

# Ion exchange as a simple and effective tool for screening possible cation conductors

Vladimir B. Nalbandyan

Received: 23 June 2010 / Revised: 2 July 2010 / Accepted: 3 July 2010 / Published online: 20 July 2010  
© Springer-Verlag 2010

**Abstract** Although kinetics of the low-temperature cation exchange in mixed oxide materials (aluminates, gallates, titanates, niobates, tantalates, antimonates, phosphates etc.) cannot provide *quantitative* information on self-diffusion and ionic conductivity in the starting material due to the mixed cation effect, it is the most direct and simple *qualitative* indication of the cation mobility in the solid state. It does not need using ceramics and single crystals and thus represents a useful tool for rapid selection of prospective cation conductors for subsequent detailed studies of dense samples with electrical methods. Examples of solid electrolytes discovered owing to their ion-exchange properties are reviewed, and rational principles of the ion-exchange testing are discussed. Laws of ion-exchange equilibria are based on ionic size compliance and the principle of hard and soft acids and bases. The former is most important for alkali/alkali exchange and the latter for exchanging cations of similar size but having different electronic structures: those of the rare-gas type and those having 18- or 18+2-electron shells, like  $\text{Na}^+$  and  $\text{Ag}^+$  or  $\text{K}^+$  and  $\text{Tl}^+$ . Ion-exchange testing is especially useful for structures with non-intersecting conduction paths. It is shown that the resistivity of crystals with non-parallel and non-intersecting conduction paths cannot be described by the classical tensor formalism. Significant differences between isotope exchange, chemical ion exchange and ion conduction, quasi-one-dimensional and true one-dimensional conductors and single- and multiple-barrelled non-intersecting channels are disclosed and discussed.

**Keywords** Ion conduction · Diffusion · Exchange equilibria · Exchange kinetics · Mixed oxides · Non-intersecting channels

## Introduction

Ion exchange between a solid and a liquid (a solution or melt) is widely used in various fields of science and technology, from softening water and chromatographic separation of ions to strengthening glass and making optical waveguides. In the solid-state science, it is one of the main “chimie douce” (soft chemistry) tools for preparing new materials ([1–20] and references therein), including ionic conductors [2, 3, 5–14], battery electrode materials [6, 15–19], superconductors [20] etc., many of which cannot be prepared by other methods. Only a small part of the relevant work could be cited here. This paper discusses both historical aspects and future prospects of a very specific field: using ion exchange for screening possible solid-state cation conductors, mostly oxides with monovalent cations.

## Overview of methods for selection of promising solid electrolytes

Modern technology needs chemically stable high-conductivity solid electrolytes for use in power sources, sensors and other electrochemical devices. Design of solid electrolytes with essentially new types of structure (rather than modification of known structures) remains a challenge. Most ion-conducting structure types known up to now could only be discovered by the way of serendipity [21]. How can one select prospective ionic conductors from the huge number of known and newly prepared compounds?

V. B. Nalbandyan (✉)  
Southern Federal University,  
7 ul. Zorge,  
Rostov-on-Don 344090, Russian Federation  
e-mail: vbn@sfedu.ru

There are several computational tools enabling search for and evaluation of possible diffusion paths in known crystal structures [21], but the structure of a compound may be still unresolved, especially when single crystals are not available. In addition, essentially wide channels do not guarantee high conductivity.

Of the experimental methods, nuclear magnetic resonance and inelastic neutron scattering are effective indicators of *local* ionic motions within a confined space, but their information on *translational* motion is much less definite. In addition, using the both methods needs sophisticated and expensive instruments. Of course, direct measurement of ionic conductivities of all available candidates might be the best way to select good ionic conductors. However, there are some difficulties, too.

