Journal of Solid State Chemistry **148,** 329–332 (1999)
Article ID jssc.1999.8456, available online at http://www.idealibrary.com on

Structural Refinement by Neutron Diffraction of $La_{1.12}Li_{0.62}Ti_2O_6$

A. I. Ruiz, M. L. López,[1] M. L. Veiga, and C. Pico

Departamento de Química Inorgánica I, Facultad de Ciencias Químicas, Universidad Complutense, 28040 Madrid, Spain

Received July 16, 1999; accepted July 22, 1999

Structural characterization of $La_{1.12}Lo_{0.62}Ti_2O_6$, which is a representative member of the series $La_{1.33-x}Li_{3x}Ti_2O_6$ by neutron diffraction at several temperatures (300, 400, 600, and 800 K) is performed. Crystal refinement was carried out by the Rietveld method and confirmed that this phase adopts a tetragonal symmetry (space group: *P*4/*mmm*) with an ordered distribution of the cations on the perovskite *A* sites. © 1999 Academic Press

Key Words: **perovskite structure; crystal refinement; neutron diffraction.**

INTRODUCTION

Ionic conducting materials have received considerable attention in the last few years, especially in a family of perovskites of general formula $Ln_{(2/3)-x}Li_{3x}\square_{2/3-2x}Ti_2O_6$ (1–4) for which very high values of conductivity (10^{-5}–10^{-3} S.cm^{-1} at room temperature) were reported. Nevertheless, the crystal structures of these lithium rare-earth–metal perovskites have not been well established until now. Some authors (5–7) proposed an orthorhombic unit cell for these phases where the Li and La ions were disordered on the *A* sites and the Ti ions were fully occupying the *B* sites. An important structural feature that remains unexplained in these previous studies is the extremely low values given for *Ln*–Li distances (ca. 0.62–0.89 Å) that are clearly unacceptable. On the other hand, Fourquet *et al.* (3) reported a tetragonal cell in which the rare-earth, lithium, and vacancies are in the 12-coordinated sites with an ordered distribution. The results are based on XRD studies. From these controversies it became necessary to clarify what is the actual structure of these materials, from which one could interpret the ion conduction mechanism and other related properties.

The aim of the present work is to establish the crystal structure by means of neutron diffraction data for a representative phase, $La_{1.12}Li_{0.62}Ti_2O_6$.

EXPERIMENTAL

Polycrystalline samples $La_{1.33-x}Li_{3x}Ti_2O_6$ where $x = 0.21$ were prepared by "liquid mix" technique (8) from powdered mixtures of $La(NO_3)_3 \cdot 6H_2O$, $LiNO_3$, and TiO_2, in stoichiometric ratio, thermally treated at 1248 K for two days, as described elsewhere (9).

Chemical analysis was performed using inductively coupled plasma (ICP) spectroscopy in a JY-70 apparatus.

Neutron powder diffraction data were recorded at four different temperatures on the D1A high-resolution powder diffractometer ($\lambda = 1.9110$ Å) at the Institut Laue-Langevin (Grenoble, France). The neutron and X-ray diffraction patterns were analyzed through the Rietveld method by the Fullprof program (10). A pseudo-Voigt function was chosen to generate the lineshape of the diffraction peaks.

RESULTS AND DISCUSSION

Elemental analysis of this sample revealed a loss of lithium with respect to the initial stoichiometric amount, $La_{1.11}Li_{0.66}Ti_2O_6$, and the real composition was $La_{1.12}Li_{0.62}Ti_2O_6$.

The X-ray diffraction patterns for the title compound could be assigned to a tetragonal symmetry and they were analyzed by the Rietveld method. Powder X-ray diffraction patterns of the as-made sample revealed a single-phase material. All the observed reflections could be indexed in the space group *P*4/*mmm*, but the corresponding *R* factors were quite high (2). In principle, this fact could be due to the low scattering factor of lithium and oxygen atoms.

To clarify this uncertainty, neutron diffraction data were recorded at several temperatures ($T = 300$, 400, 600, and 800 K). Structure refinements were carried out in the same tetragonal unit cell (space group *P*4/*mmm*), but a close examination of the fitted profiles (Fig. 1) revealed the presence of a small number of extra reflections. These could not be accounted for any supercell, so they were assumed to be due to a low content ($\leq 3\%$) of a new phase, as impurity, $La_2Ti_2O_7$ (11). The concentration of $La_2Ti_2O_7$, that was

---

[1] To whom correspondence should be addressed. Fax: +34-91 3944352; E-mail: marisal@eucmax.sim.ucm.es.

