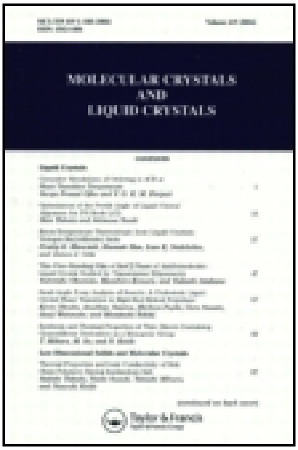

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Crystal Structures and Resistivities of $La_{1/3}Li_xNbO_3$

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Crystal Structures and Resistivities of $La_{1/3}Li_xNbO_3$

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We introduced different amounts of Li^+ ions into $La_{1/3}NbO_3$ with an A-site-deficient perovskite structure and determined crystal structures of the resultant oxides $La_{1/3}Li_xNbO_3$ ($x = 0$, 0.075, and 0.444). Reflections arising from superstructures appeared in their neutron powder diffraction patterns. Rietveld refinements revealed that the superstructures result from tilting of NbO_6 octahedra and ordering of cations and vacancies at A sites. $La_{1/3}Li_xNbO_3$ varied from an insulator to a semiconductor with increasing x.

Keywords: crystal structure; neutron diffraction; Rietveld analysis; resistivity

INTRODUCTION

Lithium-ion conductors have aroused interest widely in connection with their uses for solid electrolytes in electrochemical devices[1]. Li^+ ions can be inserted into channels or cavities of many transition-metal oxides by either chemical or electrochemical means[2,3]. Li-intercalated/deintercalated niobium oxides exhibit conductive properties caused by the mixed valence of Nb. For example, layered compounds, $Li_{1-x}NbO_2$[4] and $KLi_xCa_2Nb_3O_{10}$[5,6], showed superconductivity below 5.5 K and 6 K, respectively. Lithium ions can be also incorporated into the lattice of $La_{1/3}NbO_3$ with an orthorhombic perovskite structure (space group: Pmmm) [7,8]. In $La_{1/3}NbO_3$, a three-dimensional Nb–O network is made up of NbO_6 octahedra sharing corners. La^{3+} ions statistically occupy 2/3 of 1a positions ($z = 0$, A_1 site) whereas 1c positions ($z = 1/2$, A_2 site) are completely vacant. Kawakami *et al*[9]. synthesized $La_{(1-x)/3}Li_xNbO_3$ and determined their ionic conductivities.

The present study deals with crystal structures and resistivities, ρ, of $La_{1/3}Li_xNbO_3$ ($x = 0$, 0.075, and 0.444). We analyzed their superstructures by time-of-flight (TOF) neutron powder diffraction, paying attention to their structural peculiarities.

EXPERIMENTAL

$La_{1/3}NbO_3$ was prepared from a mixture of La_2O_3 (99.99%) and Nb_2O_5 (99.9%) in a 1:3 amount-of-substance ratio. The mixture was pelletized and calcined at 1520 K for 48 h in air. The product was molded into a bar and sintered several times at 1580 K for 36 h with intermediate grinding. Li^+ ions were introduced into $La_{1/3}NbO_3$ by soaking it in a 15 wt% *n*-hexane solution of *n*-buthylithium at room temperature for 1 and 10 weeks in a glove box filled with a high-purity Ar gas. Li contents, x, determined by ICP emission spectroscopy were 0.075 and 0.444 for the Li insertion for 1 and 10 weeks, respectively. TOF neutron powder diffraction data of the Li-free and Li-doped samples were collected at room temperature on the Vega diffractometer at the KENS. Resistivities were measured by the conventional four-probe method with currents of 10^{-3}–20 mA from room temperature down to 15 K.

