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The Structure Determination of $La_{2/3-x}Li_{3x}\square_{1/3-2x}TiO_3$ by the Powder Neutron and X-ray Diffraction

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ABSTRACT

$La_{2/3-x}Li_{3x}\square_{1/3-2x}TiO_3$ compounds with x=0.13 and 0.12 were prepared by slow cooling (x=0.13) and rapid quenching (x=0.12) into the liquid nitrogen after sintering at 1350°C for 6 h. Their crystal structure has been determined by Rietveld refinement of both the powder neutron and X-ray diffraction data. From neutron diffraction data, we found that the main phase was not tetragonal (P4/mmm), but trigonal ($R\bar{3}cH$). The refinement of neutron diffraction for the slow cooled samples were in a good agreement with a new model; a mixture of trigonal ($R\bar{3}cH$, 45.7 wt%), tetragonal (p4/mmm, 37.0 wt%), and $Li_{0.57}Ti_{0.86}O_2$ (pbnm, 17.2 wt%), but the quenched sample was found not to contain tetragonal (p4/mmm). X-ray diffraction data couldn't be well fitted because of the poor scattering factor of lithium ions and the similar reflection patterns among trigonal ($R\bar{3}cH$), tetragonal (p4/mmm), and cubic ($Pm\bar{3}m$). We also knew that one transport bottlenecks is destroyed by one La vacancy in the case of trigonal ($R\bar{3}cH$).

Key words : $La_{0.5}Li_{0.5}TiO_3$, Rietveld refinement, Neutron diffraction, XRD diffraction, Trigonal ($R\bar{3}cH$)

1. Introduction

Development of stable solid compounds with high ion conductivity is very important to design all solid state batteries. Lithium based electrolytes have been known as promising materials with high ionic conductivity for lithium batteries. Much work has been focused on $La_{2/3-x}Li_{3x}\square_{1/3-2x}TiO_3$ system. Inaguma *et al.*[1] reported a polycrystalline $Li_{0.5}La_{0.5}TiO_3$ showing conductivity as high as 1×10^{-3} S/cm at room temperature. The electrical properties have been well characterized by many researchers. But the definite structure of $La_{0.5}Li_{0.5}TiO_3$ compound was not yet determined. Since Brous *et al.*[2] first reported in 1953 that $La_{0.5}Li_{0.5}TiO_3$ has a cubic perovskite structure, there have been many suggestions about its structure. Orthorhombic perovskite[3] and tetragonal tungsten bronze[4] were continuously claimed, but these structures were not enough to explain x-ray diffraction patterns for $La_{0.5}Li_{0.5}TiO_3$. Recently tetragonal p4/mmm with the double period of c-axis and based on cubic was simulated and the superlattice lines were considered to correspond to the ordering of La^{3+} and Li^+ or vacancy.[5] Kawai and Kuwano[6] also reported that superstructure reflections observed are consistent with a superlattice consisting of the stacking of two perovskite subcells. Fourquet *et al.*[7] analyzed the structure of $La_{0.5}Li_{0.5}TiO_3$ by the Rietveld method from the X-ray diffraction data and by simulation of high resolution electron microscopy images. But unfortunately they couldn't refine the exact occupancy of Li^+, La^{3+} at A-site due to low scattering factor of lithium ions. Harada *et al.*[8] have reported that the quenched sample was well indexed in a simple cubic perovskite ($Pm\bar{3}m$) and did not appear any superlattice peaks on XRD pattern and the ordered samples (the parameter of order $S\approx0.55-0.7$) had lower conductivity than the quenched (disordered) samples in the range $x>0.08$ in the system of $La_{2/3-x}Li_{3x}\square_{1/3-2x}TiO_3$. The discordance in these structural studies led to a vague understanding of the mechanism for the high ionic conductivity. In order to work out some problems above, both neutron diffraction and x-ray diffraction were measured and then refined by Rietveld method. We would ultimately determine the structure of $La_{2/3-x}Li_{3x}\square_{1/3-2x}TiO_3$ and understand the conducting mechanism as well.

