

Rational design of solid materials: A case study of lithium-ion conductors

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

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

In the absence of a reliable method for *a priori* prediction of structure and properties of inorganic solid materials, an experimental approach involving a systematic study of composition, structure and properties combined with chemical intuition based on previous experience is likely to be a viable alternative to the problem of rational design of inorganic materials. The approach is illustrated by taking perovskite lithium-ion conductors as an example.

NOWADAYS, rational design of materials is a popular refrain among materials scientists¹⁻³. Everyone wants to rationally design materials possessing desired structure and properties for technological applications. While we materials scientists seem to know all the materials properties that are technologically important⁴, there are very few instances of rational design of materials based on *a priori* prediction of structure and properties. This dichotomy between what we want and what has been achieved in materials design could not have been brought out more effectively than by John Maddox, the previous editor of *Nature*, who declared that materials design was a 'scandal'⁵. The 'scandal' he was referring to pertains to our inability to predict *a priori* the structure and properties of crystalline solids. It is so glaring even today that we are unable to identify any crystalline material with proven or potential technological application that has been prepared by design⁶. Whether it is yttria-stabilized zirconia that finds application in solid oxide fuel cells, or lithium intercalation compounds such as LiMX_2 ($M = \text{Ti, Co, Ni}$; $X = \text{S, O}$) and Li/graphite that are used as electrodes in rechargeable lithium batteries, or the frequency-doubling nonlinear optical materials such as KTiOPO_4 and LiNbO_3 , or the oxidation catalysts based on vanadyl phosphates and bismuth molybdates that are employed for selective oxidation of *n*-butane to maleic anhydride and propylene to acrolein, respectively, or the exotic condensed metal-cluster compounds typified by NaMo_4O_6 , or, for that matter, the ubiquitous high T_c superconducting cuprates typified by $\text{YBa}_2\text{Cu}_3\text{O}_7$ – all are products of more or less chance discovery (serendipity) rather than materials of rational design. It must however be remembered that it

is the painstaking perseverance of experienced and dedicated minds and hands that was behind translating each one of the chance-discoveries into products of reality. So, if rational design of materials has not been possible, what are the causes and what is the solution?

The problem is simple: we cannot predict reliably the structures of extended inorganic solids from first-principles theoretical approach, let alone predicting their stability and properties, despite all the advances in quantum chemistry and computational methods. While it may be possible to predict in a limited way the existence of new compositions within a given structural family by analogy with already known phases, guided by chemical intuition based on previous experience⁷⁻⁹, prediction of entirely new inorganic phases and their structures and properties is too daunting a task at present. Strangely, even if we are able to predict the possible existence of novel solids either intuitively or on the basis of a theoretical approach, the problem of synthesis is equally formidable. The example of sp^3 -bonded carbon nitride, C_3N_4 , would serve to illustrate the point. Although this material has been predicted to exist and possess 'harder than diamond' properties on the basis of density functional theory^{10,11}, all the conventional approaches to its synthesis have not been successful so far¹². Instances like this involving metastable states call for innovative synthetic approaches.

Talking of synthesis of extended inorganic solids, a few points have to be made. The retrosynthetic approach *a la* Corey¹³, used successfully for the covalent synthesis of organic molecules, as well as the self-assembly approach *a la* Lehn¹⁴, Whitesides *et al.*¹⁵ and others^{16,17} used successfully for the synthesis of noncovalent assemblages of molecular solids are of no avail when it comes to synthesis of extended inorganic solids. The reasons are obvious: not only are we unable to predict kinetically-controlled reaction pathways that will enable a retrosynthetic approach, but also are we unable to identify simpler molecular units (synthons and tectons) that could be assembled together to obtain extended inorganic solids of our choice. Therefore, in this field, one relies on rather primitive synthetic methods¹⁸⁻²⁰ and constantly strives to develop new methods based on chemistry^{18,20-22}; a knowledge of crystal chemistry,

*For correspondence. (e-mail: gopal@sscu.iisc.ernet.in)

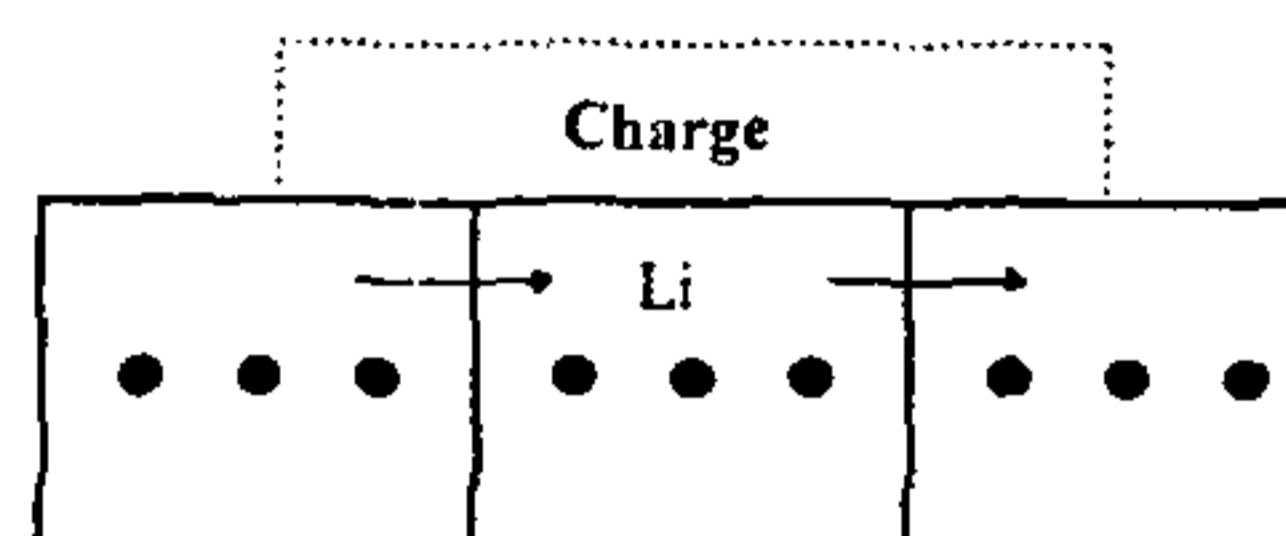
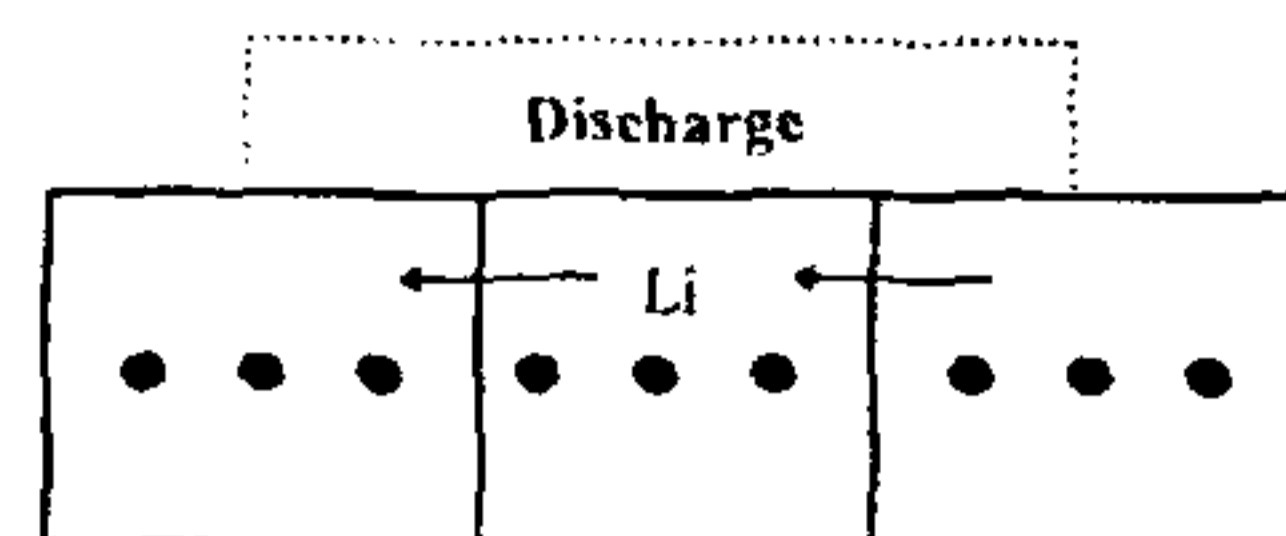
bonding, chemical reactivity, thermodynamics and kinetics is of great help to the inorganic synthetic chemist.

