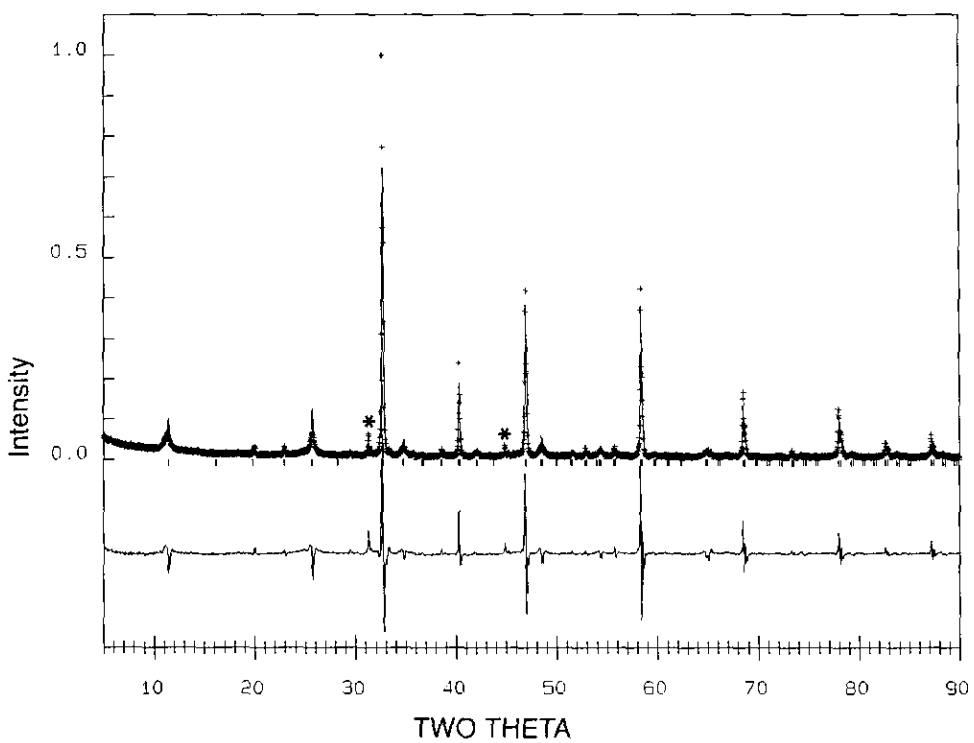

FIG. 1. Experimental X-ray diffraction pattern for $La_{0.5}Li_{0.5}TiO_3$ (crosses) and result of the profile refinement: calculated pattern (continuous line), difference (bottom line), and allowed Bragg reflections (vertical bars). The S.G. used was $P4mm$.

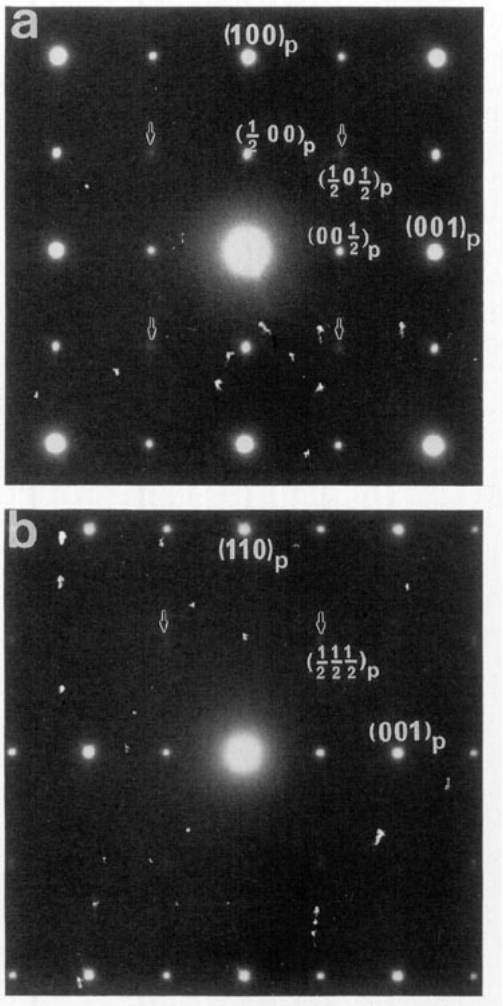

FIG. 2. Electron diffraction patterns of $La_{0.5}Li_{0.5}TiO_3$ indexed on the basis of the cubic perovskite cell: (a) $[010]_p$ zone axis; (b) $[110]_p$ zone axis.

