

# Ionic conductivity in lithium compounds\*

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The electrical and structural properties of lithium compounds which present predominantly ionic conductivity are reviewed and relationships between structure and electrical properties are, where possible, discussed. A few results on lithium silico-aluminate glasses are also reported.

## Introduction

Among the different solid electrolytes, lithium conductors could possibly play an important role in the development of high power density batteries if a compound (or compounds) could be found which exhibits room temperature electrical conductivity values comparable with those of some already known silver or sodium-conducting electrolytes, such as silver- or sodium-substituted beta-alumina or  $\text{RbAg}_4\text{I}_5$ .

The investigation of the transport properties of different lithium compounds, crystallizing in different structures, could also be helpful in discussing the behaviour of the lithium ion, which seems to be rather intriguing, at least when compared with that of ions like silver and sodium, which, in spite of their larger size appear to be definitely more mobile.

The influence of parameters such as the anion polarizability, which is of overwhelming importance in the case of molten salts [1-3] might also be important in the case of lithium-substituted  $\beta$ -alumina or in  $\beta$ -spodumene (see below). These compounds have very open structures, such as to allow a direct comparison of their transport properties with those of molten salts.

Evidence of such an influence could be obtained by considering the size effect of the cation on the self-diffusion coefficients over a number of differently substituted  $\beta$ -aluminas or by considering the influence of the value of the ratio of the cationic and anionic radius on the activation energy for the conductivity.

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As an example we have reported in Fig. 1 the results of measurements of self-diffusion coefficients in substituted  $\beta$ -aluminas [4] which show that a certain limiting size of the inserted cation exists; over or below it the ionic mobility is considerably depressed.

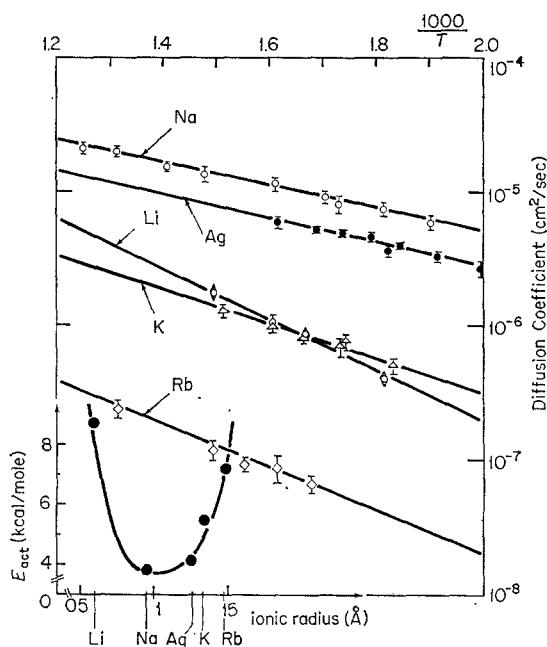


Fig. 1. Self-diffusion coefficients of different cations in alkali-substituted  $\beta$ -alumina (from ref. 4). On the bottom left the experimental activation energies are plotted as a function of the ionic radius of the cations.

Apparently sodium and silver are the most mobile ions, in spite of the fact that both thermodynamic and structural considerations [4, 5] indicate that the most stable  $\beta$ -aluminas are the potassium- and sodium-substituted ones.

In order to gain more insight into the transport properties of lithium electrolytes, electrical and structural properties of lithium compounds will be reviewed. Three main groups of compounds can be distinguished, namely:

(a) Compounds such as the lithium halides which present predominant Schottky disorder. They could be doped with altrivalent cations only to a limited extent and in every case the transport mechanism should be of the hopping type. One expects high conductivity values only at temperatures comparable with the melting point.

(b) Compounds which present a frame of big anions and, consequently, a cation lattice with multiple and energetically equivalent positions for each lattice cation. Frenkel type of disorder in the cationic sublattice is apparently imperative. Compounds of this type are polymorphic. The form stable at high temperatures, just below the melting point, could exhibit, as in the case of  $\text{Li}_2\text{SO}_4$  and  $\text{Li}_2\text{WO}_4$ , values of the activation energy for the conductivity comparable with those of molten salts (0.2–0.3 eV).

