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The Structure and Ionic Conductivity of $Li_{0.5\text{-}y}Na_yLa_{0.5}\{Nb,Ta\}_2O_6$ System

S.D. Kobylianska, O.I. V’yunov*, O.N. Gavrilenko and A.G. Belous

Abstract. *We have synthesized* $Li_{0.5-y}Na_yLa_{0.5}$ Nb_2O_6 *and* $Li_{0.5\text{-}y}Na_yLa_{0.5}$ Ta_2O_6 *defect perovskite solid solutions with* $0 < y \leq 0.5$*. Lithium ion diffusion in the investigated system exhibits no percolation effect. In the* $Li_{0.5\text{-}y}Na_yLa_{0.5}$ Nb_2O_6 *system, the ionic conductivity as a function of sodium content has a maximum due to two competing factors: the increase in perovskite cell volume and the decrease in lithium ion concentration. The ionic conductivity of* $Li_{0.5\text{-}y}Na_yLa_{0.5}$ Ta_2O_6 *samples decreases with sodium content.*

Key words: niobates, tantalates, solid-state reactions, ionic conductivity, NMR.

I. INTRODUCTION

Solid-state lithium ion conductors are of great interest because of their potential use in electrochemical devices such as solid electrolytes, electrodes or ion-selective membranes. Substituted solid solutions $Li_{3x}La_{2/3-x}\ {}_{1/3-2x}TiO_3$ with defect perovskites are among the best Li^+-ion conducting solid electrolytes ($\sigma \sim 10^{-3}$ S/cm at 290 K) [1-3]. The considerable vacancy concentration and high density of lithium migration channels in the structure of $Li_{3x}La_{2/3\text{-}x}\ {}_{4/3\text{-}2x}M_2O_6$ (M = Nb, Ta) defect perovskite solid solutions enabled the fabrication of good lithium ion conductors based on them ($\sigma \sim 10^{-5}$ to 10^{-4} S/cm at 290 K) [2, 3]. There is substantial evidence [8, 10] that, at a sufficiently high lithium concentration in such systems, the reduction in σ is due not only to the decrease in vacancy ( ) concentration but also to the size effect associated with the migration channel size (the area of the narrowest section, a bottleneck, formed by four corner-shared oxygen octahedra).

Interesting results were obtained by substituting Na^+ (r = 1.02 Å) for Li^+ (r = 0.74 Å) in $Li_{3x}La_{2/3-x\urcorner}\ {}_{1/3-2x}TiO_3$ [6]. Neutron diffraction and NMR data demonstrate that the alkali-metal and lanthanum ions in the perovskite structure of $Li_{3x-y}Na_yLa_{2/3-x\urcorner}\ {}_{1/3-2x}TiO_3$ occupy inequivalent crystallographic sites: the Li^+ is displaced toward the center position in the faces of the unit cell, and the Na^+ and La^{+3} reside on the A site. For y > 0.2, the lithium conductivity drops sharply [3]. This fact was interpreted on the basis of percolation theory [4], which assumes that the ion conductivity decreases drastically when the amount of vacant sites in the conduction network approaches the percolation threshold. Niobates and tantalates have a higher concentration of vacancies than titanates; however, the nature of ionic conduction in such materials is unknown.

The aim of this work was to elucidate the nature of ionic conduction in $Li_{0.5\text{-}y}Na_yLa_{0.5}$ $\{Nb,Ta\}_2O_6$ system in which lithium ions are partially substituted by sodium ions.

II. EXPERIMENTAL SECTION

$Li_{0.5-y}Na_yLa_{0.5}$ M_2O_6 samples (M = Nb, Ta) with y = 0, 0.1, 0.2, 0.3, 0.4, 0.43, 0.46, 0.48, and 0.5 were prepared by solid-state reactions technique. The synthesis procedure was similar to that described in detail earlier [5]. Samples were sintered at temperatures from 1470 to 1750 K for 2 h.

The resultant materials were characterized by X-ray diffraction (XRD). XRD patterns were collected on a DRON-4-07 powder diffractometer (CuK_α radiation). Structural parameters were determined by the Rietveld profile analysis method using XRD data.

In electrical measurements, we used samples 12 mm in diameter and 1 mm in thickness. Pt electrodes (0.5 μm) were deposited by electron-beam evaporation. The impedance of our samples was measured from 100 Hz to 1 MHz with a Solartron Analytical 1260A impedance/gain-phase analyzer. The electrical equivalent circuit and its components were identified using the Frequency Response Analyser 4.7 program.

^7Li nuclear magnetic resonance (NMR) spectra were measured on a Bruker Avance 400 spectrometer at frequencies of 155.51 and 105.84 MHz and temperatures from 235 to 350 K. The chemical shift was determined relative to the NMR profile function parameters (broad Gaussian and narrow Lorentzian components) were determined using the PeakFit program.

III. RESULTS AND DISCUTION

XRD showed that regardless of the sodium content, the sintered materials were single-phase and had an orthorhombic defect perovskite structure (sp. gr. Pmmm) in the range of $0 < y \leq 0.5$.

Because the large ion Na^+ is incapable of participating in ionic transport in such systems [6], the ionic conductivity of $Li_{0.5-y}Na_yLa_{0.5\urcorner}$ M_2O_6 (M = Nb, Ta) is determined by Li^+ transport. From the impedance data, we obtained the composition dependences of the total ionic conductivity (bulk and grain-boundary components) shown in Fig. 1. Sodium substitution for lithium increases the 290K ionic conductivity of $Li_{0.5\text{-}y}Na_yLa_{0.5\urcorner}$ Nb_2O_6 from σ = 6.85×10^{-6} S/cm at y = 0 to 1.28×10^{-5} S/cm at y = 0.43 (Fig. 1, curve 2). Further increase in y sharply reduces σ.