describe the structure of $La_{0.5}Li_{0.5}TiO_3$, the latter possibility cannot be totally discarded and one can index the electron diffraction patterns by considering the diagonal cell, assuming the existence of a domain structure. Figure 3 schematically shows the diffraction pattern of Fig.

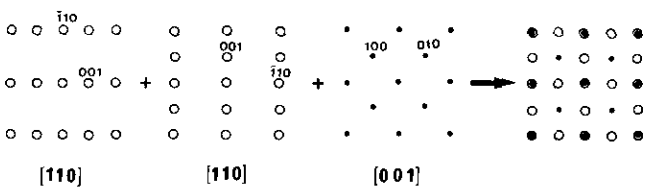

FIG. 3. Schematic interpretation of the diffraction pattern shown in Fig. 2a. The apparently cubic symmetry ($2a_p \times 2a_p \times 2a_p$) is interpreted as a combination of three sets of microdomains of a tetragonal cell ($2^{1/2}a_p \times 2^{1/2}a_p \times 2a_p$ and circular permutations) a diagonal supercell of the perovskite basic cell a_p.

2a as due to the contribution of three domains of a diagonal cell. A similar scheme can explain the spots of Fig. 2b and indeed any other orientation since it will be always due to the contribution of the three domains changing orientation upon tilting. The above scheme clearly shows a twin case that has frequently been found in other perovskites and related compounds (8, 9), including the mineral perovskite, $CaTiO_3$ (10). In this, the individual correspond to the three equivalent orientations of the doubled c axis along the x, y, and z directions. The diagonal cell derives from the perovskite by a shift of the oxygen ions that can be considered simply as a tilt of the TiO_6 octahedra. Coming back to the X-ray diffraction pattern of Fig. 1, we can index it with this diagonal cell (labels $(hkl)_d$). If the ($\frac{1}{2}$ Li + $\frac{1}{2}$ La) were disordered, a body-centered (I) cell would result. In this, $h + k + l = 2n + 1$ should be forbidden, while they appear in Fig. 1. Alternatively, with a 1 : 1 Li/La ordering along c, no centering would exist and these reflections would be allowed, as observed. It appears, then, that the $La_{0.5}Li_{0.5}TiO_3$ structure is a tetragonal diagonal perovskite with a 1 : 1 Li/La ordering along c. A tilt of the octahedra could also be present. Obviously, a full crystal structure determination will be required to definitely settle this point.

(*b*) *Microstructure*

Figure 4 shows an electron micrograph of a crystal viewed along the $[010]_p$ direction. A microdomain structure can clearly be seen. As indicated by arrows, domains with a spacing of 7.6 Å (c-axis) related by a 90° rotation with respect each other are the first feature of note. The 3.8 Å spacing of the basic cell is also visible. This obviously corresponds to the d_{110} of the proposed diagonal cell. This agrees with the information inferred from electron diffraction experiments if one takes the diagonal cell to describe the structure of the oxide. The third domain, needed to complete the scheme of Fig. 3, is also clearly seen. Close to the crystal edge, fringes corresponding to the (100) and (010) planes of the diagonal perovskite (5.4 × 5.4 Å) are resolved. Obviously, this domain is in a $[001]_p <> [001]_d$ orientation. The patchwork contrast observed is then due, as in the case of $CaTiO_3$ and related perovskites (9, 10), to the presence of three domains where the c-axis is oriented along the three space directions. Obviously the presence of three sets of domains $2^{1/2}a_p \times 2^{1/2}a_p \times 2a_p$ will suffice to explain this picture. Thus a double cell seems unnecessary to describe this phase.