(c) Compounds with layer or tunnel structures. Such compounds are anisotropic with respect to the electrical transport properties and the transport mechanism could be different from the thermally activated one, as in the case of compounds of the type (a) and (b). Compounds belonging to this last group are lithium-substituted  $\beta$ -alumina,  $\beta$ -spodumene and some mixed (electronic-ionic) conductors, like lithium ferrites and lithium bronzes.

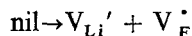
A rather wide set of examples will be discussed but some numerical values here could be largely approximate, because lithium conductors require difficult experimental problems to be solved, in order to obtain reliable results.

### Group (a) compounds

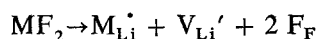
To this group belong the lithium halides, which all crystallize with the rocksalt structure. Schottky disorder prevails, cations are much more mobile than the anions and electronic conductivity is absent [6–7]. Within lithium halides, LiF is definitely the best known with respect to the electrical transport parameters [8, 9, 10].

Pure LiF exhibits intrinsic conductivity at

temperatures higher than about 600°C; in both pure and  $\text{Ca}^{2+}$ ,  $\text{Sr}^{2+}$  and  $\text{Mg}^{2+}$  doped LiF, the motion of lithium vacancies is shown to contribute overwhelmingly to the electrical conductivity. Vacancies arise from intrinsic disorder, according to the following equations



and from altrivalent cation doping



As one could see from Fig. 2, which refers to

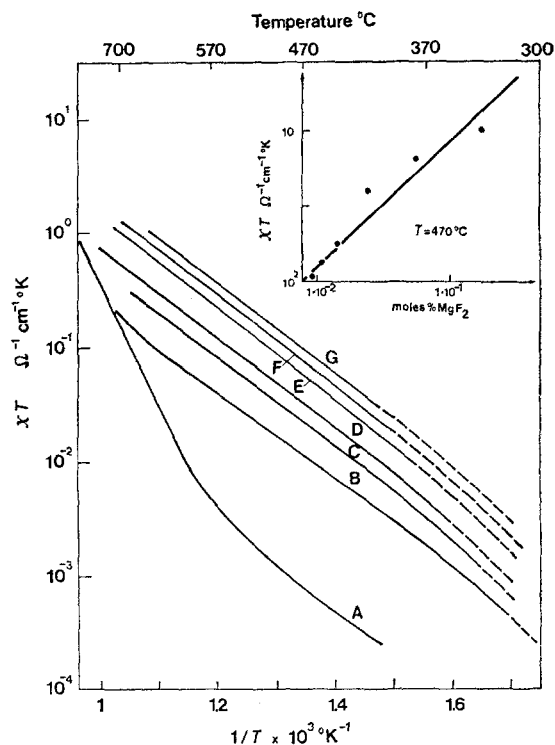


Fig. 2. Electrical conductivity of LiF-MgF<sub>2</sub> mixed crystals (from ref. 10). A: pure LiF. B:  $6 \times 10^{-3}$  moles % MgF<sub>2</sub>. C:  $1.3 \times 10^{-2}$ . D:  $2.4 \times 10^{-2}$ . E:  $4.3 \times 10^{-2}$ . F:  $7.7 \times 10^{-2}$ . G:  $1.2 \times 10^{-1}$ .

Mg doping, when varying the  $\text{Mg}^{2+}$  content from 100 to 1000 ppm the electrical conductivity varies by about one order of magnitude, thus indicating that a simple linear relationship exists between the dopant concentration and the conductivity.

Other lithium halides have been studied by Haven [8] and LiI, recently, also by Jackson and Young [11]. From their results one could recognize a systematic increase in the electrical conductivity of the pure halides, caused by the

decrease of both the activation enthalpy of motion and the enthalpy of formation of vacancies (see Table I) as the ionic radius of the anion increases.

Whereas in the case of doped LiCl and LiBr the conductivity depends linearly on the bivalent cation dope concentration, the conductivity of LiI seems to be practically independent of the dope concentration.

This kind of dependence could be attributed [8] to a Frenkel type of disorder in the cationic sublattice\* or even to a type of disorder like that found in the high temperature form of AgI or  $\text{RbAg}_4\text{I}_5$  (see group (b) compounds).