The ionic conductivity of $Li_{0.5\text{-}y}Na_yLa_{0.5}$ Ta_2O_6 samples decreases with sodium content from σ = 2.06×10^{-5} S/cm at y = 0 to 6.4×10^{-7} S/cm at y = 0.48.

Vernadskii Institute of General & Inorganic Chemistry, Kyiv, Ukraine

* vyunov@ionc.kiev.ua

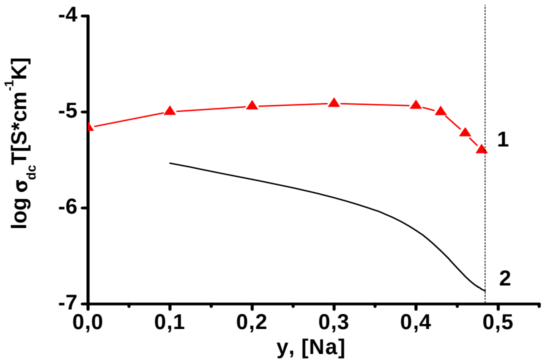

Fig. 1. Conductivity as a function of sodium content for $Li_{0.5-y}Na_yLa_{0.5}$┐ Nb_2O_6 (1) and $Li_{0.5-y}Na_yLa_{0.5}$ Ta_2O_6 (2).

The ionic conductivity of such systems is known to have a maximum at a certain migration channel size [3]. Analysis of the data in Fig. 1 leads us to conclude that the ionic conductivity of the $Li_{0.5-y}Na_yLa_{0.5}$ Nb_2O_6 samples is influenced by two competing factors, depending on *y*. On the one hand, an increase in *y* leads to an increase in *V* and, accordingly in ionic conductivity. On the other hand, increasing the Na^+ concentration reduces the lithium concentration in the system and, hence, the conductivity. The competition between these effects results in a maximum in lithium ion conductivity as a function of *y*.

In $Li_{0.5-y}Na_yLa_{0.5}$ Ta_2O_6 system, the conductivity of sample decreases with increasing of sodium content (Fig. 1, curve 2). The difference between the conductivity of Nb- and Ta-containing systems occurs due to different lithium losses during sintering. Ceramics $Li_{0.5-y}Na_yLa_{0.5}$ Ta_2O_6 were sintered at ~ 1750 K that is 150-200 K higher than $Li_{0.5-y}Na_yLa_{0.5}$ Nb_2O_6. Higher lithium losses in Ta-containing samples lead to the fact that increasing in unit cell with *y* has no positive effect on the conductivity.

^{7}Li MAS-NMR spectra of samples in both systems are formed by two signals that have been ascribed to Li ions with different mobilities. The central transition mainly corresponds to mobile Li ions (Li ions in the z = ½ plane) and satellite transitions to Li ions with restricted mobility (Li ions in the z = 0 plane). The decrease in central transition to satellite transitions ratio upon sodium substitution for lithium (Fig. 2, curve 1) points to an increase in lithium mobility, which may be due to the increase in unit cell volume. ^{7}Li MAS-NMR spectra of the $Li_{0.5-y}Na_yLa_{0.5}$ Ta_2O_6 system showed that mobility of Li decreases as the Na content increases producing the enlargement of the spectral region occupied by spinning sidebands. The intensity of narrow sidebands increases at the expense of the large ones, indicating that exchange processes between z = 0 and z= ½ planes are progressively eliminated and part of Li becomes localized when the Na content increases (Fig. 2, curve 2). In Ref. [3] this is explained by the fact that for y = 0-0.1, lithium ions are located in the plane z = ½. In this *y* range, the intensity of the satellites is minimal. With increasing of lithium (y > 0.1), Li^+ ions begin to fill the plane z = 0, thus increasing the intensity of transitions associated with localized motion of lithium.

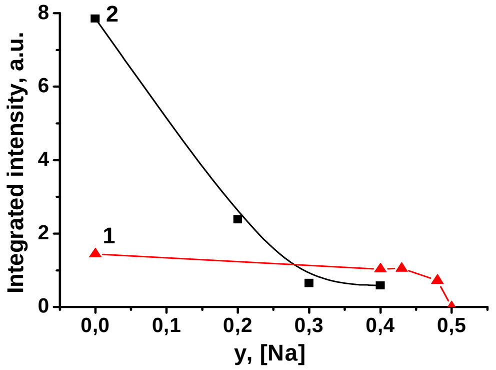

Fig. 2. The ratio of the integrated intensities of the central peak to the satellite peaks in the dependences of NMR for $Li_{0.5-y}Na_yLa_{0.5}$┐ Nb_2O_6 (1) and $Li_{0.5-y}Na_yLa_{0.5}$ Ta_2O_6 (2).

IV. CONCLUSIONS

The present results demonstrate that $Li_{0.5-y}Na_yLa_{0.5}$┐ Nb_2O_6 and $Li_{0.5-y}Na_yLa_{0.5}$ Ta_2O_6 systems have a defect perovskite structure (orthorhombic symmetry, sp. gr. Pmmm) in the range of $0 < y \leq 0.5$. The ionic conductivity of $Li_{0.5-y}Na_yLa_{0.5}$┐ Nb_2O_6 as a function of sodium content has a maximum due to two competing factors: the increase in perovskite cell volume and the decrease in lithium ion concentration. In the $Li_{0.5-y}Na_yLa_{0.5}$ Ta_2O_6 system, the ionic conductivity as a function of sodium content decreases due to significant loss of lithium during sintering of ceramics.

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