What then is the solution for the problem of rational design of inorganic materials? While it may not be possible to write down a set of infallible predictive rules for rational synthesis of inorganic materials in the foreseeable future, it is possible to address the problem by an experimentalist approach, going in small steps from the known to the unknown, and in the process, realizing meaningful targets. The recent synthesis of lithium-ion conductors in our laboratory is an example of such an approach which has yielded a modest measure of success in our efforts towards rational design. We describe here the details of this work.

Lithium batteries

It is widely recognized that lithium batteries²³⁻²⁵ are the most likely candidates for meeting the portable power requirements of the next millennium, be it for traction of zero-emission electric vehicles or as a source of power in fail-safe military devices or for that matter in consumer electronics (cellular phones, video recorders and laptop computers). The choice of lithium batteries over Ni-MH, Ni-Cd and the ubiquitous lead acid batteries is based on the favourable gravimetric and volumetric energy densities, coupled with excellent cycle life and safety records. A rechargeable lithium battery (Figure 1) consists of a cathode, an anode and an electrolyte – all containing or compatible with lithium. Lithium is the choice material for achieving high power densities because of its low atomic weight coupled with a high electropositive character. Two battery configurations are possible: one uses lithium metal or an alloy of lithium as the negative electrode, a nonaqueous electrolyte containing lithium-ions and a lithium intercalation compound such as Li_xTiS_2 or $\text{Li}_x\text{V}_6\text{O}_{13}$ as the positive electrode. The idea of using layered or framework materials that can reversibly accept and release lithium-ions as positive electrodes was indeed a major milestone^{26,27} in the development of lithium batteries. However, the main problem with lithium metal anode batteries is that the cycle life is generally limited by corrosion reactions occurring at the lithium–electrolyte interface, leading to total cell failure and serious safety hazard. The second configuration (Figure 1) is an answer to some of these problems, where the metallic lithium anode is replaced by another insertion compound, namely Li_nC_m (C_m = graphite), that is capable of releasing (discharging) and accepting (charging) large quantities of lithium. The total electrochemical process in this configuration essentially involves cyclic transfer of lithium-ions between two insertion electrodes. In this configuration, the battery is effectively a concentration cell wherein lithium-ions ‘rock’ from one electrode to

LITHIUM BATTERIES



Cathode Electrolyte Anode

Intercalation Compounds

Li-metal or Carbon

Net reactions :

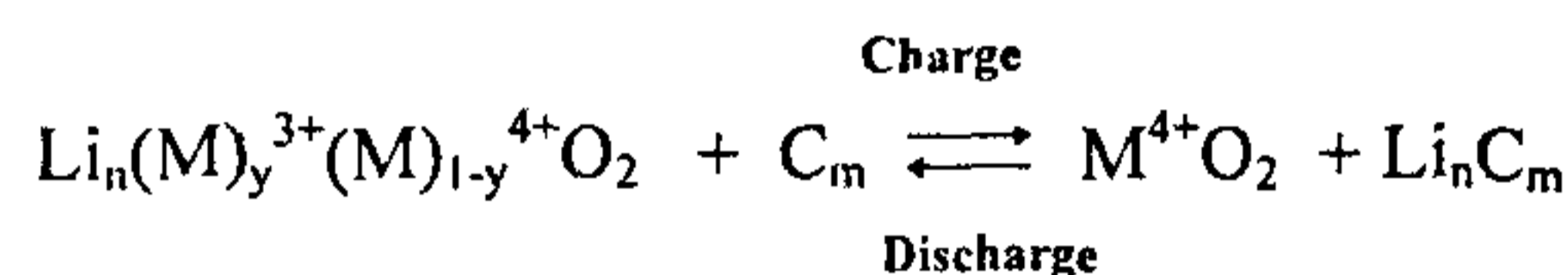
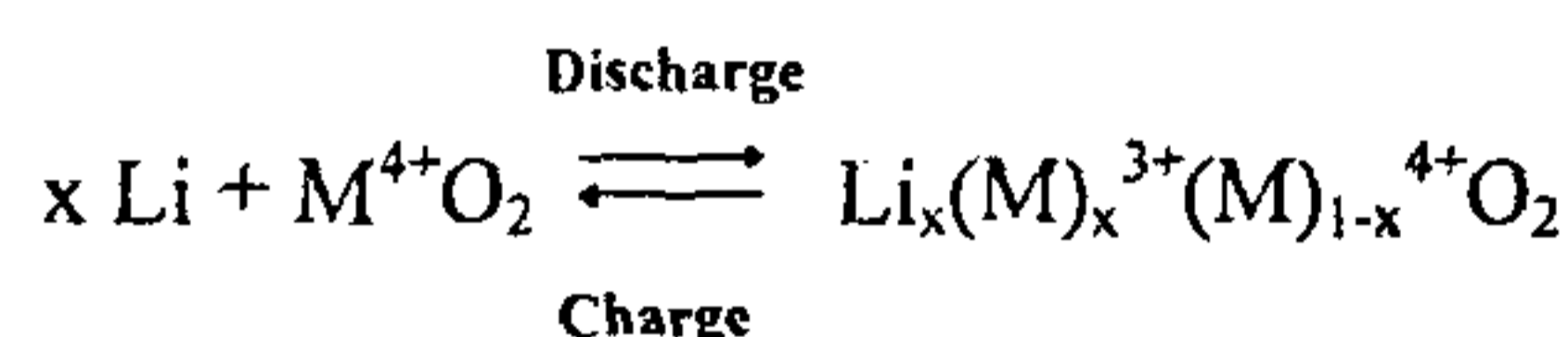


Figure 1. Schematic diagram illustrating a rechargeable lithium battery.

the other; accordingly, such batteries using intercalation compounds for both cathode and anode are called ‘rocking-chair’ batteries²⁸. The rocking-chair idea has been realized in commercial Japanese batteries which employ lithium intercalated graphite (Li_nC_m) as the anode, LiCoO_2 or LiMn_2O_4 as the cathode and a solution of lithium salt such as LiPF_6 in a mixture of ethylene carbonate and dimethyl carbonate as solvent. The recognition^{28,29} that a material like graphite, which can reversibly intercalate lithium at low voltages, could be used as anode instead of lithium metal and the experimental realization³⁰ that oxides such as LiCoO_2 would be better (high voltage) cathode materials than Li_xTiS_2 are important milestones in the development of commercial ‘rocking-chair’ batteries.