- (a) First, one needs essentially dense samples: single crystals or ceramics. With plastic phases, such as halides or chalcogenides of silver or copper (I), there is no problem: High density may be achieved by cold pressing the powders. However, this is not the case with oxide materials discussed here. They are usually hard and brittle, and this prevents obtaining dense samples with good contact of grains and reliable conductivity values by mere cold pressing. The conductivity will be usually underestimated due to poor contacts but may sometimes be overestimated due to surface conductivity, especially in humid environment. For preparing dense samples of the brittle materials, high-temperature sintering or single-crystal growth are necessary, both procedures being difficult and time-consuming, not to mention possible volatilisation of components, incongruent melting etc.
- (b) When ceramic samples are available, further problems arise: proper selection of electrode materials, their attachment to the sample and separation of the three contributions to the impedance of the resulting electrochemical cell—those from the electrolyte itself, from the grain boundaries and from the polarization of the electrolyte/electrode interface. For solving the last problem, analysis of the complex immittance measured in a wide frequency range is now the established procedure [22–25]. However, its results are sometimes ambiguous because the same spectra may be described with entirely different equivalent circuits. Thus, independent confirmations are desirable, e.g. by four-probe (AC or DC) measurements or by studying relation between resistance and length of the sample [26]. In some crystals, extremely high values of the “dc conductivity” have been deduced from measurements in the megahertz or gigahertz range [27, 28], with no confirmation of real ion transport other than “rattling” within a confined space.
- (c) In mixed conductors, it may be difficult to measure the ionic contribution in presence of dominating electronic conductivity [29].
- (d) For one-dimensional ionic conductors, measurements on ceramic samples result in conductivities several orders of magnitude lower than those in the “easy” direction; with single crystals, there may be a problem of proper choosing measurement direction (see “Ionic conductivity, diffusion and exchange in non-intersecting channels” section for details).

All the problems (a)–(d) may be effectively solved, but this needs large amount of work and it is worth doing only with selected materials: those having crystal structures favourable for the ion transport and/or showing unambiguous signs of fast ion diffusion [1–8, 30] in ion-exchange experiments discussed below.

### Self-diffusion and chemical diffusion

The well-known Nernst–Einstein equation establishes relation between ionic diffusivity and ionic conductivity. However, measurement of the self-diffusivity seems even more complicated than conductivity experiments because it needs radioactive isotope tracers and also dense samples, preferably single crystals. In contrast, chemical diffusivity may be easily controlled by chemical analysis and therefore is much easier and convenient for the screening purposes. In addition, at least one structure is known which exhibits ion conduction and ion exchange but not isotope exchange (see “Ionic conductivity, diffusion and exchange in non-intersecting channels” section).

In the most important case of a solid-state cation conductor with intersecting diffusion paths forming a two- or three-dimensional net, counterdiffusion of ions can occur, in contrast to Clearfield’s statement [3]. Then, exchange of two monovalent cations represents a special case of chemical diffusion where diffusion fluxes of the two cations in opposite directions should be equal to maintain the electroneutrality. If they are not, an electric field appears which accelerates the “slow” ions and hampers the motion of the “fast” ions until their fluxes become equal. The overall interdiffusion coefficient for this process is then given by the following relation [3, 31]:

$$D = D_1 D_2 / (x_1 D_1 + x_2 D_2)$$

where  $D_1$  and  $D_2$  are self-diffusivities of the two cations and  $x_1$  and  $x_2$  are their molar fractions in the corresponding sublattice ( $x_1 + x_2 = 1$ ). If  $x_1 D_1 \ll x_2 D_2$ , then  $D \approx D_1 / x_2$ . Thus, the chemical diffusion is controlled by the diffusivity of the

“slow” ion and/or the minority ion. The above equation, however, is of little use because the self-diffusivities of the components within the resulting solid solution are usually unknown and may be expected to be much less than those in the corresponding end members. This is the so-called mixed alkali (or mixed cation) effect: In isovalent substitutional solid solutions, the compositional dependences of ionic conductivity (and therefore diffusivity) and activation energy usually display a minimum and maximum, respectively. The effect is well-known in glasses [32, 33] and crystalline cation conductors such as polyaluminates, polygallates etc. ([21] and references therein). The conductivity minimum is most pronounced at low temperatures (due to the larger activation energies) and with great ionic radii differences. Thus, ion-exchange kinetics (in contrast to isotope-exchange kinetics) cannot provide *quantitative* information about ionic conductivity of the starting material but remains a very useful *qualitative* indication of its cation mobility.