2. Experimental Procedure

The samples of $La_{0.5}Li_{0.5}TiO_3$ compound were synthesized from a stoichiometric amount of reagent grade Li_2CO_3 (99.0%), La_2O_3 (99.99%), and TiO_2 (99.90%). These reagents were weighed and ground together with ethanol to form a homogenous mixture. The zirconia balls were used as a media. Mixed powder was calcined at 800°C for 4 h and subsequently at 1150°C for 12 h in air. The calcined powder was ground by attrition mill and pressed into pallets with a thickness of 5~7 mm and a diameter of 15 mm under the pressure of 1000 psi. These samples were sintered in air at 1350°C for 6 h and were allowed to cool in the furnace. Some

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samples were quenched into liquid nitrogen to confirm the high temperature phase of 1350°C.

The chemical composition of samples was determined by Thermo Jarrel Ash, AtomScan 25 Inductively Coupled Plasma (ICP) spectroscopy.

The neutron diffraction data were collected at the wave length of 1.8343 Å on High Resolution Powder Diffraction (HRPD) at the Korea Atomic Energy Research Institute. Experimental conditions are as follows; Monochromator: Ge(331), Take-off angle($2\theta_M$): 90°, Collimators: 6', 10', 20' - 30' - 10', Detector : 32 ^{3}He detectors (5° apart), 2θ range : 10° - 159.95°, Sample Can: Vanadum.

X-ray powder diffraction data were collected using Siemens D5005 diffractometer with variable incident and scattering slits set to V6/V6 (6 mm) and back monochromator using CuKα radiation. X-ray diffraction data for the Rietveld refinement were collected in a step-scanning mode in the 2θ range of 10°~120° with a step width of 0.02° and a step time of 30s.

Indexing of the powder neutron diffraction patterns was achieved with the powder cell program.[9] The structural analysis from x-ray and neutron diffraction data was performed via Rietveld refinement method using the Fullprof program[10] and the quantitative analysis were carried out using neutron diffraction data for quenched and slow cooled samples.[10-12] In order to understand the mechanism of the high conductivity, the bond lengths and the bottle neck size were calculated by the computer program of ATOMS[13] from the results of the Rietveld analysis on neutron diffraction data.

3. Results and Discussion

ICP chemical analysis revealed that lithium was partially evaporated during high temperature treatment. Compositions were found to be $La_{0.53}Li_{0.40}TiO_3$ ($La_{2/3-x}Li_{3x}\square_{1/3-2x}TiO_3$ with x=0.13) for slow cooled sample and $La_{0.55}Li_{0.36}TiO_3$ ($La_{2/3-x}Li_{3x}\square_{1/3-2x}TiO_3$ with x=0.12) for quenched sample.

The Rietveld refinement for the structural analysis of $La_{0.5}Li_{0.5}TiO_3$ compound from x-ray diffraction data has been already performed by Fourquet *et al.*,[7] but they had reglected the contribution of Li^+ ion due to the poor value of its scattering factor. In other word, the lithium content at 1a and 1b sites of tetragonal (p4/mmm) unit cell couldn't be calculated. In addition, X-ray diffraction data didn't provide a reliable agreement between the observed and calculated patterns. So we used neutron diffraction with the high resolution to overcome these problems. Fig. 1 shows the results of the Rietveld refinement between the observed and calculated patterns for the neutron diffraction data, which was performed using only tetragonal (p4/mmm). The refined sample was sintered at 1350°C for 6 h and then slow cooled. As shown in Fig. 1, a space group p4/mmm was well fitted to only super lattice peaks and it didn't include the closed-circle and star marked peaks. This fact implies that tetragonal (p4/mmm) might not be an accurate space group, or

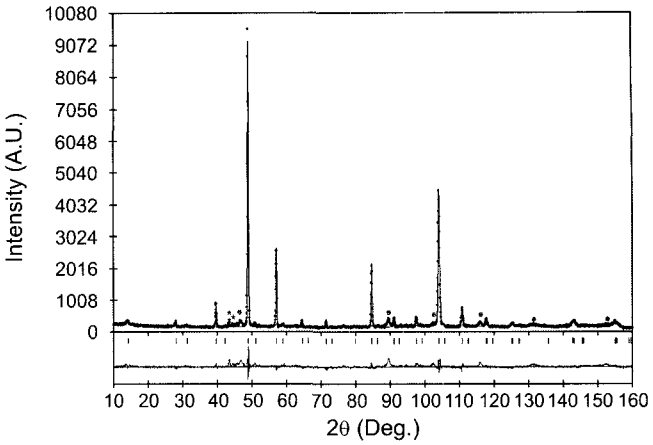

Fig. 1. Calculated(solid line) and observed(dotted line) neutron diffraction patterns and residuals for $La_{0.53}Li_{0.40}TiO_3$ prepared by slow cooling from 1350°C. Vertical bars indicate Bragg reflections. This pattern (p4/mmm, tetragonal) covers super lattice lines except for closed circle-marked and star-marked peaks.