Notwithstanding several attractive performance characteristics of present-day ‘rocking-chair’ lithium batteries, they do not seem to be the ultimate answer to the technological needs²⁵. Considerable research effort is

underway in advanced countries to bring down the cost, to increase the energy density and to realize the batteries in flexible and plastic configurations. For example, efforts are underway to find iron-based lithium compounds³¹ for positive electrodes, instead of LiCoO_2 , LiMn_2O_4 and LiNiO_2 , which would bring down the cost and make them environmentally benign. Similarly, research is directed towards developing high-capacity lithium storage materials that can replace the currently used lithium-intercalated graphite anodes; use of high capacity lithium storage materials such as tin(II)-based amorphous oxide has been shown³² to improve considerably the specific coulombic capacity for uptake and release of lithium. Major research efforts are however required to replace the currently used liquid and polymer electrolytes with ionic conducting solid state electrolytes, especially to realize flexible and plastic batteries as well as high-temperature all-solid-state batteries.

Lithium-ion conductors

At present, there is a great interest to develop solid lithium-ion conductors for use as *electrolytes* in all-solid state lithium batteries^{33,34}. Availability of a suitable solid electrolyte material that could replace the currently used liquid/polymer electrolytes in lithium batteries would greatly contribute to the development of lithium battery technology by enabling fabrication of flexible, compact and leak-proof batteries of desired geometry²⁵. Two major directions are pursued for this purpose. One is to render the currently used polymer-based electrolytes (such as polyethylene oxide (PEO)-lithium salt complexes) into solid nanocomposites³⁵ by adding solid plasticizers (such as TiO_2 or Al_2O_3). The composite, while retaining the conductivity properties brings down the operational temperature considerably to near-room temperature. Further optimization is still very much required for practical application of these materials in lithium batteries.

The other approach³³ is to find solid materials that possess the required conduction and other properties for application as electrolytes in lithium batteries. While a material exhibiting a high conductivity ($\sigma \sim 10^{-4}$ S/cm) at near-room temperature and chemical stability at electrolyte-electrode interface, which could be rendered into thin films, could replace currently used liquid/polymer-based electrolytes, a solid that possesses the following characteristics would be an ideal electrolyte material for the development of all-solid-state batteries operating at high-temperatures³³ (400–600°C). (i) The solid should have a high ionic conductivity at operating temperatures ($\sigma \approx 0.1$ S/cm at 400°C) but much less conductivity at storage temperature to avoid self-discharge. (ii) It should have negligible electronic conductivity at all

temperatures. (iii) It should be stable in contact with lithium-containing anodes. Above all, it should be easy to fabricate, inexpensive and environmentally benign. Although research efforts over the last three decades have yielded several lithium-ion conductors, both crystalline and noncrystalline (Table 1), none of them seem to possess all the characteristics listed above. Among the several crystalline lithium-ion conductors, two structure types are particularly attractive for further research and development. They are the lithium-containing NASICON phosphates³⁶ and perovskite-based oxides³⁷ typified by $(\text{Li}, \text{La})\text{TiO}_3$.

Framework phosphates, $\text{LiM}_2(\text{PO}_4)_3$ ($\text{M}^{\text{IV}} = \text{Ge}, \text{Ti}, \text{Zr}, \text{Hf}$) of NASICON structure (Figure 2) have been widely investigated for lithium-ion conduction³⁶. There is an interesting correlation between the conductivity parameters and the unit cell volume of these materials.

Table 1. Selected lithium-ion conductors

Compound	Dimensionality	σ (S/cm)	T (°C)	E_a (eV)
LiI	3D	1.0×10^{-7}	25	0.43
Li_3N	2D	4.0×10^{-4}	25	0.30
Li- β -alumina	2D	1.3×10^{-4}	25	0.19
LiAlSiO_4	1D	4.7×10^{-5}	25	0.95
$\text{Li}_{1.4}\text{Zn}(\text{GeO}_4)_4$ (LISICON)	3D	0.125	300	0.50
$\text{Li}_{4.4}\text{Al}_{0.4}\text{Si}_{0.6}\text{O}_4$	3D	8.0×10^{-3}	300	0.56
$\text{LiTi}_2(\text{PO}_4)_3$	3D	2.0×10^{-6}	30	0.30
$\text{La}_{0.55}\text{Li}_{0.36}\square_{0.09}\text{TiO}_3$	3D	1.5×10^{-3}	30	0.33
$0.20\text{Li}_2\text{O}-0.55\text{SiO}_2-0.25\text{P}_2\text{O}_5$	glass	8.0×10^{-7}	150	0.42

