$LiSr_{1.65}\square_{0.35}B_{1.3}B'_{1.7}O_9$ (B = Ti, Zr; B′ = Nb, Ta): New Lithium Ion Conductors Based on the Perovskite Structure[†]

V. Thangadurai, A. K. Shukla, and J. Gopalakrishnan*

Solid State and Structural Chemistry Unit, Indian Institute of Science,
Bangalore 560 012, India

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We describe the design and synthesis of new lithium ion conductors with the formula, $LiSr_{1.65}\square_{0.35}B_{1.3}B'_{1.7}O_9$ ($\square$ = vacancy; B = Ti, Zr; B′ = Nb, Ta), on the basis of a systematic consideration of the composition−structure−property correlations in the well-known lithium-ion conductor, $La_{(2/3)-x}Li_{3x}\square_{(1/3)-2x}TiO_3$ (**I**), as well as the perovskite oxides in Li-A-B,B′-O (A = Ca, Sr, Ba; B = Ti, Zr; B′ = Nb, Ta) systems. A high lithium-ion conductivity of ca. 0.12 S/cm at 360 °C is exhibited by $LiSr_{1.65}\square_{0.35}Ti_{1.3}Ta_{1.7}O_9$ (**III**) and $LiSr_{1.65}\square_{0.35}Zr_{1.3}Ta_{1.7}O_9$ (**IV**), of which the latter containing stable Zr(IV) and Ta(V) oxidation states is likely to be a candidate electrolyte material for all-solid-state lithium battery application. More importantly, we believe the approach described here could be extended to synthesize newer, possibly better, lithium ion conductors.

Introduction

A lithium ion conducting solid that possesses the following characteristics would be an ideal electrolyte material for the development of all-solid-state lithium batteries, especially for operation at high (400−600 °C) temperatures.[1] (i) The material should have a high ionic conductivity at operating temperatures (ca. 0.1 S/cm at 400 °C), but much less conductivity at room temperature. (ii) It should have negligible electronic conductivity at all temperatures. (iii) It should be stable in contact with electrode materials, especially with lithium-containing anodes. Above all, it should be inexpensive, easy to produce, and environmentally benign. Although several families of inorganic solids that exhibit fast lithium ion conduction are known at present,[1] none of them comprise *all* the characteristics listed above. Accordingly, considerable research effort currently is directed toward developing new lithium ion conductors[1,2] for application as electrolytes in all-solid-state lithium batteries.

Among the several families of fast lithium ion conducting solids known presently, a perovskite-type lithium-lanthanum titanate that exhibits a bulk ionic conductivity[3] of ca. 1×10^{-3} S/cm at room temperature[4] has recently attracted a great deal of attention. After the report of a high ionic conductivity in this system by Inaguma et al.,[4] subsequent work[5−8] has revealed the details of structure and the possible mechanism of lithium ion conduction in this material. The ionic conducting phase is a nonstoichiometric perovskite, $La_{(2/3)-x}Li_{3x}\square_{(1/3)-2x}TiO_3$ (**I**) ($\square$ = vacancy), which is stable over the composition range, $0.06 < x < 0.14$, of which the $x = 0.12$ member is the best ionic conductor (bulk conductivity $\sigma = 1.53 \times 10^{-3}$ S/cm at 25 °C). Although as-prepared samples of this phase exhibit a tetragonal perovskite structure ($a \simeq a_p$; $c \simeq 2a_p$, where a_p is the lattice parameter of cubic perovskite) with an unequal distribution of Li, La, and A-site vacancies in the alternate layers along the *c*-axis, samples quenched from 1350 °C are cubic exhibiting the highest conductivity.[6] Effect of pressure[7] and chemical substitution[2a,2b,5b,8] in **I** have revealed that conduction occurs by site percolation of Li^+ ions involving A-site vacancies in the ABO_3 perovskite structure, the window of four oxygens (Figure 1) separating adjacent A-sites constituting the ‘bottleneck’ for the Li^+ ion migration. Notwithstanding these unique features which render phase **I** an excellent

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* Author to whom correspondence should be addressed.