TABLE I Unit-cell dimensions and R factors for $La_{1/3}Li_xNbO_3$

	$La_{1/3}NbO_3$	$La_{1/3}Li_{0.075}NbO_3$
a	7.81935(8) Å	7.82325(8) Å
b	7.83789(8) Å	7.84208(9) Å
c	7.91329(8) Å	7.91954(8) Å
V	484.984(9) Å^3	485.868(9) Å^3
R_{wp}	5.29%	7.65%
R_e	4.43%	8.69%
R_p	4.00%	5.76%
R_B	3.39%	3.25%

RESULTS AND DISCUSSION

The structure parameters of $La_{1/3}Li_xNbO_3$ were refined by the Rietveld method with RIETAN-98T[10]. The initial structural model for $La_{1/3}NbO_3$ was based on space group Pmmm and lattice parameters of $a = 3.909$ Å, $b = 3.917$ Å, and $c = 7.910$ Å[8]. Preliminary Rietveld analysis revealed that parts of reflections could not be assigned to the Pmmm phase. On the other hand, all the reflections could be indexed on the basis of an orthorhombic superlattice with $a = 7.819$ Å $\approx 2a_p$, $b = 7.838$ Å $\approx 2a_p$, and $c = 7.913$ Å $\approx 2a_p$, where a_p denotes the typical lattice parameter of a cubic perovskite-type compound. Reflection conditions, $h = 2n$ for $h0l$, $k = 2n$ for $0kl$, and $h + k = 2n$ for $hk0$, show the space group of $La_{1/3}NbO_3$ to be Cmmm, which differs from Pmmm reported previously[7,8].

Our Rietveld refinement adopting Cmmm and the new superstructure afforded lattice parameters and R factors listed in Table I. Final structure parameters are tabulated in Table II. Figure 1 gives Rietveld-refinement patterns plotted against the lattice-plane spacing, d.

In $La_{1/3}NbO_3$, La^{3+} ions occupy only part of A_1 positions, which causes displacements of Nb, O3, O4, and O5 atoms from their ideal positions on the $z = 1/4$ plane and alternate formation of long (2.070 Å) and short (1.903 Å) Nb–O bonds along the c-axis. The unit-cell dimensions of $a \approx b \approx 2a_p$ result from the tilting of NbO_6 octahedra, as demonstrated in Fig. 2.

TABLE II Occupancies, g, fractional coordinates, and isotropic atomic displacement parameters, B, for $La_{1/3}NbO_3$ ($Z = 8$)

Atom	Site	g	x	y	z	B / Å^2
La	4i	2/3	0	1/4	0	0.37(4)
Nb	8o	1	1/4	0	0.26022(3)	1.00(4)
O1	4g	1	0.22874(5)	0	0	1.18(9)
O2	4h	1	0.27126(5)	0	1/2	1.09(9)
O3	4k	1	0	0	0.25413(9)	1.14(9)
O4	4l	1	0	1/2	0.21316(9)	0.62(7)
O5	8m	1	1/4	1/4	0.23427(9)	1.11(8)

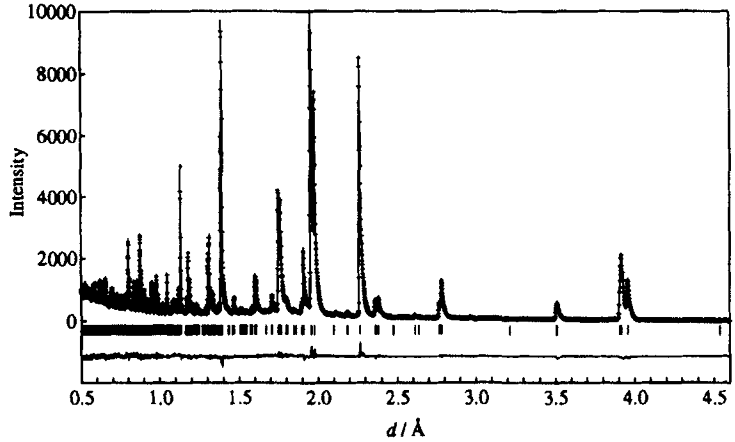

FIGURE 1 Observed (plus marks), calculated (upper solid line), and difference (lower solid line) patterns of $La_{1/3}NbO_3$.

The unit-cell dimensions and *R* factors, and final structure parameters for $La_{1/3}Li_{0.075}NbO_3$ are tabulated in Tables I and III, respectively. Li^+ ions proved to occupy A_1 positions randomly. The uptake of the small amount of Li^+ ions resulted in a slight increase in *V* and further shifting of Nb from its ideal positions: $z = 0.26022$ for $x = 0$ and $z = 0.26104$ for $x = 0.075$.