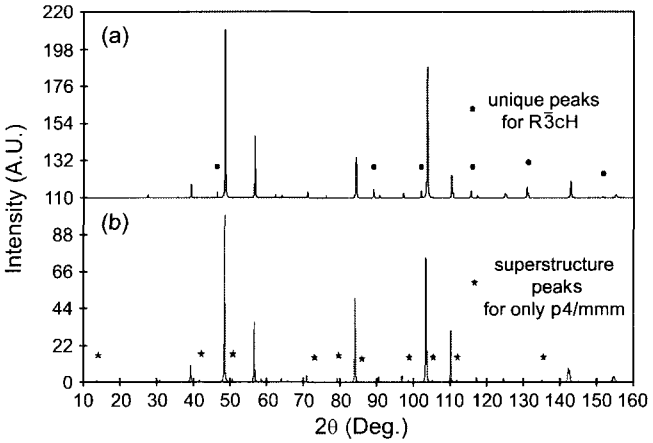

Fig. 2. Simulated neutron diffraction patterns for $La_{0.5}Li_{0.5}TiO_3$; (a) trigonal (R3̄cH) model and (b) tetragonal (p4/mmm).

antiphases could exist in this compound. We assumed that another phases might co-exist in addition to tetragonal (p4/mmm).

Fig. 2 shows the simulated neutron diffraction patterns of trigonal (R3̄cH) and tetragonal (p4/mmm) for $La_{0.5}Li_{0.5}TiO_3$ compound. When Fig. 1 was compared with Fig. 2, we could know that solid-circled peaks marked in Fig. 1 were well indexed in a neutron diffraction pattern of trigonal (R3̄cH), which was simulated in Fig. 2(a). Star-marked peaks of Fig. 1 corresponded to the reflections of $Li_{0.57}Ti_{0.86}O_2$(Pbnm).[14]

From these results, we finally conducted the Rietveld refinement to confirm the existence of trigonal (R3̄cH). The simulated trigonal (R3̄cH) in Fig. 2(a) was well refined in the observed neutron diffraction data. The results are presented in Fig. 3. The refined parameters are summarized in Tables 1 and 2. R factors seem to confirm the validity of this structural model. Consequently this experiment experienced that tetragonal (p4/mmm) was not the main phase of $La_{0.5}Li_{0.5}TiO_3$ compound and the sample sintered at 1350°C

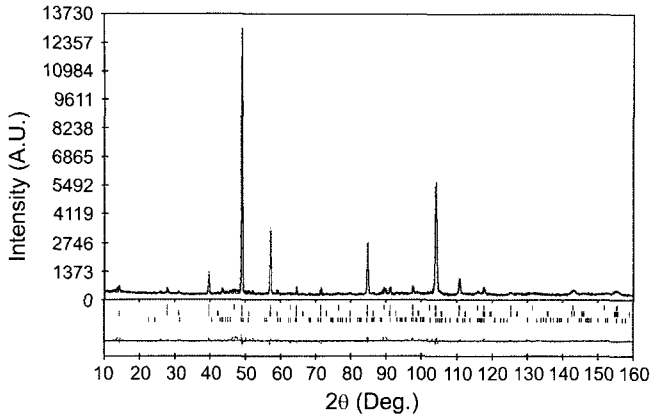

Fig. 3. Calculated(solid line) and observed(dotted line) neutron diffraction patterns and residuals for $La_{0.53}Li_{0.40}TiO_3$ sintered at 1350°C for 6 h and then slow cooled. The 1st, 2nd, and 3rd vertical bars from above indicate Bragg reflections of $La_{0.52}Li_{0.22}TiO_3$ (R$\bar{3}$cH), $La_{0.62}Li_{0.38}TiO_3$ (p4/mmm), $Li_{0.57}Ti_{0.86}O_2$ (pbnm) respectively. Observed neutron diffraction was well refined by three phases.