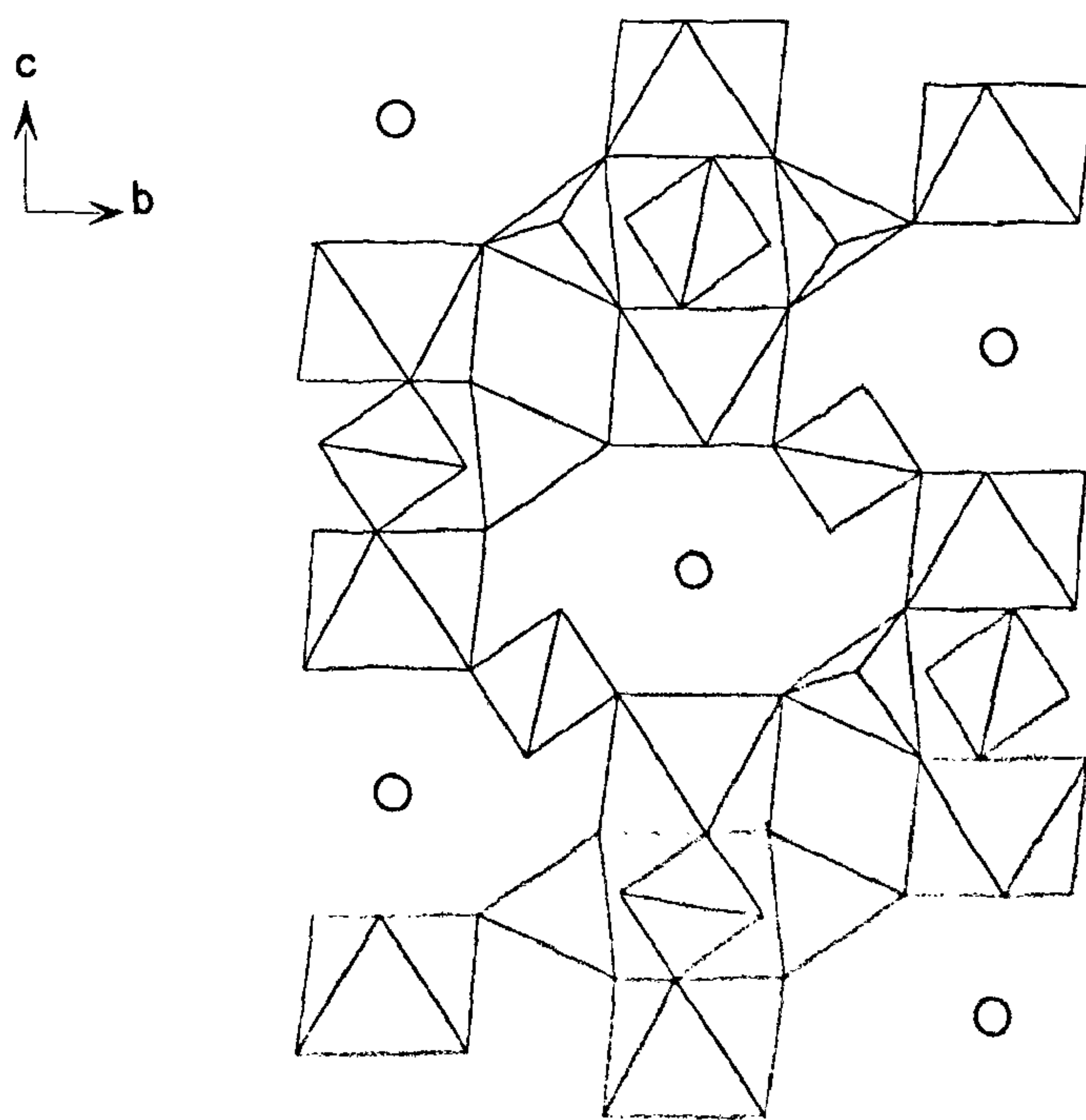


Figure 2. $\text{LiM}^{\text{IV}}\text{M}^{\text{III}}(\text{PO}_4)_3$ -NASICON structure showing the positions of Li^+ within the $\text{M}_2(\text{PO}_4)_3$ framework.

$\text{LiTi}_2(\text{PO}_4)_3$ which has a cell volume of 1309 \AA^3 exhibits the highest conductivity ($\sigma \approx 10^{-6} \text{ S/cm}$ at room temperature) and lowest activation energy ($E_a = 0.30 \text{ eV}$) among the $\text{LiM}_2(\text{PO}_4)_3$ materials. Isostructural materials having larger or smaller unit cell volumes exhibit lower conductivities and higher activation energies, revealing that there is an optimal cell volume (optimal tunnel size) which is favourable for a high lithium-ion conduction in this structure. Another important point is that there is a considerable grain boundary contribution³⁴ to the resistivity of these materials which can be substantially eliminated by substituting trivalent metal atoms in place of Ti^{IV} . Thus, while $\text{LiTi}_2(\text{PO}_4)_3$ (porosity = 34%) itself exhibits a room temperature conductivity of $2 \times 10^{-6} \text{ S/cm}$, $\text{Li}_{1.5}\text{Ti}_{1.5}\text{Al}_{0.5}(\text{PO}_4)_3$ (porosity = 2%) exhibits a much higher conductivity ($\sigma = 2.5 \times 10^{-4} \text{ S/cm}$ at room temperature) and a lower activation energy ($E_a \approx 0.20 \text{ eV}$). Despite the attractive ionic conductive properties of $\text{Li}_{1+x}\text{Ti}_{1-x}\text{Al}_x(\text{PO}_4)_3$, there are several materials problems to be overcome before a NASICON-based solid could find application as an electrolyte in a lithium battery. A major problem is that the lithium-reducible Ti^{IV} in this material should be replaced by other metal ions that would not undergo reduction at the lithium anode. Towards this end, we synthesized³⁸ new mixed-metal NASICON phosphates with the formula $\text{LiM}^{\text{V}}\text{M}^{\text{III}}(\text{PO}_4)_3$ ($\text{M}^{\text{V}} = \text{Nb, Ta}$; $\text{M}^{\text{III}} = \text{Al, Cr, Fe}$) and investigated³⁹ their lithium-ion conductivity. We believed that once we find a stoichiometric NASICON phase possessing intrinsic conductivity properties similar to those of $\text{LiTi}_2(\text{PO}_4)_3$ but without Ti^{IV} , extraneous factors such as sinterability, porosity, grain-boundary resistance, etc. could be tailored by appropriate means to obtain a favourable conducting material for application. Our results which are summarized in Table 2 reveal that among the new phases investigated, $\text{LiTaAl}(\text{PO}_4)_3$ exhibits the highest conductivity comparable to $\text{LiTi}_2(\text{PO}_4)_3$. Interestingly, $\text{LiTaAl}(\text{PO}_4)_3$ has the smallest cell volume (1315 \AA^3) and lowest activation energy ($E_a = 0.47 \text{ eV}$) among the $\text{LiM}^{\text{V}}\text{M}^{\text{III}}(\text{PO}_4)_3$ investigated.

Thus in $\text{LiTaAl}(\text{PO}_4)_3$, we have identified a new NASICON-type lithium-ion conductor that does not contain lithium-reducible metal ions. Accordingly, we believe that the material deserves further attention towards tailoring electrolytes for solid-state lithium batteries.

We now turn to our work on lithium-ion conductors based on the perovskite structure. We believe that this work is directly relevant to the problem of rational design of inorganic materials discussed in the introductory section. A perovskite type phase in the $(\text{Li,Lu})\text{TiO}_3$ system, first reported in 1987 by Belous *et al.*⁴⁰, exhibiting a bulk ionic conductivity of $\sim 1 \times 10^{-3} \text{ S/cm}$ at room temperature has triggered off a great deal of research activity⁴¹⁻⁴³. This phase is rather unusual in that Li^+ , which is normally expected to occupy the B-site in the ABO_3 perovskite structure on the basis of ionic radius considerations, occupies the A-site. Further work⁴¹⁻⁴³ has revealed the details of structure and possible mechanism of lithium-ion conduction in this system. The ionic conducting phase is a nonstoichiometric perovskite, $\text{La}_{(2/3)-x}\text{Li}_{3x}\square_{(1/3)-2x}\text{TiO}_3$ (I) ($\square = \text{vacancy}$), which is stable over the composition range $0.06 < x < 0.14$, of which members around $x \approx 0.12$ exhibit best ionic conductivity ($\sigma \approx 1.53 \times 10^{-3} \text{ S/cm}$ at 25°C). Samples of this composition quenched from high temperatures having a cubic perovskite structure where the A-site constituents are disordered exhibit a higher conductivity than slow-cooled samples, which have a partially ordered tetragonal superstructure (Figure 3). Effect of pressure⁴⁴ and chemical substitution⁴⁵ in (I) have revealed that conduction occurs by site percolation of Li^+ involving A-site vacancies, the window of four oxygens separating adjacent A-sites constituting the 'bottleneck' for Li^+ migration. Notwithstanding these unique features which render lithium-lanthanum titanates excellent lithium-ion conductors, the facile reducibility of Ti^{IV} by lithium giving rise to appreciable electronic conduction in (I) precludes its use as electrolyte material.