Increasing *x* led to ordering of cations and vacancies at A positions. The neutron diffraction pattern of $La_{1/3}Li_{0.444}NbO_3$ exhibited tetragonal or pseudo-tetragonal symmetry. We also observed extra weak reflections whose profiles were considerably broadened in comparison with those of nearby reflections due to the Cmmm superstructure. This finding may be explained in terms of inhomogeneous Li distribution that yields domains with additional lattice distortion and dimensions exceeding the coherence length. Nevertheless, it should be noted that all the reflections can be indexed on the basis of tetragonal space group P4/m with lattice parameters $a = 17.5180(5)$ Å and $c = 7.8966(3)$ Å. The relation between this unit cell and that of the cubic perovskite is described as $a = b \approx 2\sqrt{5}\,a_p$ and $c \approx 2a_p$, or in vector representation as $\boldsymbol{a} = 4\boldsymbol{a}_p - 2\boldsymbol{b}_p$, $\boldsymbol{b} = 4\boldsymbol{b}_p + 2\boldsymbol{a}_p$, and $\boldsymbol{c} = 2\boldsymbol{c}_p$.

Transport properties dramatically changed with increasing *x*, which accom-

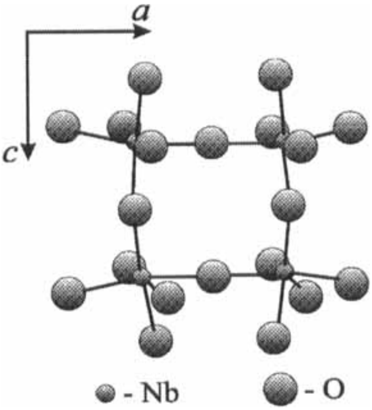

FIGURE 2 Atomic arrangement in $La_{1/3}NbO_3$.

TABLE III Structure parameters of $La_{1/3}Li_{0.075}NbO_3$ ($Z = 8$)

Atom	Site	*g*	*x*	*y*	*z*	B / Å^2
La	4i	2/3	0	1/4	0	0.29(4)
Li	4i	0.075	0	1/4	0	0.29(4)
Nb	8o	1	1/4	0	0.26104(7)	0.98(4)
O1	4g	1	0.22782(9)	0	0	1.29(9)
O2	4h	1	0.27218(9)	0	1/2	1.18(9)
O3	4k	1	0	0	0.25128(9)	1.14(9)
O4	4l	1	0	1/2	0.21073(8)	0.54(8)
O5	8m	1	1/4	1/4	0.23432(8)	1.15(7)

panied reduction of Nb^{5+} ions and changes in color from white to black. Li contents in $La_{1/3}Li_xNbO_3$ varied with the duration of soaking as well as the particle size. The typical particle size was estimated at 20 μm from SEM photographs. The resistivity of $La_{1/3}NbO_3$ was too high to measure because of its insulating property, while the Li-doped samples with $x = 0.075$ and 0.444 were both semiconducting (Fig. 3). Figure 3 shows that the resistivity at room temperature decreased and localization of electron carriers at low temperature moderated with increasing Li content owing to an increase in the number of the carriers.

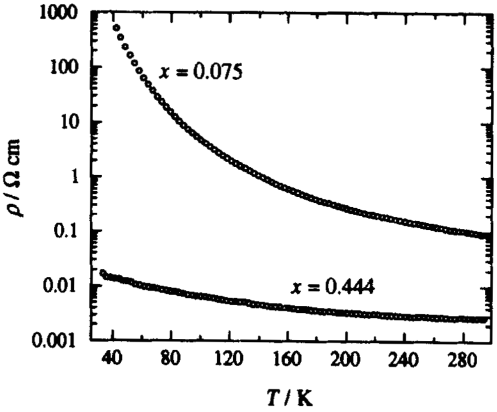

FIGURE 3 Temperature dependence of resistivity for $La_{1/3}Li_xNbO_3$.

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