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Table 1. Chemical Composition, Lattice Parameters, and Lithium ion Conductivity Data for Perovskite Oxides in the Li-A-B,B′-O (A = Ca, Sr, Ba; B = Ti, Zr; B′ = Nb, Ta) Systems

composition[a]	synthesis conditions: temperature (°C)/duration (h)	lattice parameters (Å)	$\sigma_{30\,°C}$ (S/cm)	$\sigma_{360\,°C}$ (S/cm)	E_a (eV)
$LiCaTiNbO_6$	800/12, 1150/(12 + 12), 1200/12	*b*	$< 10^{-7}$	6.3×10^{-6}	0.68 (200−700 °C)
$LiSrTiNbO_6$	800/12, 1150/(12 + 12), 1250/18	3.932(1)	$< 10^{-6}$	8.9×10^{-4}	0.42
$LiSrTiTaO_6$[c]	800/12, 1100/10, 1350-1400/4-6	3.932	5.5×10^{-4}	6.3×10^{-2}	0.33
$LiCa_2Ti_2NbO_9$	800/12, 1150/(12 + 12), 1200/24	*d*	$< 10^{-8}$	7.1×10^{-7}	1.03 (300−700 °C)
$LiSr_2Ti_2NbO_9$	800/12, 1150/(12 + 12), 1200/12	3.924(2)	$< 10^{-6}$	3.2×10^{-4}	0.34
$LiBa_2Ti_2NbO_9$	800/12, 1150/(12 + 12), 1200/12	4.031(1)	$< 10^{-7}$	2.0×10^{-5}	0.74 (200−700 °C)
$LiSr_2Ti_2TaO_9$[e]	1100/12, 1250/9	3.925(1)	3.2×10^{-5}	3.2×10^{-3}	0.27
$LiSr_{1.65}\square_{0.35}Ti_{1.3}Nb_{1.7}O_9$[e]	1100/12, 1200/6	3.932(1)	2.0×10^{-5}	4.2×10^{-2}	0.34[g]
$LiSr_{1.65}\square_{0.35}Ti_{1.3}Ta_{1.7}O_9$[e]	1100/12, 1250/6	3.932(1)	4.9×10^{-5}	0.114	0.35[g]
$LiSr_{1.65}\square_{0.35}Zr_{1.3}Ta_{1.7}O_9$[e]	1100/12, 1300/9	4.017(1)	1.3×10^{-5}	0.125	0.36[g]
$Li_{0.36}La_{0.55}\square_{0.09}TiO_3$[f]	650/2, 800/12, 1350/1	3.8710(2)	2.0×10^{-5}	0.130	0.33 (−100−60 °C)

[a] Excess (10 mol %) of Li_2CO_3 was added to compensate for the loss of lithium at high temperatures. [b] Orthorhombic: $a = 5.365(2)$; $b = 5.486(2)$; $c = 7.666(3)$ Å. [c] Data taken from ref 2c. [d] Orthorhombic: $a = 5.374(3)$; $b = 5.487(3)$; $c = 7.674(1)$ Å. [e] These samples were quenched to room temperature at the last stage. [f] For comparison, the data for cubic $Li_{0.36}La_{0.55}\square_{0.09}TiO_3$ are included (refs 4, 6). [g] Activation energies were obtained from the conductivity data in the temperature range 30−200 °C.

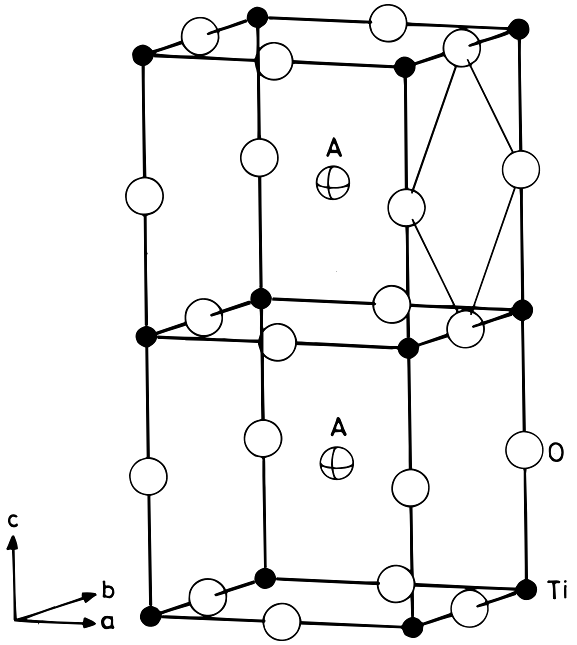

Figure 1. Idealized structure of $La_{(2/3)-x}Li_{3x}\square_{(1/3)-2x}TiO_3$ (**I**). La, Li, and vacancies(□) are distributed unequally at A-sites. A ‘bottleneck’ for the migration of the Li^+ ion is outlined.