However, such a conclusion has been questioned by the authors of [11] who found that LiI crystals containing 30–120 ppm of Mg are obtained from a melt containing from  $10^3$  to  $10^4$  ppm of Mg. They suggest that in the case of the Haven results it is likely that moisture or oxide contamination of LiI have been combined with the added Mg, as MgO, which precipitates and therefore reduces the effective concentration of  $\text{Mg}^{++}$  in the solid LiI by several orders of magnitude.

Actually there is no proof that the last two authors interpreted their own results correctly, as it is hard to infer any phenomenological law expressing the concentration dependence of the electrical conductivity from their measurements, due to the very narrow range of concentrations investigated.

From the experimental evidence of the independence of the activation enthalpy for motion of the ionic size (see Table I for numerical values and [8, 9, 10] for details of the calculation of enthalpy for motion values from the overall activation energy) one might conclude that the transport mechanism is the same in LiCl, LiBr and LiI, where size parameters only affect the values of formation of defects.

### Group (b) compounds

Early in this century it was recognized that a number of ionic compounds exhibited 'abnormally' high electrical conductivity at low tempera-

\*It should be noted that, whereas  $\text{Cu}^+$  is accommodated in tetrahedral sites in AgCl and AgBr,  $\text{Li}^+$  can be accommodated in octahedral sites in the same salts [7].

tures (200–300°C) when compared with the normal values of electrical conductivity presented by the ionic conductors belonging to the first group.

In Fig. 3 some examples are reported of the abnormally high conductivity exhibited by compounds derived from AgI [12–17]. One notices that with the exception of  $\beta\text{-Ag}_3\text{SI}$ , only the  $\alpha$ -forms, stable at high temperature, exhibit anomalous values, whereas at temperatures lower than the transition temperature conductivities are of the same order of those of compounds belonging to the first group.

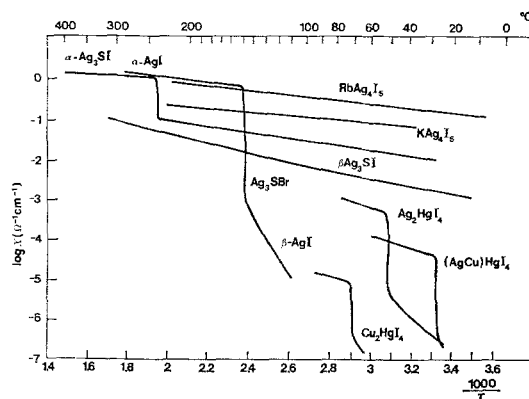


Fig. 3. Electrical conductivity of  $\text{Ag}^+$ -conductors.

The main reason for this difference has been recognized to lie in the disordered structures of the cationic sublattice of the  $\alpha$ -forms, where the cations are distributed over a number of tetrahedral and octahedral 'interstices'. The same behaviour is presented by the  $\alpha$ -form of  $\text{Li}_2\text{SO}_4$  and  $\text{Li}_2\text{WO}_4$  although the high temperature form is stable in a narrower range of temperature and the transition temperature is higher than those observed in compounds derived from the AgI structures, as is shown in Fig. 4.

The high temperature forms of both  $\text{Li}_2\text{SO}_4$  [18] and  $\text{Li}_2\text{WO}_4$  [19] (as well as that of lithium molybdate [20], which, however, does not present anomalous conductivity) adopt [5] a spinel-type cubic close-packed array of oxygen atoms (32 per unit cell) with a total number of 64 tetrahedral and 32 octahedral holes. The  $\text{Li}^+$  ions as well as  $\text{W}^{6+}$ ,  $\text{S}^{6+}$  and  $\text{Mo}^{6+}$  ions are distributed over these holes. According to Førlund [21], who studied the high temperature form of  $\text{Li}_2\text{SO}_4$ , lithium is distributed among

Table 1.