Table 2. Chemical composition, lattice parameters and total ionic conductivity data for NASICON-type phosphates $\text{LiM}^{\text{V}}\text{M}^{\text{III}}(\text{PO}_4)_3$ [$\text{M}^{\text{V}} = \text{Nb, Ta}$; $\text{M}^{\text{III}} = \text{Al, Cr, Fe}$]

Composition	Lattice parameters			$\sigma_{30^\circ\text{C}}$ (S/cm)	$\sigma_{350^\circ\text{C}}$ (S/cm)	E_a (eV)
	$a_h(\text{\AA})$	$c_h(\text{\AA})$	$V(\text{\AA}^3)$			
$\text{LiNbFe}(\text{PO}_4)_3$	8.593(3)	21.715(8)	1388	$< 10^{-8}$	6.6×10^{-6}	0.85 (210–600°C)
$\text{LiTaAl}(\text{PO}_4)_3$	8.542(6)	20.815(5)	1315	6.5×10^{-7}	1.0×10^{-2}	0.47 (30–250°C)
$\text{LiTaCr}(\text{PO}_4)_3$	8.535(6)	21.551(8)	1360	$< 10^{-7}$	3.7×10^{-4}	0.49 (80–300°C)
$\text{LiTaFe}(\text{PO}_4)_3$	8.608(6)	21.753(6)	1395	$< 10^{-7}$	3.0×10^{-4}	0.86 (150–350°C)
$\text{LiTi}_2(\text{PO}_4)_3^a$	8.512	20.858	1310	2.0×10^{-6}	6.3×10^{-3}	0.30 (30–200°C)
$\text{LiZr}_2(\text{PO}_4)_3^b$	8.850	22.240	1508	3.2×10^{-10}	5.0×10^{-3}	0.43 (300–400°C)

^aData taken from literature. ^bThe high temperature rhombohedral cell parameters are given. At low-temperatures, $\text{LiZr}_2(\text{PO}_4)_3$ has a monoclinic cell with $a = 15.299(1)$, $b = 8.940(1)$, $c = 8.612(2) \text{ \AA}$, $\beta = 125.98(2)$.

We believed that it should be possible to design perovskite type lithium-ion conductors that retain the attractive features of (I) but eliminate the reduction problem by a suitable choice of A and B atoms in the perovskite and related structures. First, we wanted to establish the role of dimensionality on lithium-ion conduction of perovskite-related oxides. For this purpose, we prepared⁴⁶ new layered perovskite oxides, LiLnTiO_4 ($\text{Ln} = \text{La}, \text{Nd}$), by a soft-chemical route starting from NaLnTiO_4 . The new materials adopt a 2D-layered structure related to Sr_2TiO_4 (K_2NiF_4), where Li and Ln atoms are ordered in alternate interlayer sites between sheets of $\text{TiO}_{4/2}\text{O}_2$ octahedra (Figure 4). The ionic conductivity of LiLaTiO_4 is much lower than that of the 3D-perovskite oxide in $(\text{Li}, \text{La})\text{TiO}_3$ system, revealing that a 2D structure does not favour a high lithium-ion conductivity.

Since a 3D-perovskite structure appeared to be more favourable than the corresponding 2D structure for lithium-ion conduction, we investigated⁴⁷ several stoichiometric oxides of the formulae, $\text{LiABB}'\text{O}_6$ and $\text{LiA}_2\text{B}_2\text{B}'\text{O}_9$, in $\text{Li}-\text{A}-\text{B}-\text{B}'-\text{O}$ ($\text{A} = \text{Ca}, \text{Sr}, \text{Ba}$; $\text{B} = \text{Ti}, \text{Zr}$; $\text{B}' = \text{Nb}, \text{Ta}$) systems in an attempt to determine the factors that control lithium-ion conduction in perovskite oxides. Our experimental investigations summarized in Table 3 and Figure 5 have led us to conclude that (i) conductivity increases with increasing pentavalent (B') metal, as seen by comparing the data for LiSrTiNbO_6 and $\text{LiSr}_2\text{Ti}_2\text{B}'\text{O}_9$ ($\text{B}' = \text{Nb}, \text{Ta}$), (ii) for oxides of the same formula, the $\text{B}' = \text{Ta}$ compounds exhibit a higher

conductivity than the corresponding $\text{B}' = \text{Nb}$ compounds. This is evident from the conductivity data for the pairs of oxides, LiSrTiNbO_6 , LiSrTiTaO_6 and $\text{LiSr}_2\text{Ti}_2\text{NbO}_9$, $\text{LiSr}_2\text{Ti}_2\text{TaO}_9$; and (iii) for oxides of the same formula, the strontium compounds exhibit a higher conductivity than the corresponding calcium or barium compounds. This conclusion is based on the data for $\text{LiA}_2\text{Ti}_2\text{NbO}_9$ ($\text{A} = \text{Ca}, \text{Sr}, \text{Ba}$).

Similar correlations between chemical composition and lithium-ion conductivity in $\text{La}_{(2/3)-x}\text{Li}_{3x}\square_{(1/3)-2x}\text{TiO}_3$ (I) are found in the literature. For example, substitution of the larger strontium for lanthanum in (I) increases the ionic conductivity, whereas substitution of smaller lanthanides (Pr, Nd, Sm) for lanthanum in (I) decreases the ionic conductivity. This effect has been understood in terms of the increase/decrease of the 'bottleneck' size due to the substitution of larger/smaller cations at the lanthanum site. Corroborative evidence for this observation is provided by pressure effect studies on (I). An increase in the conductivity due to Nb/Ta substitution for Ti in derivatives of (I) has been understood in terms of the increase in B-O bond strength with increasing oxidation state of the B atom, which in turn weakens the A-O bond in ABO_3 perovskites in general.

The higher conductivity of the tantalum oxides than that of the corresponding niobium oxides is most likely related to the HOMO-LUMO gap between oxygen 2p and the metal (Nb/Ta) d^0 states⁴⁸; this gap in turn determines the off-centre distortion of $\text{NbO}_6/\text{TaO}_6$ octahedra. 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 equal. Presumably, a less distorted TaO_6 octahedron seems to be more