Li^+ ion conductor, the facile reducibility of Ti^{4+} by lithium giving rise to appreciable electronic conduction in **I** precludes its use as an electrolyte material in lithium batteries.[1a,9]

We believed that it should be possible to design perovskite-type lithium ion conductors that retain the attractive features of **I** but avoid the reduction problem, by a suitable choice of A- and B-cations in the ABO_3 perovskite structure. For this purpose, we investigated several perovskite oxides in the Li-A-B,B′-O system, where A = Ca, Sr, Ba; B = Ti, Zr; B′ = Nb, Ta. In light of work already reported on **I** and related phases, our investigations have enabled us to design new lithium ion conductors of the formula, $LiSr_{1.65}\square_{0.35}B_{1.3}B'_{1.7}O_9$ (B = Ti, Zr; B′ = Nb, Ta), of which the B = Ti, Zr and B′ = Ta members (**III** and **IV**) are excellent ionic conductors exhibiting a high conductivity of 0.11−0.12 S/cm at 360 °C. We believe that the zirconium phase, $LiSr_{1.65}\square_{0.35}Zr_{1.3}Ta_{1.7}O_9$ (**IV**), would be an attractive material for electrolyte application because a reduction of Zr(IV) and Ta(V) by elemental lithium is most unlikely under operating conditions.

Experimental Section

Several perovskite oxide compositions corresponding to the general formulas $A'ABB'O_6$ and $A'A_2B_2B'O_9$ in Li-A-B,B′-O (A = Ca, Sr, Ba; B = Ti, Zr; B′ = Nb, Ta) systems were prepared by reacting appropriate oxide/carbonate mixtures at elevated temperatures in air. Single-phase materials were obtained by repeated grinding, pelletizing and heating. Table 1 lists the compositions and synthesis conditions together with lattice parameters and conductivity data. Structure characterization was made by powder X-ray diffraction (XRD) (Siemens- D5005 X-ray diffractometer, CuK_α radiation), and unit cell parameters of the single-phase materials were obtained by least-squares refinement of the powder XRD data (Figure 2). Lithium ion conductivities were measured on sintered pellets coated with gold paste using a HP4194A Impedance/Gain-Phase Analyzer across the frequency range 100 Hz to 15 MHz in the temperature range 30−700 °C in air. Because it was not possible to separate bulk and grain boundary contributions to the total conductivity, especially at high temperatures, we uniformly obtained the total ionic conductivity of the samples from the low-frequency intercepts of the impedance plots. Typical impedance plots are shown in Figure 3.

Results and Discussion

To understand the factors that control lithium ion conduction in perovskite oxides, we investigated several stoichiometric perovskite oxides of the formulas $A'ABB'O_6$ and $A'A_2B_2B'O_9$ in Li-A-B,B′-O (A = Ca, Sr, Ba; B = Ti, Zr; B′ = Nb, Ta) systems. From the data given in Table 1 and Figure 4, we concluded that: (i) conductivity increases with increasing pentavalent (B′) ion content in the oxides. This can be seen by comparing the data for $LiSrTiNbO_6$ and $LiSr_2Ti_2B'O_9$ (B′ = Nb, Ta). (ii) For oxides of the same formula, the B′ = Ta compounds exhibit a higher conductivity than the corresponding B′ = Nb compounds. This is evident from the conductivity