Group	System or compound	Conductivity equations*	Enthalpy of motion (eV)	Enthalpy of formation of defects (eV)	Diffusion coefficients (cm <sup>2</sup> sec <sup>-1</sup> )	Remarks	References
(a)	LiF	$x = \frac{1.6 \times 10^9}{T} \exp\left(\frac{-1.99}{kT}\right)$	0.65	2.68		Single crystal samples	[8, 9, 10]
(a)	LiCl	$x = 2.51 \times 10^6 \exp\left(\frac{-1.47}{kT}\right)$	0.41	2.12		Single crystal samples	[8]
(a)	LiBr	$x = 1.41 \times 10^6 \exp\left(\frac{-1.29}{kT}\right)$	0.39	1.80		Single crystal samples	[8]
(a)	LiI	$x = 0.96 \times 10^6 \exp\left(\frac{-1.05}{kT}\right)$	0.38 [8] 0.43 [11]	1.34 [8] 1.06 [11]		Single crystal samples	[8, 11]
(b)	Li <sub>2</sub> SO <sub>4</sub>	$x = -3.29 + 6.89 \times 10^2 t$ $+ 0.53 \times 10^{-6} t^2 (\Omega^{-1} \text{cm}^{-1})$ ( <i>t</i> in deg C)	0.36		$D_{\text{Li}^+} = 10.99 \times 10^{-5}$ ( $T = 800^\circ\text{C}$ ) $D_{\text{Li}^+} = 3.54 \times 10^{-5}$ ( $T = 600^\circ\text{C}$ )	Polycrystalline samples	[18, 19, 21]
(b)	Li <sub>2</sub> WO <sub>4</sub>	$x = 104.2 \exp\left(\frac{-0.36}{kT}\right)$	0.36			Polycrystalline samples	[18, 19, 21]
(c)	Li-doped SiO <sub>2</sub> glass	$x = 8.5 \times 10^{-2} \exp\left(\frac{-1.01}{kT}\right)$				Doping level 100 ppm	[41]
(c)	Li-substituted β-alumina		0.38		$D_{\text{Li}^+} = 14.5 \times 10^{-4} \exp\left(\frac{-0.377}{kT}\right)$		[4]
(c)	(Na-substituted β-alumina)		0.165		$D_{\text{Na}^+} = 2.4 \times 10^{-4} \exp\left(\frac{-0.165}{kT}\right)$		[4]
(c)	β-spodumene	$x = 79.4 \exp\left(\frac{-1.16}{kT}\right)$				The composition of β-spo-dumene is Li <sub>2</sub> O·Al <sub>2</sub> O <sub>3</sub> ·4SiO <sub>2</sub>	[41]
(c)	Li <sub>2</sub> O - SiO <sub>2</sub> glass	$1.28 \leq E_{\text{act}} \leq 0.60$ $6.7 \leq x_{\text{Li}_2\text{O}} \leq 39.8$ mole %					[42, 43]
(c)	Lithium borate glasses	$0.95 \leq E_{\text{act}} \leq 0.65$ $7.9 \leq x_{\text{Li}_2\text{O}} \leq 4.65$ mole %			$E_{\text{act}} = 0.22 \text{ eV}$ $28.6 \leq x_{\text{Li}_2\text{O}} \leq 37$ mole %		[44]

\* Activation energies are given in eV

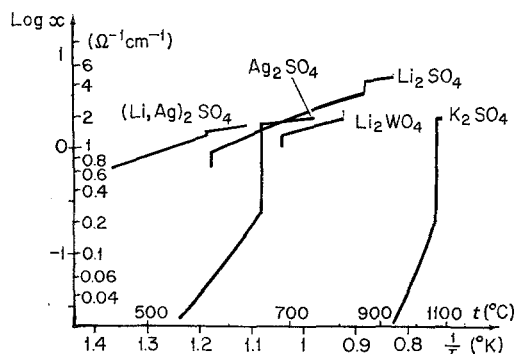


Fig. 4. Electrical conductivity of  $\text{Li}_2\text{SO}_4$ ,  $\text{Li}_2\text{WO}_4$  and other  $\text{MeXO}_4$ -type compounds (ref. 18).

two kinds of octahedral holes differently coordinated by the sulphate group.

This degree of intrinsic disorder (which is, however, much less important than in the case of the  $\text{AgI}$  structure) explains the high electrical conductivity values of the  $\alpha$ -form of both lithium sulphate and tungstate. Note that in the case of tungstate the transition is sluggish, whereas in the case of sulphate a sudden jump of the conductivity is observed corresponding to the transition temperature. On the basis of the activation enthalpies reported in Table I one could also remark that the overall activation enthalpy is lower than that corresponding to the pure motion term of the lithium halides.

The transport mechanism remains the hopping type and does not differ very much from that of lithium ions in the melt.