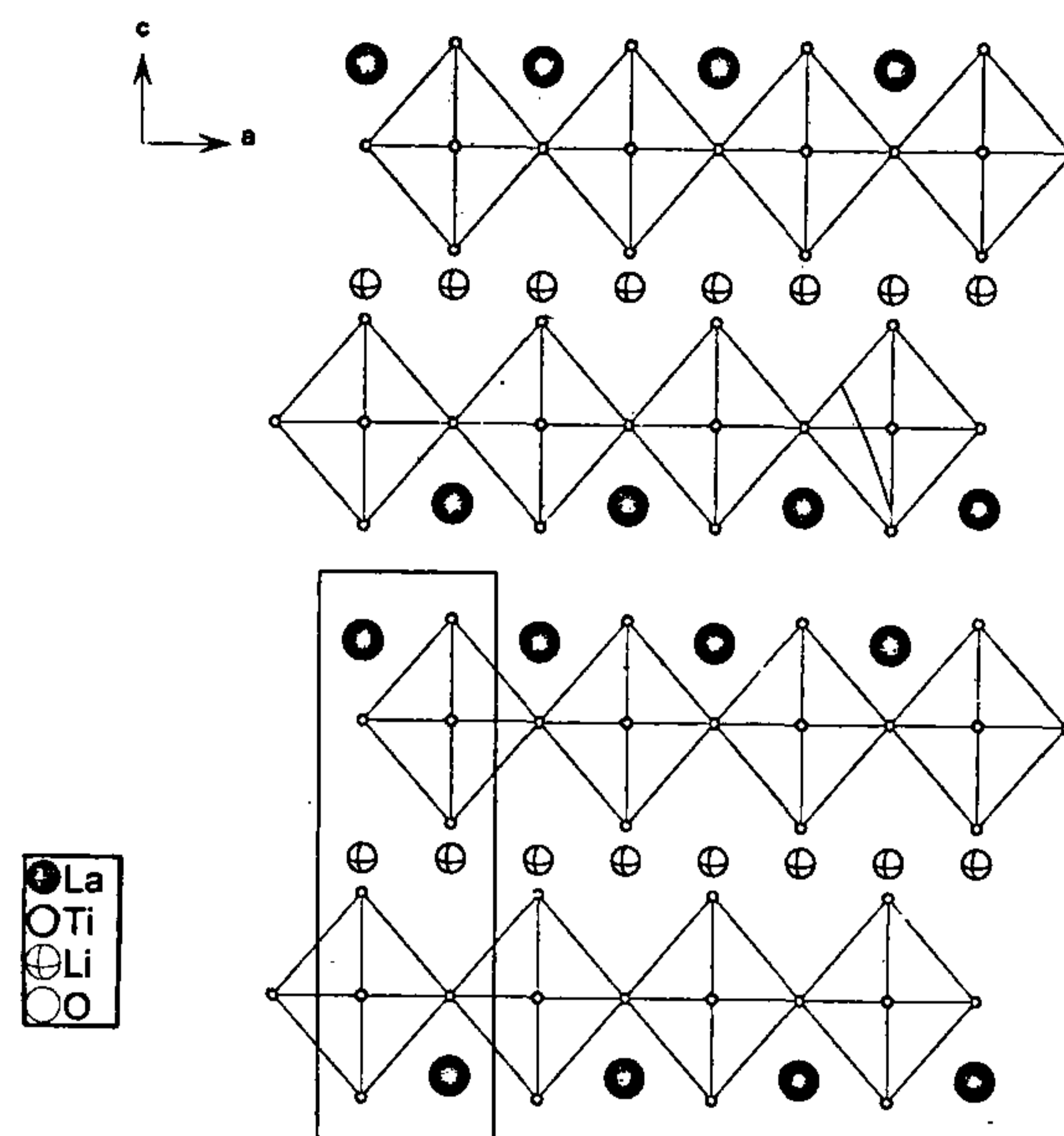


Figure 4. Layered perovskite structure of LiLaTiO_4 .

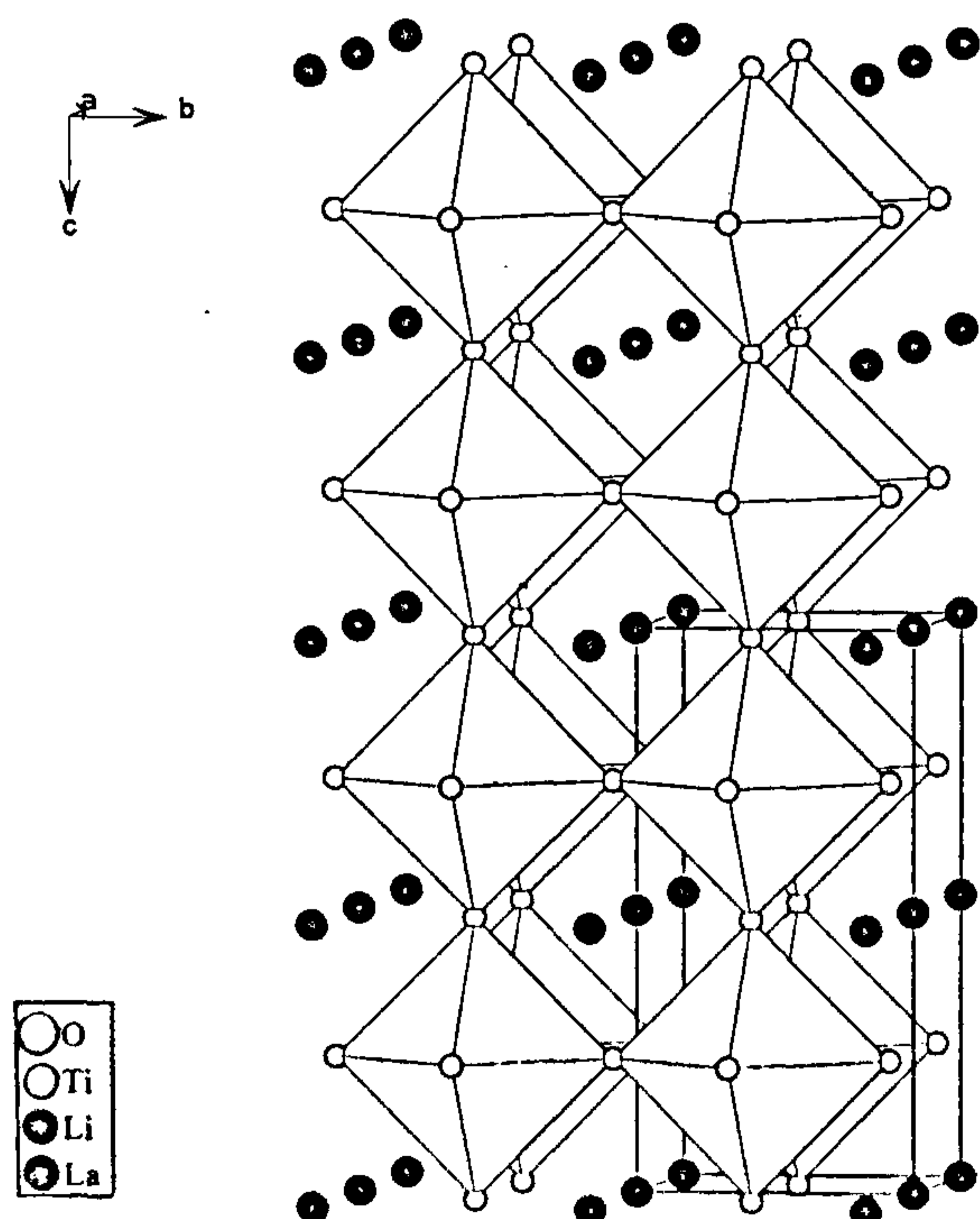


Figure 3. Tetragonal superstructure of $(\text{Li}, \text{La})\text{TiO}_3$ perovskite.