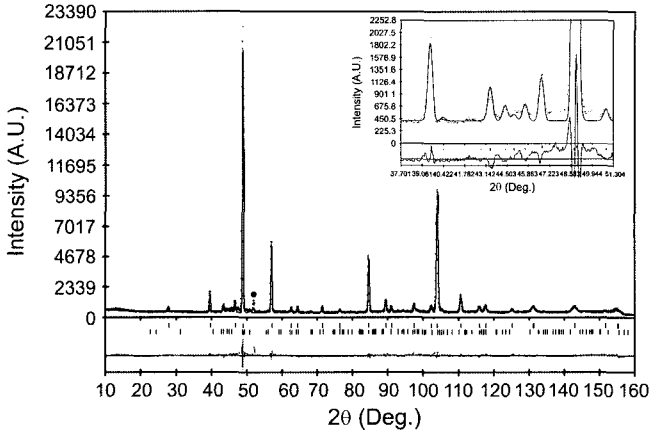

Fig. 4. Calculated(solid line) and observed(dotted line) neutron diffraction patterns and residuals for $La_{0.55}Li_{0.36}TiO_3$ sintered at 1350°C for 6 h and then quenched into the liquid nitrogen. The 1st and 2nd vertical bars from above indicate Bragg reflections of $La_{0.53}Li_{0.20}TiO_3$ (R$\bar{3}$cH) and $Li_{0.57}Ti_{0.86}O_2$ (pbnm) respectively. A mark with closed-circle represents an unknown phase.

was a mixture among trigonal (R$\bar{3}$cH, 45.7 wt%), tetragonal (p4/mmm, 37.0 wt%), and $Li_{0.57}Ti_{0.86}O_2$ (Pbnm,17.2 wt%). Minor phases were reported by several authors: $La_2Li_2Ti_3O_{10}$ by Kawai and Kuwano,[6] $Li_2Ti_3O_7$ by Fourquest *et al.*,[7] and $La_2Ti_2O_7$ by Ruiz *et al.*[15] But in this study, these minor phases were not observed at all. As can be seen in the inserted figure of the Fig. 4, the minor peaks those were not identified as major phase matched well with $Li_{0.57}Ti_{0.86}O_2$, which exists as minor phase in this study.

On the other hand, the quenched sample from 1350°C didnt contain any superstructure peaks which belong to tetragonal (p4/mmm). Fig. 4 presents the results of the refinement for the neutron diffraction of a quenched sample. As shown in Fig. 4, the superstructure lines that appeared at

Table 1. Results of Rietveld Refinement of Neutron Diffraction for $La_{2/3-x}Li_{3x}\square_{1/3-2x}TiO_3$ with x=0.13 and 0.12

Space group	R$\bar{3}$cH	P4/mmm	Pbnm
unitcell	Trigonal	Tetragonal	Orthorhombic
Number of reflections	52	70	115
a	5.4807(6) 5.4825(3)*	3.8728(1)	5.0223(8) 5.0193(8)*
b	5.4807(6) 5.4825(3)*	3.8728(1)	9.5676(15) 9.5657(14)*
c	13.4214(27) 13.4249(14)*	7.7614(2)	2.9469(4) 2.9495(4)*
α	90	90	90
β	90	90	90
γ	120	90	90
Wt%	45.74% 81.33%*	37.03%	17.23% 18.67%*
Bragg R-factor	8.26 5.88*	8.33	37.5 45.6*
R_P		7.61 8.48*	
R_{wp}		10.4 11.7*	
R_e		5.04 4.00*	

**x=0.12, the sample quenched from 1350°C.*
- In the case of $Li_{057}Ti_{0.86}O_2$ (3'rd phase) scale factor and unit-cell parameters were only refined

$$R_p = 100\sum|Y_{io}-Y_{ic}|/\sum Y_{io}$$

$$R_{wp} = 100\left[\sum w_i(Y_{io}-Y_{ic})^2/\sum Y_{io}^2\right]^{1/2}$$

$$R_{exp} = \left[(N-P)\sum w_i Y_{io}^2\right]^{1/2}$$

$$R_B = 100\sum\left||F_{io}|^2-|F_{ic}|^2\right|/\sum|F_{io}|^2$$

Y_{ic}: calculated intensity, Y_{io}: observed intensity.
N-P: # of observation(stepes) – # of least-squares parameters.