A great amount of experimental data shows that good cation conductors always show very fast ion-exchange kinetics—of course, in optimal conditions only, as discussed in “Ion-exchange equilibria and rational principles of the ion-exchange testing” section. E.g. for 1-mm-sized single crystals of  $\beta$ -alumina in molten  $\text{KNO}_3$ , half-conversion time is less than 5 min at 350 °C [34]. Even in one-dimensional sodium channels of the two framework structures shown in Fig. 1a, b, complete silver substitution

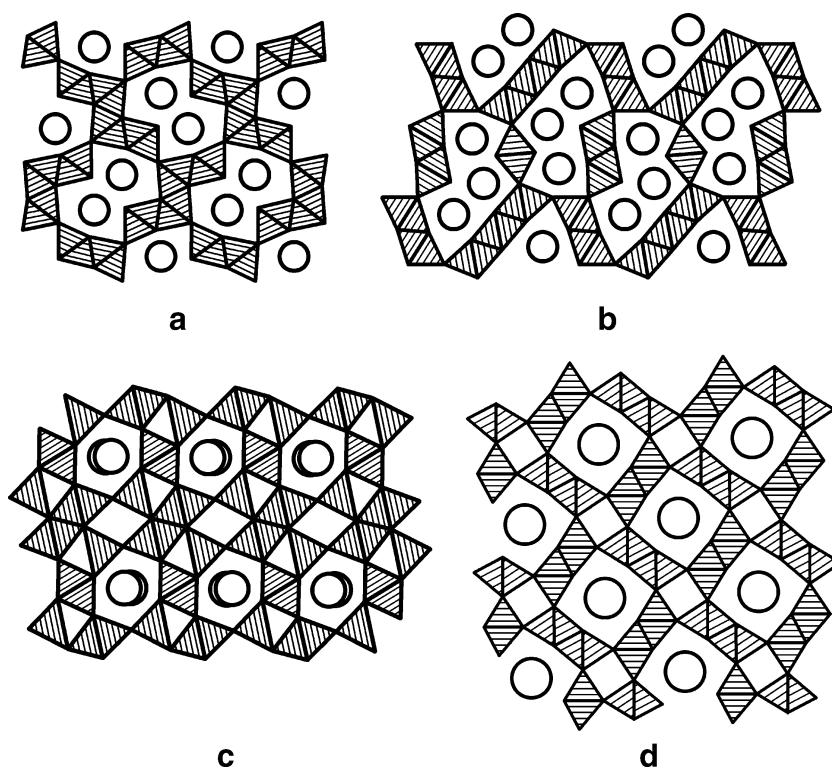
for sodium in a 2- to 3-mm-long crystal (ca.  $10^7$  ions in a channel!) takes few minutes at 300–320 °C [2, 35, 36]. Note that initially [35], we used much longer ion-exchange treatments, but later experiments showed that it was redundant.

Ion exchange is a necessary, but not sufficient, condition for fast ion conduction [1, 3]; the opinion that a fast ion-conducting solid does not necessarily undergo fast ion exchange [6] has not been supported by the experimental data and, probably, is based on experiments performed under unfavourable conditions. Actually, a powder that do not exchange its monovalent cations rapidly *in optimal conditions* discussed in “Ion-exchange equilibria and rational principles of the ion-exchange testing” section is of no interest from the cationic conductivity point of view, although not all cation exchangers (e.g. zeolites) are very good cation conductors.

#### Some examples of cation conductors discovered and studied owing to ion-exchange reactions

The discovery of the high sodium ion conductivity in  $\beta$ -alumina followed by development of sodium–sulphur battery [34, 37] and boom on  $\beta$ - and  $\beta''$ -alumina type electrolytes (many hundreds papers and patents, only four of them being cited here [9–11, 38]) was inspired by the works on cation-exchange reactions published by Toropov

**Fig. 1** Four framework crystal structures with one-dimensional cation conduction channels projected along the channel axis [21]: **a**  $\text{Na}_x(\text{M,Ti})_2\text{O}_4$ ; **b**  $\text{Na}_{2+x}(\text{M,Ti})_4\text{O}_9$ ; **c**  $\text{Na}_{0.7}\text{Ga}_{4.7}\text{Ti}_{0.3}\text{O}_8$ ; **d** hollandite-type  $\text{K}_x(\text{M,Ti})_4\text{O}_8$ .  $\text{M}=\text{Mg}^{2+}$ ,  $\text{Fe}^{3+}$  and other cations of similar size.  $(\text{M,Ti})\text{O}_6$  (or  $\text{GaO}_6$ ) and  $\text{GaO}_4$  groups are shown as polyhedra and  $\text{Na}^+$  or  $\text{K}^+$  cations as balls