The fact that the Nernst-Einstein factor, [6]

$$\xi = t_+ \frac{\lambda}{F^2} \frac{RT}{D^+ z^+}$$

(where  $t_+$  is the transport number of the cation,  $\lambda$  is the equivalent conductivity and  $D^+$  is the self-diffusion coefficient), which differs from one in the case of both  $\alpha$ - $\text{AgI}$  and  $\alpha$ - $\text{Li}_2\text{SO}_4$ , but is greater than one in the former case and lower than one ( $\xi = 0.6$ ) in the latter case has been taken as a proof that, if the interstitial [6] mechanism dominates in the case of  $\text{AgI}$ , it should contribute little in the case of  $\text{Li}_2\text{SO}_4$ . Kvist [20] suggests that in the case of  $\alpha$ -lithium sulphate, a cooperative transport takes place, which involves a fairly large number of lithium ions.

This kind of mechanism recalls an analogous

situation presented by  $\text{CaO}$ -doped  $\text{ZrO}_2$ , where a cooperative transport of oxygen ions has been suggested to take place within the single microdomains of an ordered superstructure [22].

Relevant parameters of the electrical conductivity and self-diffusion coefficients of compounds of the  $\text{Li}_2\text{XO}_4$ -type are reported in Table I.

A spinel type structure is also adopted by the solid solutions of  $\text{Li}_2\text{MoO}_3$  and  $\text{Li}_6\text{MoO}_7$  [23]; this structure is that of  $\text{Li}_2\text{SnO}_3$ , with  $\text{Li}^+$  ions and  $\text{Mo}^{2+}$  ions distributed over the interstices between the oxygen ions, so that planes exist filled by oxygen ions alone, alkali ions alone and by alkali and molybdenum ions together [24] (see Fig. 5).

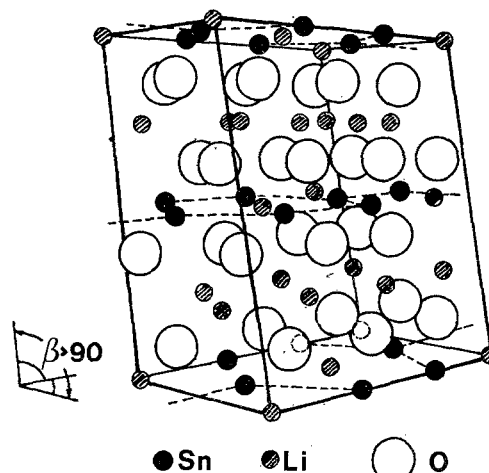


Fig. 5. Structure of  $\text{Li}_2\text{SnO}_3$  (from ref. 24).

Although the electrical conductivities of such compounds are unknown, we could imagine that lithium ions might move with relative ease along the less dense planes, as in the case of sulphates.

Better known are the electrical properties of  $\text{LiFeO}_2$  (lithium ferrite) and  $\text{LiFe}_5\text{O}_8$  (lithium ferrosphenel) which have a structure of the  $\text{NaCl}$  type, where cations are distributed in a disordered or ordered fashion among the equivalent lattice sites [25, 26, 27], the order-disorder temperature being around  $660^\circ\text{C}$  for lithium ferrite and  $745^\circ\text{C}$  for lithium ferrosphenel. D.c. electrical conductivity experiments carried out by Kato [25, 26] show that ionic conduction is present in these compounds coupled with electronic conductivity. As a consequence of the

Table 2.

System	Ref.	$T_{tr}$ °C	$\rho$ 25°C		Activation Energy (eV)	
			Disordered form	Ordered Form	Disordered	Ordered
LiFeO <sub>2</sub>	22	660 ± 2	~ MΩ	~ 1000 MΩ	~ 0.3 100 ≤ T ≤ 300°C ~ 1.4 (T > 680°C)	0.65 ≤ E <sub>a</sub> ≤ 0.9 200 ≤ T ≤ 400°C
LiFe <sub>5</sub> O <sub>8</sub>	23	745 ± 1	~ 2-3 KΩ	~ 100 MΩ	~ 0.20 130 ≤ T ≤ 500°C 1.2 ÷ 1.4 (T > 745°C)	~ 0.60 200 ≤ T ≤ 500°C

low values of the activation enthalpy for the conductivity for both compounds in the disordered state (about 5000 cal/mole), their behaviour has been compared with that of AgI or Ag<sub>2</sub>HgI<sub>4</sub>.