the slow cooled samples of Fig. 3 disappeared or became weaker and broader. In terms of superstructure lattice, this agreed with the result of Y. Harada *et al.*[8] They have reported that all the XRD reflections of the quenched sample were indexed in a simple cubic perovskite unit cell (pm$\bar{3}$m). But in this study of neutron diffraction for the quenched sample, we could find that the main phase was not a simple cubic perovskite (pm$\bar{3}$m) but trigonal (R$\bar{3}$cH). A small amount of $Li_{0.57}Ti_{0.86}O_2$ and an unknown phase were detected. The refined parameters are summarized in Tables 1 and 2. The unit cell parameters and volume of the quenched sample were larger than those of the slow cooled sample. The final R values obtained for the neutron refinement of the sample quenched from 1350°C had a little larger than those for the slow cooled sample. This may be due to the existence of an unknown phase.

From the refinement results of the slow cooled and rapid

Table 2. Crystallographic Characteristics of $La_{2/3-x}Li_{3x}\square_{1/3-2x}TiO_3$ with x=0.13 and 0.12 Obtained from Rietveld Refinement of Neutron Diffraction

1. R$\bar{3}$cH, Z=6

Atom	Position	X	Y	Z	Biso.	Occupancy factor
La	6a	0	0	0.25	1.469 0.268*	0.174(7) 0.177(1)*
Li	18d	0.5	0	0	7.960 7.458*	0.072(29) 0.066(17)*
Ti	6b	0	0	0	2.283 1.142*	0.333
O	18e	0.5285(0) 0.5279(3)*	0	0.25	3.360 1.743*	1.000

*x=0.12, the quenched sample from 1350°C.

2. P4/mmm, Z=2

Atom	Position	X	Y	Z	Biso.	Occupancy factor
La1	1a	0	0	0	0.224	0.114(5)
Li1	1a	0	0	0	0.224	0.136(5)
La2	1b	0	0	0.5	1.015	0.197(5)
Li2	1b	0	0	0.5	1.015	0.053(5)
Ti	2h	0.5	0.5	0.2465(0)	0.495	0.500
O1	1c	0.5	0.5	0	2.311	0.250
O2	1d	0.5	0.5	0.5	1.687	0.250
O3	4i	0	0.5	0.2643(0)	1.301	1.000

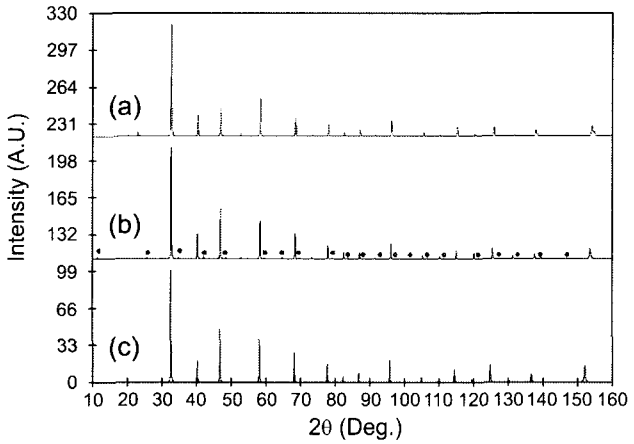

Fig. 5. Simulated X-ray diffraction patterns of (a) trigonal (R$\bar{3}$cH) model, (b) tetragonal (p4/mmm) model, and (c) cubic (pm$\bar{3}$m) model. The differences between trigonal and tetragonal are superstructure lines (solid closed circles). Trigonal and cubic is very similar.

quenched samples, trigonal (R$\bar{3}$cH) was consequently proved to be a main phase of $La_{2/3-x}Li_{3x}\square_{1/3-2x}TiO_3$ compound. Tetragonal (p4/mmm) seems to be created by the ordering of La^{3+}, Li^+ ions and vacancy and the contraction of unit cell during the cooling process.