Table 3. 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	Lattice parameters (Å)	$\sigma_{30^\circ\text{C}}$ (S/cm)	$\sigma_{360^\circ\text{C}}$ (S/cm)	E_a (eV)
LiCaTiNbO ₆	orthorhombic: $a = 5.365(2)$, $b = 5.486(2)$, $c = 7.666(3)$	$< 10^{-7}$	6.3×10^{-6}	0.68
LiSrTiNbO ₆	3.932(1)	$< 10^{-6}$	8.9×10^{-4}	0.42
LiSrTiTaO ₆	3.932(1)	5.5×10^{-4}	6.3×10^{-2}	0.33
LiCa ₂ Ti ₂ NbO ₉	orthorhombic: $a = 5.374(3)$, $b = 5.487(3)$, $c = 7.674(1)$	$< 10^{-8}$	7.1×10^{-7}	1.03
LiSr ₂ Ti ₂ NbO ₉	3.924(2)	$< 10^{-6}$	3.2×10^{-4}	0.34
LiBa ₂ Ti ₂ NbO ₉	4.031(1)	$< 10^{-7}$	2.0×10^{-5}	0.74
LiSr ₂ Ti ₂ TaO ₉	3.925(1)	3.2×10^{-5}	3.2×10^{-3}	0.27
LiSr _{1.65} □ _{0.35} Ti _{1.3} Nb _{1.7} O ₉	3.932(1)	2.0×10^{-5}	4.2×10^{-2}	0.34
LiSr _{1.65} □ _{0.35} Ti _{1.3} Ta _{1.7} O ₉	3.932(1)	4.9×10^{-5}	0.114	0.35
LiSr _{1.65} □ _{0.35} Zr _{1.3} Ta _{1.7} O ₉	4.017(1)	1.3×10^{-5}	0.125	0.36
Li _{0.36} La _{0.55} □ _{0.09} TiO ₃ ^a	3.8710(2)	2.0×10^{-5}	0.130	0.33

^aFor comparison, the literature data for this phase in (Li, La)TiO₃ system are included.

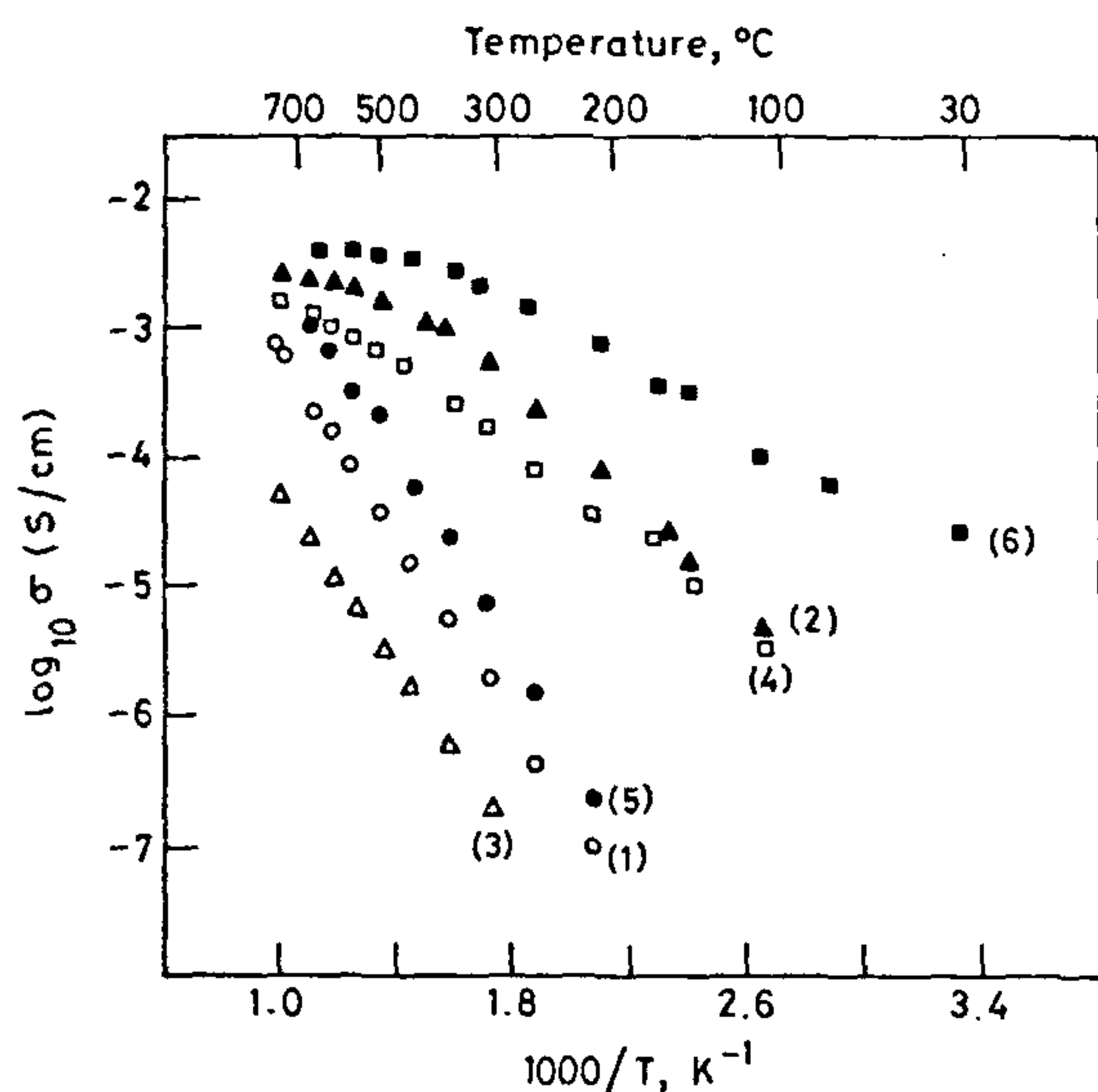


Figure 5. Temperature dependence of lithium-ion conductivity of LiABB'O₆ and LiA₂B₂B'O₉ perovskites; (1) LiCaTiNbO₆, (2) LiSrTiNbO₆, (3) LiCa₂Ti₂NbO₉, (4) LiSr₂Ti₂NbO₉, (5) LiBa₂Ti₂NbO₉ and (6) LiSr₂Ti₂TaO₉ (from ref. 47).

favourable for lithium-ion conduction than a strongly distorted NbO₆ 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 is obtained when the total concentration of lithium and A-site is 0.44–0.45, this value being higher than the site percolation threshold (0.3117) for the simple cubic lattice. Presumably, this concentration ensures the presence of at least one vacancy/Li⁺ adjacent to every Li⁺/vacancy.

Taking into account the foregoing factors which influence lithium-ion conduction in perovskite oxides, we

arrived at the composition, LiSr_{1.65}□_{0.35}B_{1.3}B'_{1.7}O₉ (B = Ti; B' = Nb, Ta) (II) which optimizes all the factors. Thus, we have chosen Sr in preference to Ca or Ba for the A-site, because Sr provides the optimal 'bottleneck' size for lithium-ion migration, the Sr content (0.55) per ABO₃ formula being the same as the La content of the best lithium-ion conducting composition of (I). The total concentration of lithium and A-site vacancies is 0.45 per ABO₃ formula – a value that is known to give maximum lithium-ion conductivity in (I). The composition we have chosen 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 were readily obtained by reacting the constituents at 1200°C followed by quenching the sample to room temperature. Between the two phases, the tantalum oxide exhibited a higher ionic conductivity than the niobium oxide (Figure 6), as expected. The conductivity of this phase is comparable to that of the best conductors in the lanthanum-lithium titanate series (I).