Although the image obtained does not allow the determination of the atomic arrangement at the microdomain boundaries, the contrast observed in several wide boundaries between domains with $[110]_d$ orientation suggests the presence of another type of domain. The lattice peri-

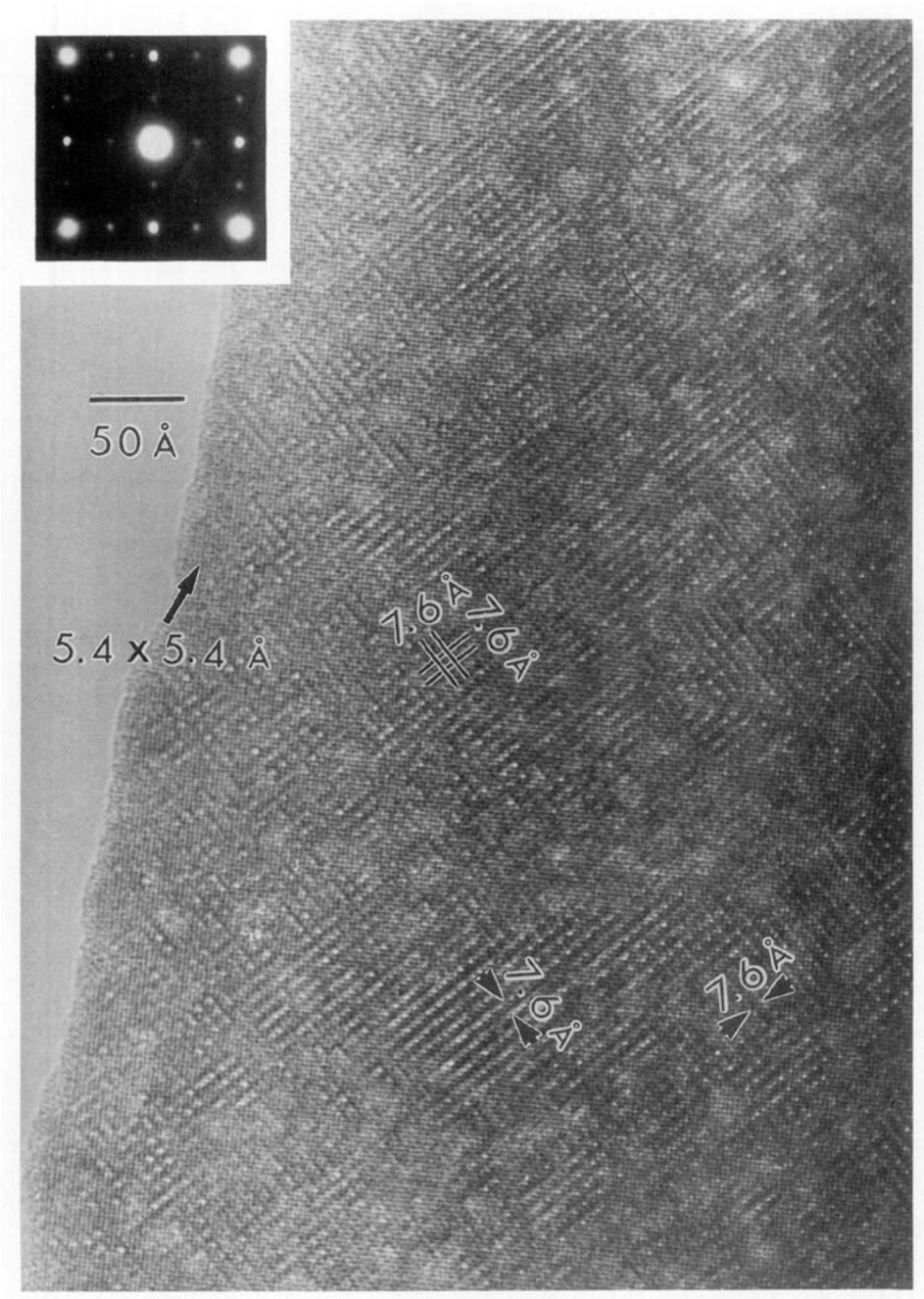

FIG. 4. High resolution electron microscope image corresponding to a $La_{0.5}Li_{0.5}TiO_3$ crystal.