Fourquet *et al.*[7] have previously performed the Rietveld refinement on the X-ray diffraction data using a model (tetragonal, p4/mmm). In this study, the structure of $La_{2/3-x}$

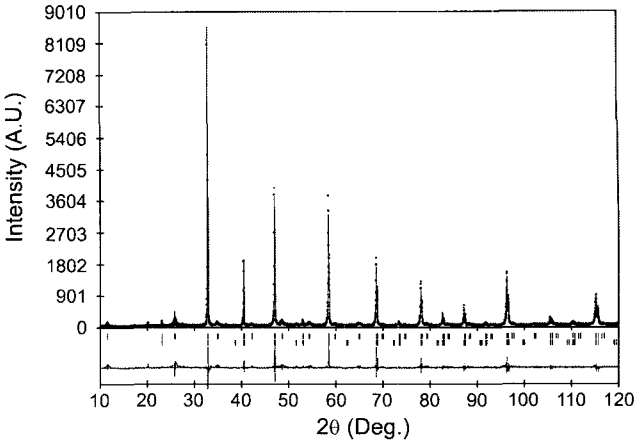

Fig. 6. Calculated(solid line) and observed(dotted line) X-ray diffraction patterns and residuals for $La_{0.53}Li_{0.40}TiO_3$ sintered at 1350°C and slow cooled. The 1st and 2nd vertical bars indicate Bragg reflections of trigonal (R$\bar{3}$cH) and tetragonal (p4/mmm) respectively. This figure shows that the refinement of X-ray diffraction is worse than that of neutron diffraction.

Table 3. Results of Rietveld Refinement of X-ray Diffraction for $La_{0.53}Li_{0.40}TiO_3$ Prepared by Slow Cooling after Sintering at 1350°C for 6 h

Space group	R$\bar{3}$cH	P4/mmm
Unitcell	Trigonal	Tetragonal
Number of reflections	126	152
A	5.4775(2)	3.8738(3)
B	5.4775(2)	3.8738(3)
C	13.4207(8)	7.7501(1)
	90	90
	90	90
	120	90
Vol.	348.846	116.303
Bragg R-factor	15.3	14.5
R_P	14.7	
R_{wp}	19.5	
R_e	9.23	

Intensities of $Li_{0.16}TiO_2$ (3'rd phase) were too weak to be refined

$Li_{3x}\square_{1/3-2x}TiO_3$ compound was also studied by X-ray diffraction on the basis of the results from the neutron diffraction. Fig. 6 shows the results of the refinement. When X-ray diffraction data were refined using a new model; a mixture of trigonal (R$\bar{3}$cH) and tetragonal (p4/mmm), we couldn't obtain better R values than the neutron diffraction. This result was attributed to the facts that lithium atoms had a low scattering factor and that the pattern of cubic (pm$\bar{3}$m), tetragonal (p4/mmm) based on cubic and trigonal (R$\bar{3}$cH) had similar reflections in x-ray diffraction profile. The simulated patterns are presented in Fig. 5. Their differences were so small that we couldn't recognize the existence of trigonal (R$\bar{3}$cH) from X-ray diffraction data at the first stage. Though our R values obtained from the refinement of