0022-4596/99 $30.00

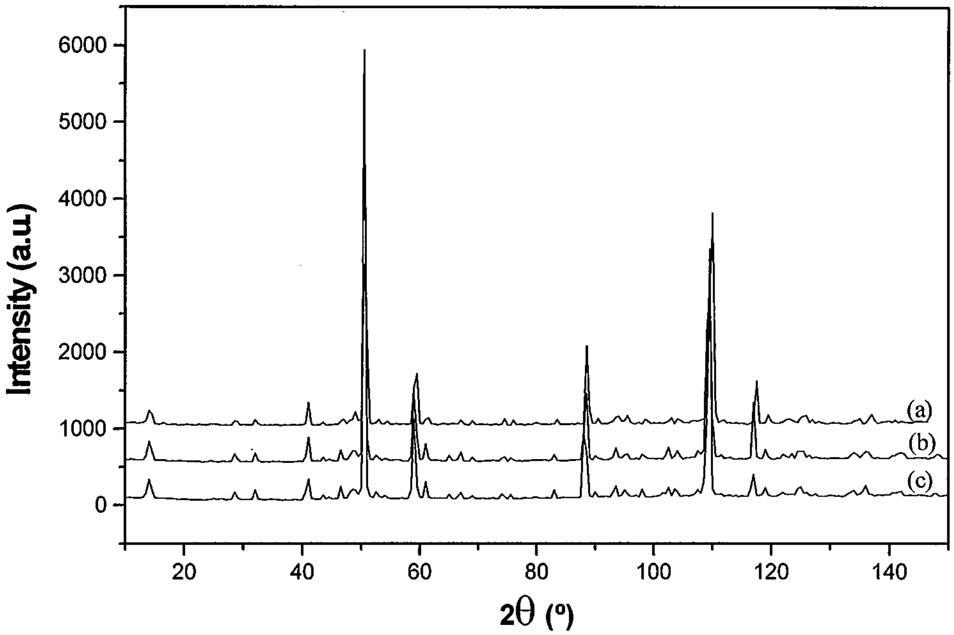

FIG 1. Powder neutron diffraction of $La_{1.12}Li_{0.62}Ti_2O_6$ at (a) 300, (b) 600, and (c) 800 K.

not detected in the X-ray patterns was included in the refinement as a second phase.

The observed, calculated, and difference neutron diffraction profiles at 800 K, are shown in Fig. 2 (in which the above extra lines are marked with asterisks). Refinement details are summarized in Table 1 and the new R factors seem to confirm the validity of this structural model. The variation of cell parameters (a and c) of this compound as a function of temperature is shown in Table 1 and their values increase with the temperature.

All atom positions are located in special sites, where the z value of Ti and O1 must be calculated. Atomic coordinates

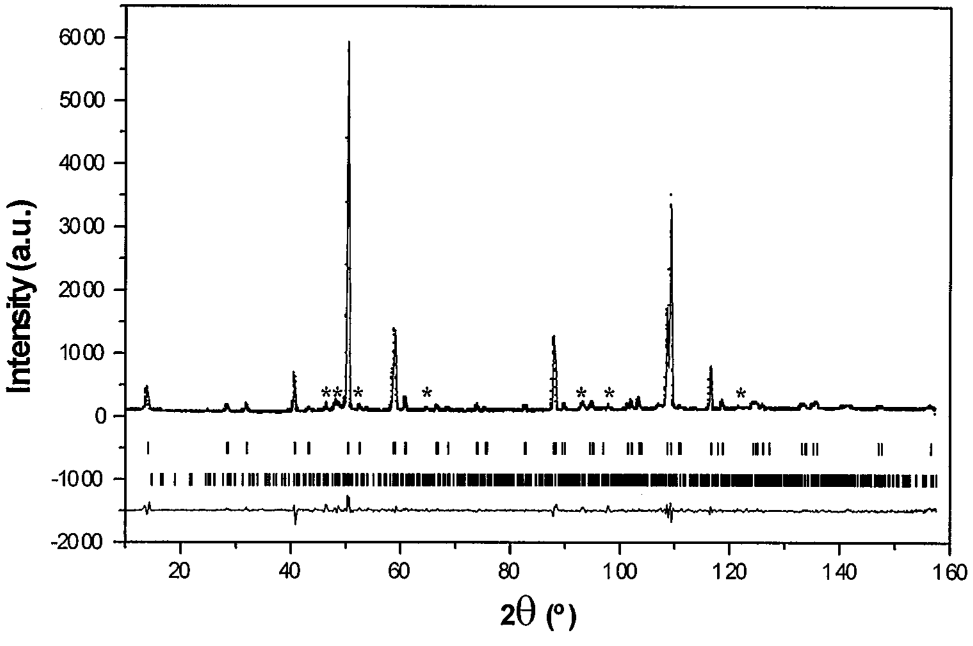

FIG 2. Calculated (dots) and observed (line) ND patterns and difference spectrum for $La_{1.12}Li_{0.62}Ti_2O_6$ at 800 K.