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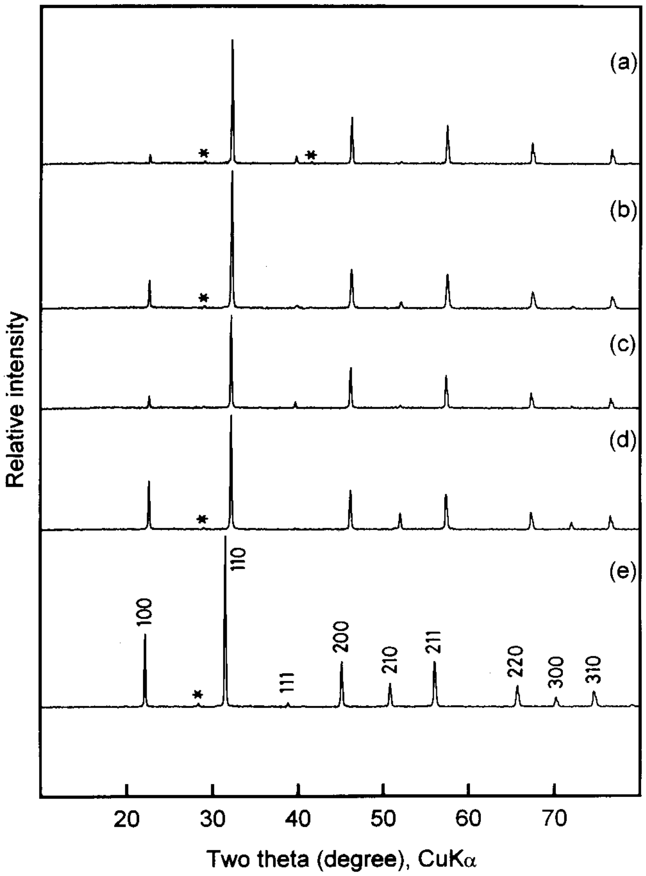

Figure 2. Powder XRD patterns (CuKα) of (a) $LiSrTiNbO_6$, (b) $LiSr_2Ti_2TaO_9$, (c) $LiSr_{1.65}\square_{0.35}Ti_{1.3}Nb_{1.7}O_9$, (d) $LiSr_{1.65}\square_{0.35}Ti_{1.3}Ta_{1.7}O_9$, and (e) $LiSr_{1.65}\square_{0.35}Zr_{1.3}Ta_{1.7}O_9$. Weak reflections caused by an unidentified impurity are marked by asterisks.

data for the pairs of oxides, $LiSrTiNbO_6$, $LiSrTiTaO_6$, $LiSr_2Ti_2NbO_9$, and $LiSr_2Ti_2TaO_9$. (iii) For oxides of the same formula, the strontium compounds exhibit a higher conductivity than the corresponding calcium or barium compounds. This is seen from the data for $LiA_2Ti_2NbO_9$ (A = Ca, Sr, Ba). The lower conductivity of the calcium compound could be caused by its lower (orthorhombic) symmetry (Table 1). The 'rolling over' of the conductivity of some of the more conducting samples in Figure 4 could be caused by the tilting of BO_6 octahedra at higher temperatures. A similar behavior has been reported for $La_{(2/3)-x}Li_{3x}\square_{(1/3)-2x}TiO_3$ (**I**), and the conductivity data at higher temperatures have been fitted to a Vogel–Tamman–Fulcher model.[9a]

Similar correlations between chemical composition and lithium ion conductivity in $La_{(2/3)-x}Li_{3x}\square_{(1/3)-2x}TiO_3$ (**I**) have been pointed out in the literature. For example, Inaguma et al.[2a] reported that substitution of the larger strontium ion for lanthanum in **I** increases the ionic conductivity, whereas substitution of smaller lanthanides (Pr, Nd, Sm) for lanthanum in **I** decreases the ionic conductivity.[2b] This effect has been understood[7] in terms of the increase/decrease of the 'bottleneck' size caused by the substitution of larger/smaller cations at the lanthanum site. Corroborative evidence for this observation is provided by pressure-effect studies[7b] on **I**. An increase in the conductivity due to Nb/Ta substitution for Ti in derivatives of **I** has been attributed to a shallow electrostatic potential[10] at the A-sites which arises from an increased B–O bond strength.[8] In general, it is known that in ABO_3 perovskite oxides, increase of B–O bond strength due to increasing oxidation state of B weakens the A–O bond strength and vice versa, owing to the interaction of A and B ions competing for the same oxygen 2p orbitals.[11]

A larger conductivity of the tantalum oxides than that of the corresponding niobium oxides is not easily understood. The effect is most likely related to the highest occupied molecular orbital (HOMO)–lowest unoccupied molecular orbital (LUMO) gap between oxygen 2p and the metal d^0 states of Nb/Ta, which in turn determines the distortion of NbO_6/TaO_6 octahedra.[12] Since this gap would be larger for Ta than for Nb oxides, TaO_6 octahedra would be less distorted than NbO_6 octahedra, other factors being constant. Presumably, a less distorted TaO_6 octahedron seems to be more favorable for lithium ion conduction than a strongly distorted NbO_6 octahedron (where the distortion is perhaps frozen).