odicity within it, 7.6 × 7.6 Å (see Fig. 4), is obviously not consistent with the diagonal cell. Optical diffraction experiments carried out in different small areas confirm that, in those regions, the corresponding cell needs to be considered as doubled in at least two directions. Figure 5a shows the optical diffraction pattern of a domain oriented along the $[110]_d$ direction, while Fig. 5b corresponds to a domain where the existence of a double cell is clear. Although, due to the small size of the domains, a total separation of the diffraction effects arising from each microdomain was not possible, these data do indeed indicate that some domains correspond to a cell where both *a* and *b* are doubled. The existence of domains with a double cell would not be detected by electron diffraction since the other three sets of twin domains of the diagonal cell produce together the same diffraction pattern as the double cell.

An explanation of the complicated experimental observations just described is not obvious since neither the cubic nor the diagonal cells are consistent with all data. A

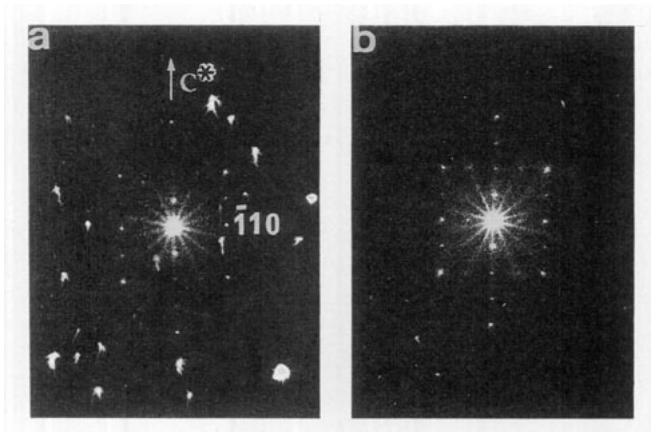

FIG. 5. Optical diffraction patterns from two different domains of Fig. 4: (a) $[110]_d$, (b) boundary between two perpendicular $[110]_d$ oriented domains giving a double cell $2a_p \times 2a_p$.

tentative model would consider, again, an ordering between lanthanum and lithium in a diagonal cell. Let us consider that a layer of lithium alternates with a layer of lanthanum along the c-direction of a $2^{1/2}a_p \times 2^{1/2}a_p \times 2a_p$ cell. The only fact without explanation, the existence of domains where the double cell is observed, can be now assigned to the coalescence of the two different orientations of the [110] domains of the diagonal cell. That is, the regions where the double cell can be seen correspond to the borderline of the two different [110] microdomains. This is illustrated in Fig. 6a, where the two different domains and the interface are schematically shown. The organization at the boundary would represent a defect of lanthanum, since some of these atoms have to be replaced by lithium. This atomic deficiency can be compensated if, on another boundary, the roles of Li and La are just opposite. Obviously, this would maintain the overall composition throughout the crystal. On the other hand, Fig. 6b shows a perfect match between both domains and the consequent absence of the double cell.

Figure 7 shows an enlargement of a small area of the diffraction pattern presented in Fig. 2a. The spots are now indexed, taking into account the presence of the three domains of the diagonal cell. An additional feature can be now seen. Although very weakly, cross shaped diffuse spots along the $[100]_p$ and $[010]_p$ directions can be seen. Although the microdomain texture of $La_{0.5}Li_{0.5}TiO_3$ does not appear clearly ordered, we think that the above