Apparently the lack of any information about the ratio of the electronic to the ionic conductivity does not allow any definitive conclusion about the behaviour of these compounds, nor a valid comparison of their properties with those of AgI and related compounds, although it has been done. It is, however, remarkable that in these compounds the room temperature values of the electrical conductivity of disordered samples is several orders of magnitude higher than that of the corresponding ordered samples, as is seen in Table 2.

#### Group (c) compounds (layer and tunnel structures)

Some compounds which have structures derived from the spinel structure belong to this group, as well as compounds with more complicated structures which originate from those of ReO<sub>3</sub> and TiO<sub>2</sub> (shear structures).

In the case of spinel-types of structures,  $\beta$ -aluminas and ferrites are well-known examples. Here spinel blocks exist (see Fig. 6) sheared by planes (mirror planes) in which all the sodium ions occur.

Whereas in the past some doubts existed about the possible stability of a form of beta-alumina (which is known to have the empirical formula Na<sub>2</sub>O.11 Al<sub>2</sub>O<sub>3</sub>) with higher sodium content, it is now recognized that a form which contains about twice the quantity of Na<sub>2</sub>O (Na<sub>2</sub>O.5 Al<sub>2</sub>O<sub>3</sub>)

exists, which could be prepared at lower temperatures as compared with the 1900°C needed for the preparation of the other form [28-30].

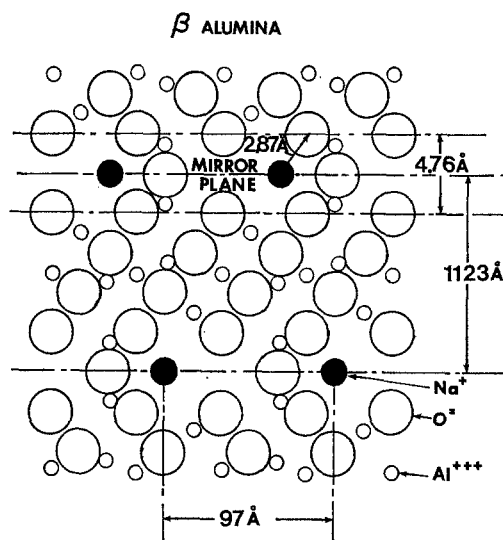


Fig. 6. Structure of  $\beta$ -alumina (from ref. 4).

As is emphasized in the Introduction, beta-alumina gives a straightforward example of the influence of the cation size on the mobility. Here there is an optimum size for a slot width which depends on the oxygen posts which keep the spinel blocks at a fixed distance apart; lithium ions, for example, are too small with respect to the slot width, and cannot move freely within the mirror plane but sit in a deep electrostatic well.

As the polarization power decreases with the increase of the ionic radius, the repulsive forces

of the outer electrons of the oxygen ions start to be more important than polarization effects and the ions move along the mirror plane.

Although it has been shown that the slot width could be changed by using isomorphous compounds such as  $K_2O \cdot 11 Fe_2O_3$  and  $Na_2O \cdot 11 Ga_2O_3$ , no significant progress has been reported in the direction of a high conductivity lithium-substituted beta-alumina. Potassium and sodium ferrites [31], on the other hand, in line with their high ionic mobility (the diffusion coefficients of alkali ions in alkali ferrites range between  $10^{-5}$  and  $10^{-6}$ , i.e. are of the same order of magnitude as found in beta-alumina) exhibit high electronic mobility, which favours their use as electrodes.

The compounds described above exhibit two-dimensional conductivity. Belonging to the same group are compounds which exhibit one-dimensional ionic conductivity. This depends on the existence in their structure of channels or tunnels, along which ions could move in the same manner as sodium ions move in the mirror plane of beta-alumina. The only known examples of tunnel structures with enhanced ionic conductivity, however, exhibit coupled ionic and electronic conductivity. Examples of such compounds are vanadium and tungsten bronzes. Lithium bronze  $Li_xV_2O_5$ , whose structure [32, 33] is schematically reported in Fig. 7, is claimed by Sienko [33, 34] to have good ionic conductivity within the range of composition  $0.30 \leq x \leq 0.60$  (beta-phase).