Besides these factors, A-site vacancy concentration is another crucial factor that helps maximize the ionic conductivity of **I**. Best ionic conduction in **I** is obtained,[5c,6] for the compositions $x = 0.11-0.12$ in the formula $La_{(2/3)-x}Li_{3x}\square_{(1/3)-2x}TiO_3$, for which the A-site vacancy concentration is 0.11–0.09. At this value of x, the total concentration of lithium and A-site vacancy is 0.44–0.45, this value being higher than the site percolation threshold (0.3117) for the simple cubic lattice.[7a] Presumably, this concentration of lithium ion and A-site vacancy seems to be the optimal value for maximizing lithium ion conduction in perovskite lattices, because it ensures the presence of at least one lithium ion or vacancy adjacent to every lithium ion in the oxide.[7a]

Last but not least, ionic conductivity of **I** is influenced by whether or not the A-site species (La, Li, and vacancies) are ordered.[6] For example, an $x = 0.12$ sample of **I** quenched from 1350 °C having a cubic structure (A-site species are disordered) has a higher conductivity (1.53×10^{-3} S/cm at 25 °C) than an annealed sample of the same composition. The latter having a tetragonal perovskite superstructure exhibits a lower conductivity (6.88×10^{-4} S/cm).

Taking into account the foregoing factors that influence lithium ion conduction in perovskite oxides, we arrived at the composition, $LiSr_{1.65}\square_{0.35}B_{1.3}B'_{1.7}O_9$ (B = Ti; B′ = Nb, Ta), which optimizes all the factors. Thus, A-site contains strontium (0.55 Sr per ABO_3 formula, the Sr content being the same as the La content of the best lithium ion conducting composition of **I**) which is expected to provide an optimal 'bottleneck' size for lithium ion migration.[7a] The total concentration of lithium and A-site vacancies is 0.45 per ABO_3 formula, a value that gives maximum lithium ion conductivity for **I**. Our composition also has a significant concentration of pentavalent (Nb/Ta) ions at the B-site which is known to promote lithium ion conduction by weakening Li–O bonds.

Cubic perovskite oxides of this composition are readily obtained by reacting an appropriate mixture of oxides/

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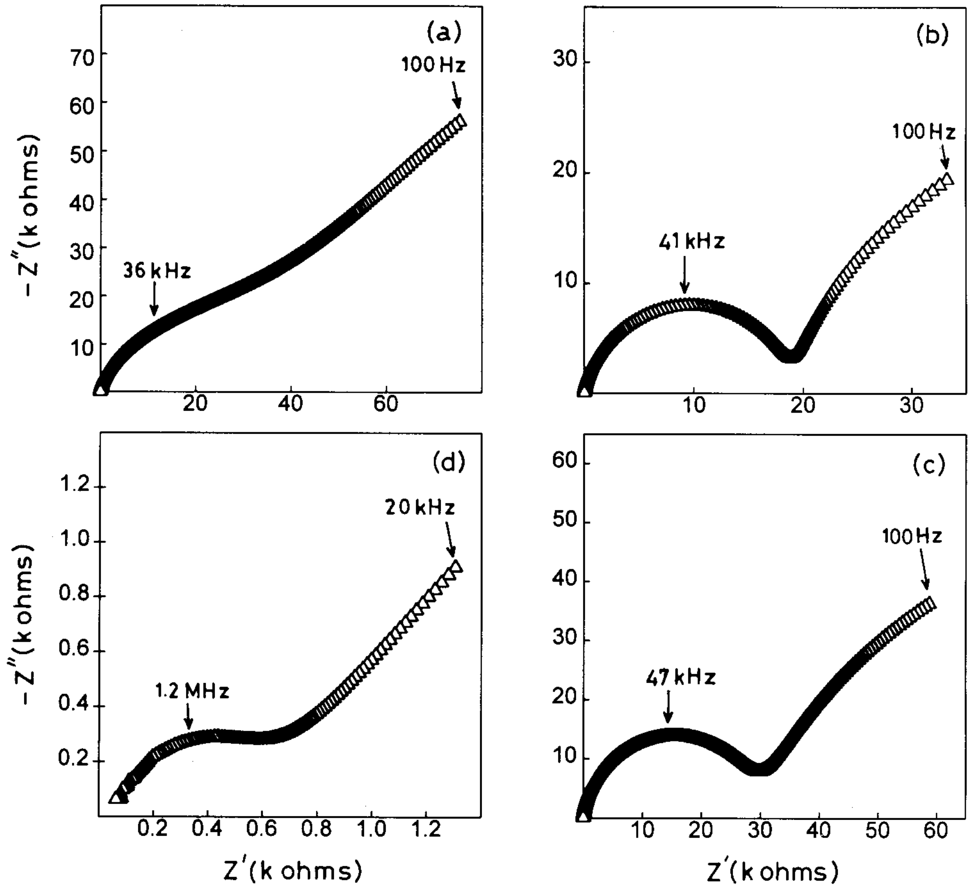