TABLE 1
Refined Crystal Data for $La_{1.12}Li_{0.62}Ti_2O_6$

	800 K	600 K	400 K	300 K
a	3.8825(3)	3.8787(5)	3.8745(8)	3.8697(8)
c	7.8079(8)	7.7991(1)	7.7836(9)	7.7756(5)
V	117.69(4)	117.33(5)	116.84(5)	116.44(6)
R_p	6.57	7.31	6.17	7.72
R_{wp}	9.11	10.2	8.24	10.7
R_{exp}	3.91	3.93	3.23	6.14
R_B	3.77	4.14	3.88	3.90

TABLE 3
Fractional Atomic Coordinates and Occupation of *A* Sites

	Coordinates		Occupation				
Temperature	z (Ti)	z (O1)	La1	La2	Li1	Li2	□
800 K	0.257(3)	0.236(7)	0.801(3)	0.310(3)	0.190(5)	0.430(3)	0.26
600 K	0.257(1)	0.236(1)	0.814(4)	0.306(1)	0.186(9)	0.434(4)	0.26
400 K	0.258(4)	0.234(4)	0.812(9)	0.308(1)	0.188(8)	0.432(5)	0.26
300 K	0.258(8)	0.237(3)	0.811(9)	0.309(1)	0.189(6)	0.431(2)	0.26

as well as both isotropic and anisotropic thermal parameters that were used in the refinement are listed in Table 2. The occupation factors for La^{3+}, Li^{+}, and vacancies and the *z*-coordinates of Ti and O1 are shown in Table 3. It can be observed that the $1a$ sites are markedly preferred by La^{3+} whereas all the vacancies are concentrated in the $z = \frac{1}{2}$ plane where the great majority of lithium is found. This fact confirms that this model is characterized by an ordered distribution of La^{3+}, Li^{+}, and vacancies on the *A* sites (1a and 1b) of the perovskite structure.

TABLE 2
Crystallographic Data for $La_{1.12}Li_{0.62}Ti_2O_6$

			U_{iso}			
Atom	Position	Atomic coordinates	800 K	600 K	400 K	300 K
La1	$1a$	0, 0, 0	0.13(5)	0.21(2)	0.13(6)	0.09(2)
La2	$1b$	$0, 0, \frac{1}{2}$				
Li1	$1a$	0, 0, 0	2.05(6)	2.82(7)	4.53(2)	4.22(3)
Li2	$1b$	$0, 0, \frac{1}{2}$				
Ti	$2h$	$\frac{1}{2}, \frac{1}{2}, z$	—	—	—	—
O1	$4i$	$0, \frac{1}{2}, z$	—	—	—	—
O2	$1c$	$\frac{1}{2}, \frac{1}{2}, 0$	—	—	—	—
O3	$1d$	$\frac{1}{2}\cdot \frac{1}{2}, \frac{1}{2}$	—	—	—	—

Anisotropic temperature factor/10^{-2} Å

		U_{aniso}			
Atom	Position	800 K	600 K	400 K	300 K
Ti	U_{11}	3.12(3)	3.16(1)	4.56(2)	3.59(7)
	U_{22}	3.12(3)	3.16(1)	4.56(2)	3.59(7)
	U_{33}	0.07(4)	− 0.05(2)	− 0.47(6)	− 0.45(2)
O1	U_{11}	0.95(4)	0.79(8)	1.73(3)	0.96(5)
	U_{22}	4.09(1)	3.83(5)	4.47(1)	3.20(2)
	U_{33}	1.28(6)	1.22(3)	1.07(2)	1.28(7)
O2	U_{11}	4.84(1)	4.67(5)	5.29(9)	4.63(6)
	U_{22}	4.84(1)	4.67(5)	5.29(9)	4.63(6)
	U_{33}	1.16(3)	1.11(7)	1.36(8)	0.48(5)
O3	U_{11}	6.90(1)	6.01(6)	7.60(5)	6.66(2)
	U_{22}	6.90(1)	6.01(6)	7.60(5)	6.66(2)
	U_{33}	0.18(7)	0.26(4)	0.03(2)	0.60(1)

Table 4 contains the most representative bond lengths as well as their comparison with the sum of Shannon ionic radii and the mean bond lengths. These data suggest that the TiO_6 octahedra are distorted along the *c*-axis with a shorter Ti–O3 distance as opposed to a longer Ti–O2 one and showing four equal Ti–O1 distances in the equatorial plane. The preferential location of the La^{3+} ions on $1a$ sites probably causes the displacement of Ti^{4+} toward the O3 atoms (2, 3). As a result of the above considerations, the La^{3+} and Li^{+} cations have a distorted 12-coordination polyhedra. Figure 3 shows the main features of this phase. Basal planes ($z = 0$) correspond to the $1a$ sites and the intermediate one ($z = \frac{1}{2}$) to the $1b$ sites.