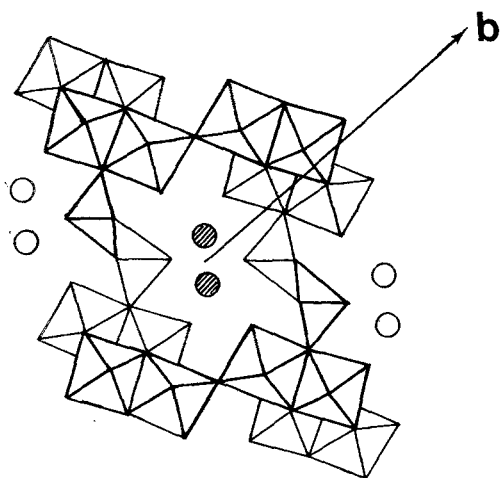


Fig. 7. Structure of  $\beta$ - $Li_xV_2O_5$  (from ref. 32).

It is apparent from Fig. 7 that large tunnels exist along the  $b$  axis where pairs of lithium ions could move. These tunnels are originated by chains of distorted octahedra and bipyramids.

Presumably other compounds with a structure derived from that of  $WO_3$ ,  $TiO_2$  and  $V_2O_5$  and exhibiting large deviations from stoichiometry could exhibit enhanced ionic conductivity.

Pure ionic conductivity is exhibited by a recently discovered class of compounds which have a structure which derives from the  $ReO_3$

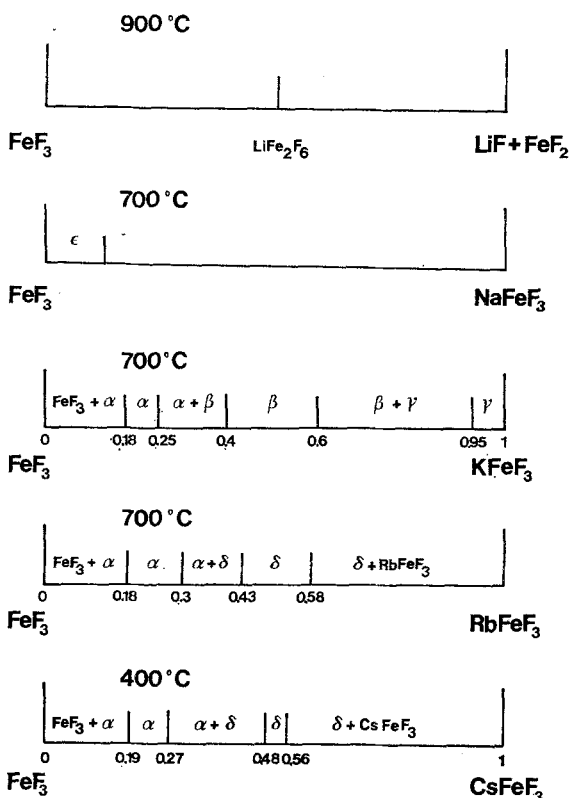


Fig. 8. Isothermal sections of the homologous series of the alkali fluorobronzes (from ref. 37).

structure. Such compounds, which have the general formula  $Me_xFeF_3$ , are called fluorobronzes and could not be considered, as in the past, as simple binary compounds between monovalent and trivalent fluorides [35–37].

As is shown in Fig. 8, where the isothermal sections of the homologous series with the alkali metals have been reported, it appears that grossly non-stoichiometric phases are stable. The existence of the latter could be explained only by considering that the electroneutrality is

maintained thanks to a valency control mechanism, due to the redox couple  $\text{Fe}^{2+}/\text{Fe}^{3+}$ . The metal-metal distance is, however, too large to allow orbital-coupling with consequent electron delocalization. These compounds are in fact insulators at room temperature.

In Fig. 9 the structure of  $\text{FeF}_3$  is reported in a

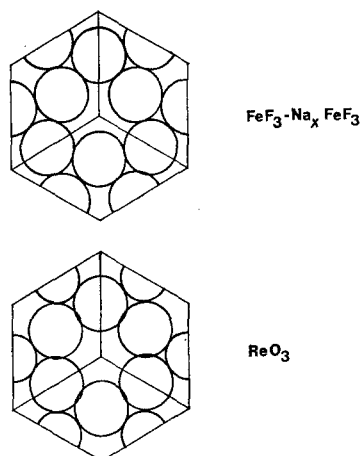


Fig. 9. Structure of a fluorobronze compared with the parent structure of  $\text{ReO}_3$  (from ref. 37).

schematic fashion, together with that of  $\text{ReO}_3$ . Inserted cations are shown to go to the large interstices.