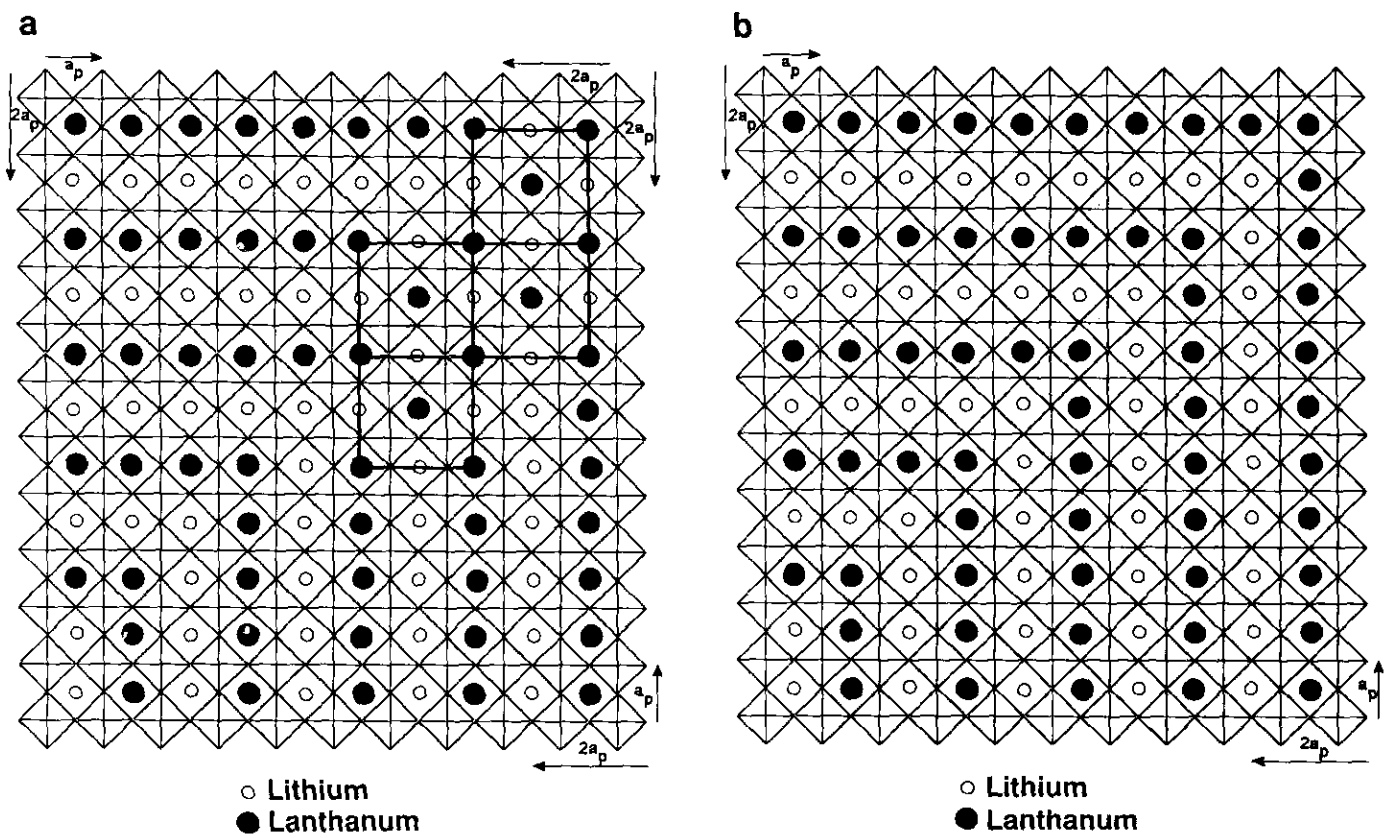

FIG. 6. Schematic representation of two [110] domains of a diagonal cell showing an ordering of lanthanum and lithium along the c-axis: (a) An ordering along two directions obtains where some lithium ions replace some lanthanum ions. (b) A situation corresponding to a perfect matching of both domains.