Some authors (5, 6) have suggested that Ln and Li cations are occupying 8-coordination sites with anomalous distances such as Nd–Li = 0.89 Å, Pr–Li = 0.62 Å, and La–Li = 0.699 or 0.866 Å. In this respect, the structural determination carried out by us gives a more accurate length for La–Li = 3.87 Å (300 K); that is, it corresponds to the distances between $1a$ and $1b$ sites in this space group.

TABLE 4
Main Interatomic Distances (Å) for $La_{1.12}Li_{0.62}Ti_2O_6$

		Temperature			
		800 K	600 K	400 K	300 K
M1[a]–O1 (× 8)		2.677(1)	2.674(4)	2.661(6)	2.671(5)
M1–O2 (× 4)		2.745(3)	2.743(1)	2.740(7)	2.736(7)
M2[b]–O1 (× 8)		2.831(8)	2.828(4)	2.834(3)	2.816(1)
M2–O3 (× 4)		2.745(2)	2.743(9)	2.740(2)	2.736(3)
Mean M–O		2.751	2.748	2.745	2.741
Shannon La–O	2.76				
Ti–O1 (× 4)		1.948(2)	1.946(3)	1.946(7)	1.942(1)
Ti–O2		2.009(8)	2.004(4)	2.005(1)	2.010(3)
Ti–O3		1.895(6)	1.895(2)	1.887(6)	1.878(7)
Mean Ti–O		1.949	1.947	1.946	1.943
Shannon Ti–O	2.005				

[a] M1 = La/Li in z = 0.

[b] M2 = La/Li in $z = \frac{1}{2}$.

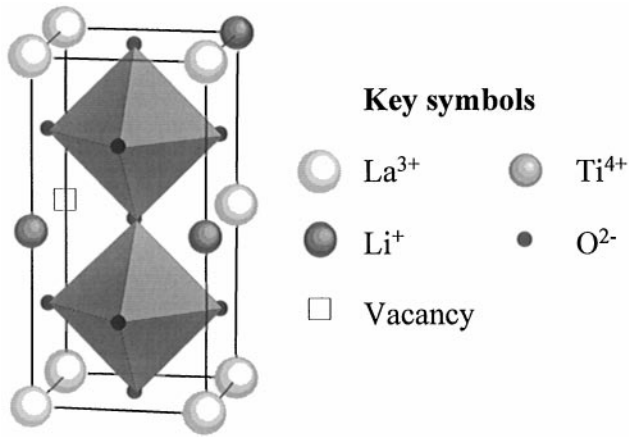

FIG 3. Structural model for $La_{1.12}Li_{0.62}Ti_2O_6$.

ACKNOWLEDGMENTS

We are indebted to the CICYT (MAT 97-0326-C04-03) for financial support. We acknowledge the ILL for collecting data of ND. One of the authors (A.I.R.) is grateful to the C.A.M. for a Beca.

REFERENCES

1. Y. Inaguma, C. Liguan, M. Itoh, T. Nakamura, T. Uchida, H. Ikuto, and M. Wakihara, *Solid State Comm.* **86,** 689 (1993).
2. A. I. Ruiz, M. L. López, M. L. Veiga, and C. Pico, *Solid State Ionics* **112,** 291 (1998).
3. J. L. Fourquet, H. Duroy, and M. P. Crosnier-López, *J. Solid State Chem.* **113,** 283 (1996).
4. C. León, M. L. Lucía, J. Santamaría, M. A. París, J. Sanz, and A. Várez, *Phys. Rev. B* **54,** 184 (1997).
5. J. M. S. Skakle, G. C. Mather, M. Morales, R. I. Smith, and A. West, *J. Mater. Chem.* **5,** 1807 (1995).
6. M. Morales and M. L. Martínez Sarrión, *J. Mater. Chem.* **8,** 1583 (1998).
7. S. García-Martín, F. García-Alvarado, A. D. Robertson, A. R. West, and M. A. Alario-Franco, *J. Solid State Chem.* **128,** 97 (1997).
8. M. Pechini, U.S. Patent 3, 231, 328 (1966).
9. I. Álvarez, M. L. Veiga, and C. Pico, *J. Alloys Comp.* **255,** 74 (1997).
10. J. Rodriguez-Carvajal, “Fullprof: A program for Rietveld refinement and pattern machine analysis,” revised version, 1994.
11. K. Scheunemann and HK. Müller-Buschbaum, *J. Inorg. Nucl. Chem.* **37,** 1879 (1975).