From the reported electrical conductivity ( $R \approx 10^8 \Omega$  at room temperature) data one should, however, conclude that a transport mechanism is operative which is different from that taking place in oxygenated bronzes.

The same behaviour is presented by the high temperature form of beta-spodumene, which can be derived from the Keatite structure.  $\beta$ -spodumene itself is a member of the family of silico-aluminates, with a composition  $\text{Li}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 4\text{SiO}_2$  (giving a 1:1 ratio between the aluminium and lithium) whose particularly attractive structural properties [38] should enhance ionic conductivity. It presents channels of about 3 Å in diameter, which run parallel to the  $a$  and  $b$  axes [39], similar to those present in zeolites. Along these channels lithium ions should move relatively freely when subjected to a convenient driving force.  $\beta$ -spodumene is endowed with cation-exchange properties, and like zeolites, those are probably limited to  $\text{H}^+$  [39]  $\text{Na}^+$  and  $\text{K}^+$  [40].

E.m.f. measurements and a.c. electrical conductivity measurements [41] have been carried out by the author on undoped and doped silica as well as on  $\beta$ -spodumene in order to get information on the type of ionic carriers and on the carrier concentration-mobility relationship in such  $\text{SiO}_2$ -based compounds. E.m.f. measurements show that the lithium ion is mobile and results of electrical conductivity measurements given in Fig. 10 illustrate that the activation

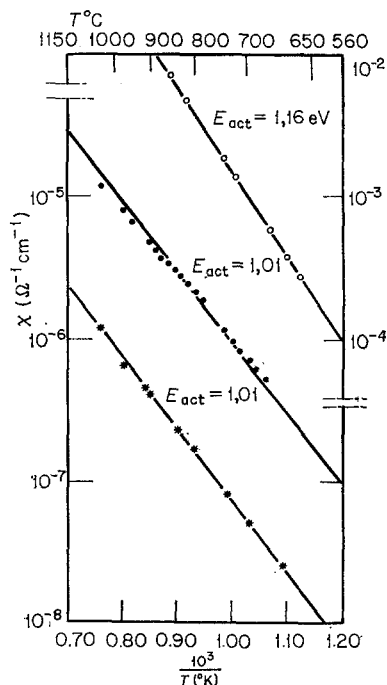


Fig. 10. Electrical conductivity of Pursil-silica, Li-doped  $\text{SiO}_2$  (100 ppm) and  $\beta$ -spodumene.

energy remains approximately constant (23–27 kcal/mole) in spite of the large variation of the lithium content, whereas the absolute value of the conductivity depends on the total lithium content with an approximately linear relationship (see also Table I for numerical values).

As in the case of both fluorobronzes and  $\beta$ -spodumene, the electrical conductivity results refer to polycrystalline samples, it is not completely excluded that the use of single crystal would reveal better transport properties.

## Conclusions

The transport behaviour of the lithium ion is exceptional because it is particularly sensitive to



the environment of polarizable anions on account of its small size.

The influence of the structure could however be masked, at least in the case of silico-aluminates, by the presence of islands of glass, so that both the mismatch between the crystals at the grain boundaries and the presence of an amorphous phase between crystals are responsible for the 'regular' behaviour observed.

This explanation is favoured by the comparable properties of the lithium metaborate glasses, which are known to be ionic conductors, with an activation energy for the electrical conductivity which is of the same order of magnitude as that observed in  $\beta$ -spodumene (15–20 kcal/mole depending on the lithium content, which ranges between 7.9 and 42.6 mole %, see Table I). In other terms, anisotropy of the electrical conductivity, due to the presence of layers or tunnels, hinders the possibility of finding excess of ionic conductivity in polycrystalline materials: here the kinetics of the overall transport process could be entirely determined by the transport across grain boundaries.

Only in the case of group (a) compounds has the behaviour of single crystals been compared with that of polycrystalline samples. Therefore definitive conclusions about the role of structure in the case of lithium compounds could be drawn only if comparison could also be made between single crystal and polycrystalline samples of group (b) and group (c) compounds.

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