Figure 3. Typical ac impedance plots for (a) $LiSr_2Ti_2TaO_9$, (b) $LiSr_{1.65}\square_{0.35}Ti_{1.3}Nb_{1.7}O_9$, (c) $LiSr_{1.65}\square_{0.35}Ti_{1.3}Ta_{1.7}O_9$, and (d) $LiSr_{1.65}\square_{0.35}Zr_{1.3}Ta_{1.7}O_9$ at 30 °C.

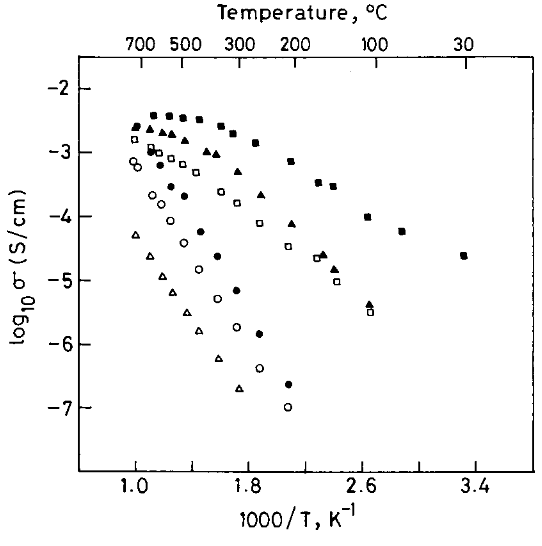

Figure 4. Arrhenius plots for the ionic conductivity of $LiABB'O_6$ and $LiA_2B_2B'O_9$ perovskites: $LiCaTiNbO_6$(○), $LiSrTiNbO_6$(▲), $LiCa_2Ti_2NbO_9$ (△), $LiSr_2Ti_2NbO_9$ (□), $LiBa_2Ti_2NbO_9$ (●), and $LiSr_2Ti_2TaO_9$ (■).

carbonates at 1200 °C followed by quenching the sample to room temperature (Table 1; Figure 2). Between the two phases, $LiSr_{1.65}\square_{0.35}Ti_{1.3}Nb_{1.7}O_9$ (**II**) and $LiSr_{1.65}\square_{0.35}Ti_{1.3}Ta_{1.7}O_9$ (**III**), the tantalum oxide (**III**) exhibits a much higher ionic conductivity than the niobium oxide (**II**) (Figure 5), the conductivity of **III** being similar to that of the best conductors in the lanthanum−lithium titanate series (**I**).[6] It must be mentioned that slow cooling of the samples does not yield single-phase cubic perovskites.