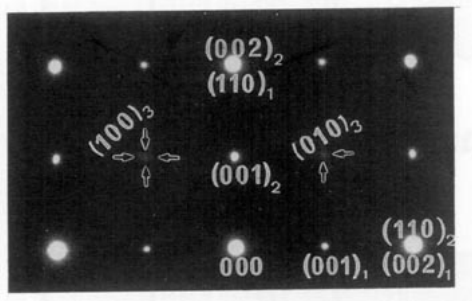

FIG. 7. Enlargement of an area of an electron diffraction pattern, taking along $[010]_p$—the same as in Fig. 2a—showing the reflections arising from each microdomain periodicity. A somewhat diffuse cross shaped group of spots can be observed (see arrows).

described effect is evidence of the existence of a quasi-periodic two-dimensional array of domains, as observed for other systems (11). From the spot spacing, a domain wall periodicity of ~78 Å can be estimated. This value indicates that the separation between quasi-ordered domain boundaries is close to $20 \times d(110)_d$. Nevertheless, this is not the case for all crystals. In others, the cross-shaped diffuse scattering is not observed, indicating that a random distribution of domains is also possible. Since these domains are very small (microdomains), a large part of the image corresponds to interfaces. However, the main feature to study in this case is not only the interface but the structure within the domains, which corresponds to the "diagonal cell."

CONCLUSIONS

$La_{0.5}Li_{0.5}TiO_3$ can be considered a tetragonal perovskite with the following cell parameters: $a = 2^{1/2}a_p$, $b = 2^{1/2}a_p$, and $c = 2a_p$ ($a_p = 3.8$ Å). It shows a microdomain texture where a quasi-periodic arrangement of domains is often present. The double cell $2a_p \times 2a_p \times 2a_p$, involving an ordering between lanthanum and lithium along three directions, has been rejected to describe the average long range structure of this compound. Nevertheless, some small domains of such a cell can be seen, probably as a microdomain boundary effect. On this basis, we propose the existence of an ordering of lanthanum and lithium in alternate layers along the c-axis to describe the intradomain structure.

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REFERENCES

1. Y. Inaguma, C. Liquan, M. Itoh, T. Nakamura, T. Uchida, H. Ikuta, and M. Wakihara, *Solid State Commun.* **86** (10), 689 (1993).
2. J. Brous, I. Fankuchen, and E. Banks, *Acta Cryst.* **6** (1), 67 (1953).
3. P. V. Putil and V. S. Chincholkar, *Indian J. Chem. Sect. A* **16** (2), 95 (1978).
4. A. M. Varaprasad, A. L. S. Mohan, D. K. Chakrabarty, and A. B. Biswas *J. Phys. C. Solid State Phys.* **12** (2), 465 (1979).
5. L. L. Kochergina, N. B. Khakhin, N. V. Porotnikov and I. Petrov, *Russ. J. Inorg. Chem.* **29** (4) (1984).
6. H. M. Rietveld, *J. Appl. Crystallogr.* **2,** 65 (1969).
7. J. Rodríguez Carvajal, "FULLPROFF Program: Rietveld Pattern Matching Analysis of Powder Patterns," Grenoble, ILL, 1990.
8. M. J. Rodríguez Henche, PhD. Thesis, Universidad Complutense, Madrid, 1985.
9. A. Vegas, M. Vallet-Regí, J. M. González-Calbet, and M. A. Alario-Franco, *Acta Crystallogr. Sect. B* **42,** 167 (1986); A. D. Berry, D. K. Gaskill, R. T. Holm, E. J. Cukauskas, R. Kaplan, and R. L. Henny, *Appl. Phys. Lett.* **52,** 1743 (1988).
10. H. F. Kay and P. C. Bailey, *Acta Crystallogr. Sect.* **10,** 219 (1957); J. J. White, R. L. Segall, J. C. Barry, and J. L. Hutchison, *Acta Crystallogr. Sect. B* **41,** 93 (1985).
11. M. Labeau, I. E. Grey, J. C. Joubert, H. Vincent, and M. A. Alario-Franco, *Acta Crystallogr. Sect. A* **38,** 753 (1982).