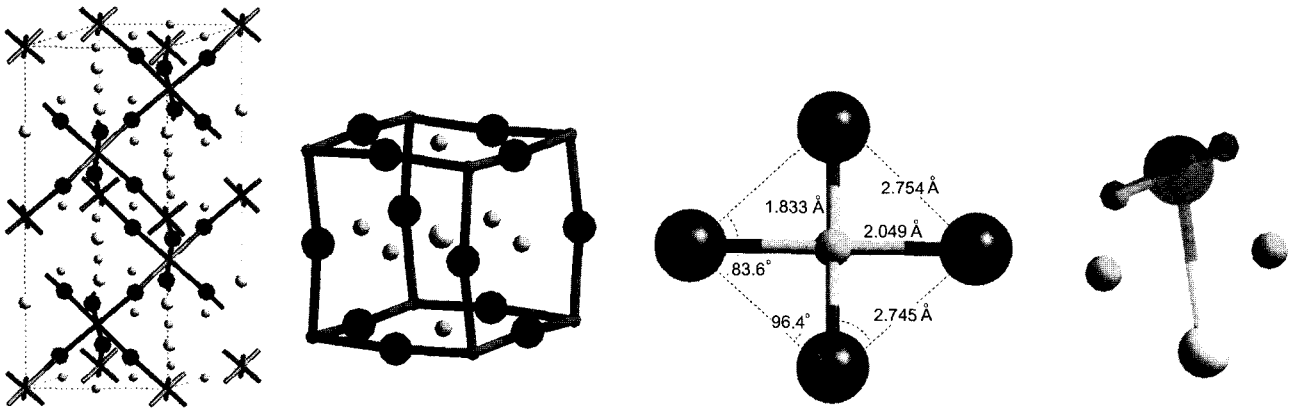

Fig. 7. Schematic figure of trigonal $La_{2/3-x}Li_{3x}\square_{1/3-2x}TiO_3$ ($R\bar{3}cH$) which show the relative location of Li (light small spheres), La (light medium spheres), Ti (dark small spheres), and O (dark large spheres). (a) unit cell, (b) pseudo-cubic unit cell, (c) Li coordination, and (d) bottleneck.

Table 4. Interatomic Distances of $La_{0.55}Li_{0.36}TiO_3$, Trigonal ($R\bar{3}cH$)

		Distance
Ti-O	×6	1.944 Å (2.005)
La-O	×6	2.745 Å
	×3	2.894 Å
	×3	2.588 Å
	Mean	2.781 Å (2.76)
Li-O	×2	2.049 Å
	×2	1.833 Å
	Mean	1.941 Å (1.99)

The bracket denotes the sum of Shannon the ionic radii[16]

X-ray diffraction data were better than that of Fourquet *et al.*,[7] they were not in a good agreement. The results of the refinement are summarized at Table 3.

The crystal structure of trigonal ($R\bar{3}cH$) unit cell is presented in Fig. 7(a). The crystallographical data were obtained from Rietveld refinement of the neutron diffraction and presented in Tables 1 and 2. Bond lengths and coordinations are tabulated in Table 4. The mean bond lengths are in good agreement with the sum of Shannon the ionic radii.[16] The Ti^{4+} ions are surrounded by six oxygen neighbors but the Ti-O-Ti angle is 170.97°. This bond angle suggest that a network of TiO_6 octahedra slightly tilted along the pseudocubic rhombohedral axes in order to optimize La-O distances as shown in Fig. 7(b). The La^{3+} ion have a distorted 12-coordination polyhedra with La-O bond lengths in the range 2.894–2.588 Å. La site occupancy is nearly 0.5 and the remaining sites are vacancies. The Li^+ ions are fourfold coordinated to oxygen ions in square plane and the Li^+ ions are placed at the middle of oxygen windows formed by four TiO_6 octahedra as shown in Fig. 7(b) and (c). The occupancy factor of Li is less than 1/6 since there are 0.5 Li ions per formula unit. The transport bottleneck located in the space between two adjacent Li sites is composed trigonal plane with two Ti, one La and one O as shown in Fig. 7(d). Because nearly half of La sites is vacancies the number of bottleneck is about 1/2. This fact means that the Li^+ mobility is proportional to the fraction of La vacancy and trigonal phase has higher conductivity. This model can be explain the result of Harada *et al.*[8] that the quenched sample has lower conductivity than the annealed sample for $Li_{0.33}La_{0.56}TiO_3$.

4. Conclusions

In this neutron diffraction study, The structure of $La_{2/3-x}Li_{3x}\square_{1/3-2x}TiO_3$ compound with x=0.13 and 0.12 is trigonal ($R\bar{3}cH$) rather than a tetragonal (p4/mmm). To be concrete, $La_{0.53}Li_{0.40}TiO_3$ compound for slow cooled sample was identified with a mixture of trigonal ($R\bar{3}cH$), tetragonal (p4/mmm), and $Li_{0.57}Ti_{0.86}O_2$ (pbnm). In addition the quenched sample, $La_{0.55}Li_{0.36}TiO_3$ was observed not to contain tetragonal (p4/mmm). It was thought that the ordered tetragonal (p4/mmm) might be formed in the course of the cooling process.

In the case of trigonal phase, La vacancy leads the break of the transport bottleneck and plays important role for the ionic conductivity.

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