Having obtained one of the best lithium-ion conductors by a rational choice of the chemical composition, we attempted to prepare a lithium-ion conductor that would not suffer a reduction of the B-site ions when in contact with lithium metal. For this purpose, we chose the composition, LiSr_{1.65}□_{0.35}Zr_{1.3}Ta_{1.7}O₉ (III), where Zr^{IV} replaces Ti^{IV} in (II). A single-phase perovskite oxide of this composition was readily obtained by reacting the constituents at 1300°C followed by quenching. The phase has a cubic perovskite structure with $a = 4.017(1)$ Å. The ionic conductivity of this phase (0.125 S/cm) is slightly higher than that of the corresponding Ti^{IV} oxide (II) (0.114 S/cm) at 360°C. Accordingly, we believe that the Zr^{IV} oxide phase (III) would be an ideal candidate that would meet the requirement of a low ionic conductivity at lower temperatures (1.3×10^{-5} S/cm at 30°C) and a high ionic conductivity

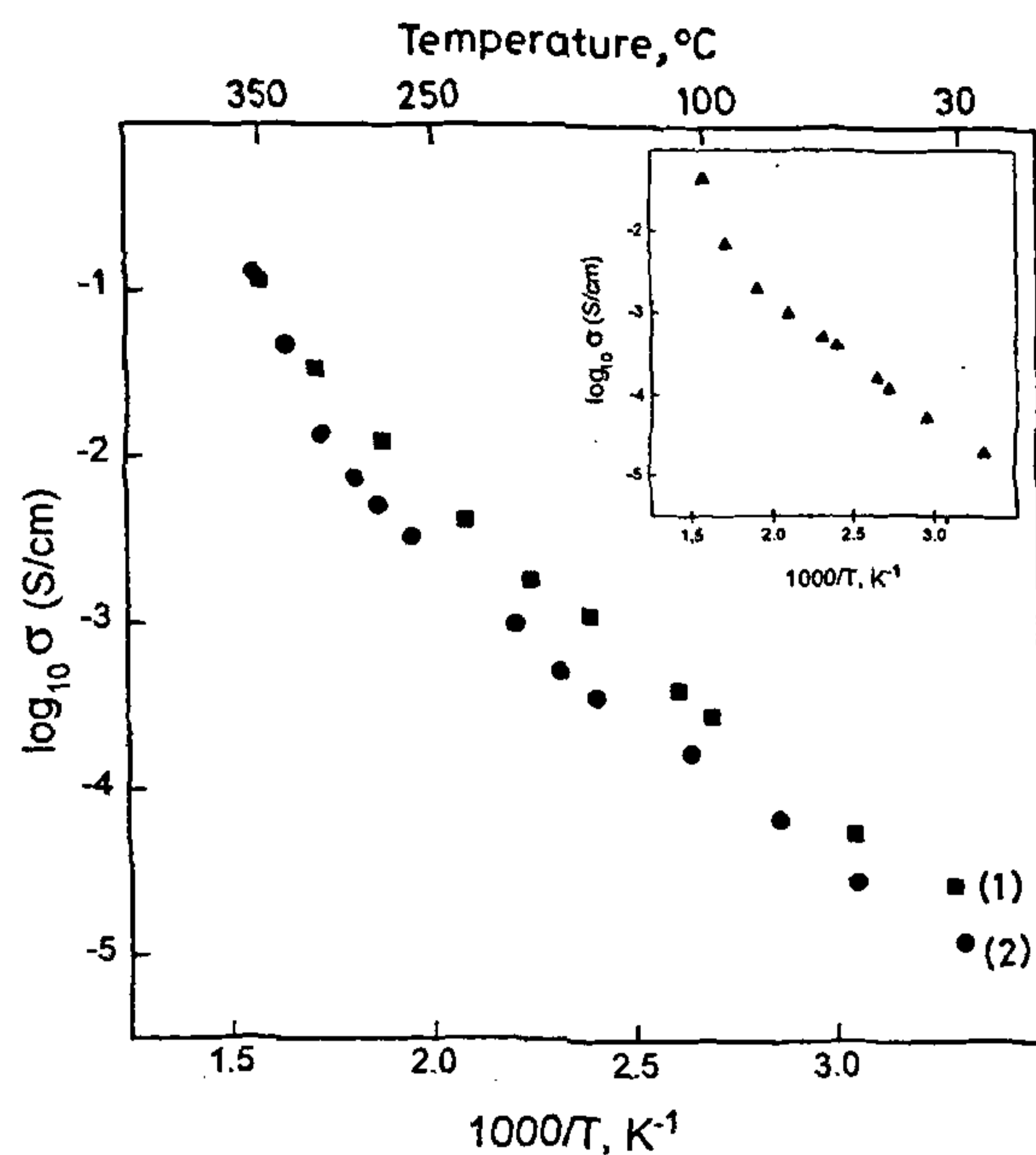


Figure 6. Temperature dependence of lithium-ion conductivity of: (1) $\text{LiSr}_{1.65}\text{Ti}_{1.3}\text{Ta}_{1.7}\text{O}_9$, and (2) $\text{LiSr}_{1.65}\text{Zr}_{1.3}\text{Ta}_{1.7}\text{O}_9$. The data for $\text{LiSr}_{1.65}\text{Ti}_{1.3}\text{Nb}_{1.7}\text{O}_9$ are shown in the inset (from ref. 47).

(~ 0.1 S/cm) at operating temperatures (400°C), required for high-temperature solid-state lithium battery application. Moreover, the material contains stable oxidation states Zr^{IV} and Ta^{V} that would not undergo reduction by lithium anode at the operating conditions.

We believe that the choice of B cations in the perovskite structure is crucial for obtaining best lithium-ion conduction. Because migration of lithium-ions in the perovskite structure is known to involve a dilatation of the 'bottleneck', accompanied by a positive volume of activation and distortion/tilting of BO_6 octahedra, d^0 cations such as Ti^{IV} , Zr^{IV} , Nb^{V} and Ta^{V} seem to be the best choices. A spatiotemporal fluctuation of B–O bond lengths caused by a disordered distribution of A-site species in the perovskite structure seems to be more favourable for facile conduction than a frozen distribution of bond lengths, as revealed by a higher ionic conductivity of cubic perovskite phase than its ordered variants. Further work to understand the dynamics of lithium-ion using local probes such as ^7Li NMR would shed more light on the mechanism of lithium-ion conduction in these materials.

Here, we have described an experimental approach to the problem of rational design of new inorganic materials, taking lithium-ion conductors as a case study. By a systematic consideration of composition–structure–property correlations in the family of lithium-containing perovskite oxides in the Li-A-B-B'-O ($\text{A} = \text{Ca}, \text{Sr}, \text{Ba}$; $\text{B} = \text{Ti}, \text{Zr}$; $\text{B}' = \text{Nb}, \text{Ta}$) systems, together with literature data on $(\text{Li}, \text{La})\text{TiO}_3$ perovskites, we have been able

to design and synthesize a new lithium-ion conductor, $\text{LiSr}_{1.65}\text{Zr}_{1.3}\text{Ta}_{1.7}\text{O}_9$, that appears a promising candidate material for application as electrolyte in all-solid-state high temperature lithium batteries. More importantly, we believe that the approach described here could be employed to synthesize other inorganic solids possessing specific materials properties.

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