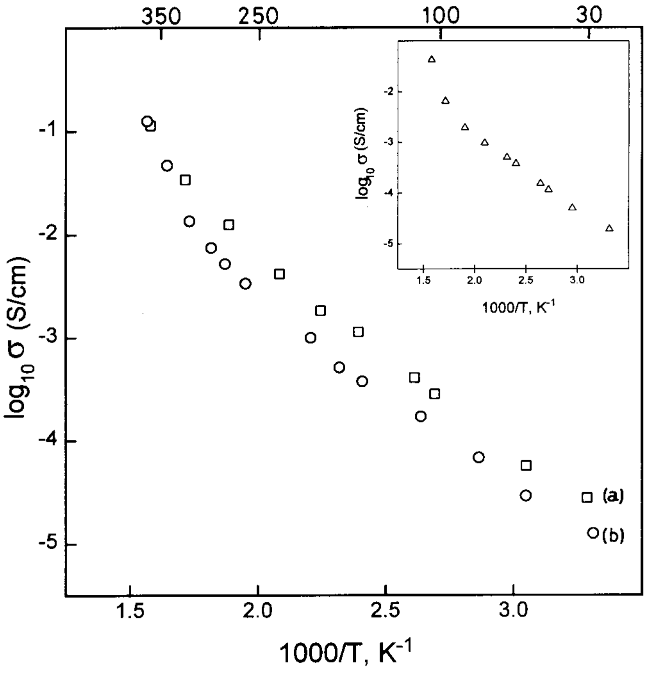

Figure 5. Arrhenius plots for the ionic conductivity of (a) $LiSr_{1.65}\square_{0.35}Ti_{1.3}Ta_{1.7}O_9$ (**III**) and (b) $LiSr_{1.65}\square_{0.35}Zr_{1.3}Ta_{1.7}O_9$ (**IV**). The data for $LiSr_{1.65}\square_{0.35}Ti_{1.3}Nb_{1.7}O_9$ (**II**) are shown in the inset.

Having succeeded in obtaining one of the best lithium ion conducting perovskite oxides by a rational choice of the chemical composition, we attempted to prepare a lithium ion conductor that will not suffer a reduction of the B-site ions when in contact with lithium. For this purpose, we chose the composition, $LiSr_{1.65}\square_{0.35}Zr_{1.3}Ta_{1.7}O_9$ (**IV**), where Zr(IV) replaces Ti(IV) in **III**. A single-phase perovskite oxide of this composition is formed (Figure 2e) by reacting the constituents at 1300 °C followed by quenching. The phase has a cubic perovskite structure with $a = 4.017(1)$Å (Table 1). The ionic conductivity data for this phase (**IV**) are shown in Figure 5. Although the conductivity of this oxide (1.3×10^{-5} S/cm at 30 °C) is lower than that of the corresponding titanium oxide (**III**) (4.9×10^{-5} S/cm at 30 °C) at room temperature, the conductivities of both the oxides become equal around 350 °C; indeed the conductivity of **IV** (0.125 S/cm) is slightly higher than that of **III** (0.114 S/cm) at 360 °C. Accordingly, we believe that the zirconium oxide phase (**IV**) would be an ideal candidate that would meet the requirement of a low ionic conductivity at lower temperatures and a high ionic conductivity (ca. 0.1 S/cm at 400 °C) at operating temperatures, required for high-temperature, solid-state lithium battery application.[1a] Moreover, because Zr(IV) and Ta(V) are stable oxidation states that resist reduction to lower states, we believe that the oxide (**IV**) would be stable toward lithium anodes at operating conditions.

Finally, a comment on the choice of B cations for the best lithium ion conduction in perovskite oxides may be in order. Because migration of lithium ions in **I** is known to involve a dilatation of the ‘bottleneck’, accompanied by a positive volume of activation[7] and distortion/tilting of TiO_6 octahedra, we believe that d^0 cations such as Ti(IV), Zr(IV), Nb(V) and Ta(V) would be the best choices for B cations in lithium ion conducting perovskite oxides, because d^0 cations are known to distort BO_6 octahedra giving rise to short and long B—O bonds.[12] A dynamic fluctuation of B—O bond lengths caused by a disordered distribution of A-site species in the perovskite structure seems to be more favorable for facile conduction than a frozen distribution of bond lengths, as revealed by a higher ionic conductivity of the cubic perovskite phase than its ordered variant[6] in **I**. Further work on the new series of oxides reported here is essential to understand these aspects.

In summary, we have shown that, by a systematic consideration of the composition−structure−property correlations in lithium-containing perovskite oxides, it is possible to design new perovskite oxides in the Li-Sr-B,B′-O (B = Ti, Zr; B′ = Nb, Ta) systems that exhibit excellent lithium ion conduction. A perovskite oxide with the formula $LiSr_{1.65}\square_{0.35}Zr_{1.3}Ta_{1.7}O_9$ (**IV**), which contains stable Zr(IV) and Ta(V), is likely to be a good candidate electrolyte material for all-solid-state lithium battery application.

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