and Stukalova as early as 1939–1940. Similarly, preparation and study of the great amount of pyrochlore-type electrolytes, e.g. ceramic conductors of  $K^+$ ,  $Na^+$  ions [7, 8] and protons [12, 13], and also pyrochlore-related rhombohedral proton conductor  $(NH_4)_4Ta_{10}WO_{30}$  [14] was stimulated by ion-exchange and crystal chemistry studies by B. Raveau and co-workers [39, 40]. Ion-exchange properties, together with crystal chemistry studies, prompted discovery of ionic conductivity in cubic  $NaSbO_3$  [7, 8], layered  $A_4Nb_6O_{17}$  ( $A=K, Na$ ) [7],  $A_7Fe_3(X_2O_7)_4$  ( $A=Na, Ag$ ;  $X=P, As$ ) [41, 42] etc.

The present author performed ion-exchange tests with several dozens of sodium-, potassium-, thallium- or lithium-containing mixed oxides (titanates, niobates, tantalates, antimonates etc.). Some of them showed little or no ion exchange in mild conditions and were discarded as solid electrolytes. In many other instances (e.g. layered  $\alpha$ - $NaFeO_2$ -related phases), observed ion-exchange properties were well predictable based on preceding work with structural analogues and thus were of little interest for the present review. Hollandite-type phases displayed moderate ion-exchange properties [43, 44], which correlated with their moderate conductivities, contrasted with an early report on extremely high potassium ion mobility, and simultaneously showed that planned use of hollandites for immobilization of radioactive caesium may be hazardous. However, the two channel structures mentioned above [35, 36] showed very rapid exchange; high ionic conductivity in one of them was confirmed by direct measurements on single crystals [45], whereas crystals of the other have not been grown sufficiently large, and the conductivity could only be measured on ceramics [46]. Two more sodium ion conductors with still unsolved structures,  $Na_4MgTi_3O_9$  [47] and  $12NaF \cdot 35Na_2O \cdot 53TiO_2$  [48], were also discovered owing to their fast silver ion exchange [49].

Complete substitution of silver for alkali facilitates the chemical analysis of crystals [45] because analytical determination of the heavy metal is easier and more accurate than determination of sodium or potassium. In other instances, incomplete ionic or tracer substitution under optimal conditions may indicate presence of a non-labile or hardly mobile cation, like sodium on gallium sites in  $Na_{1+2x}(Ga_{11-x}Na_x)O_{17}$  [38], Na(1) in ten-barrelled channels of “ $Na_{10}MgTi_{10}O_{26}$ ” [50] and the “fourth” sodium residing within a  $(NaFeSb)O_6$  layer in  $Na_4FeSbO_6$  [51].

### **Ion-exchange equilibria and rational principles of the ion-exchange testing**

As any chemical reaction, ion exchange should be considered in both thermodynamic and kinetic aspects. To be thermodynamically possible at constant pressure and

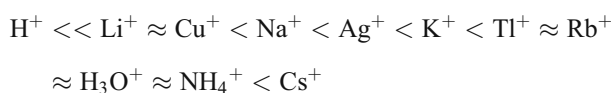
temperature, the reaction should result in negative change of the Gibbs free energy

$$\Delta G = \Delta H - T\Delta S$$

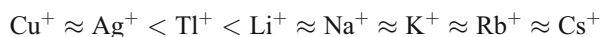
The most common, although small at moderate temperatures, driving force of all exchange reactions is an increase in the configuration entropy ( $\Delta S > 0$ ) due to formation of liquid and/or solid solutions. For isotope exchange, it is the only driving force since no considerable change in the enthalpy may be expected ( $\Delta H \approx 0$ ). For chemical exchange, the enthalpy term is usually much more important. It is hardly possible to predict  $\Delta H$  and  $\Delta S$  values quantitatively for a reaction resulting in a previously unknown product, but some empirical principles of equilibrium displacement have been formulated [2]. They are based on ionic sizes and bond character.

As far as a low-temperature topotactic reaction is concerned, the crystal structure of a potential ion exchanger should remain intact. Therefore, the size of the incoming ion must be similar to that of the outgoing ion. Too small ion may be not stabilized in the structure whereas too large ion will not be able to enter it. This is most important for rigid frameworks and less important for layered structures where interlayer distance may vary. For the salt phase, cation/anion volume relation may also play a significant role, as discussed below.

The radii of monovalent cations increase in the following series:



The role of bond character may be interpreted in terms of Pearson's hard and soft acids and bases (HSAB) theory. Soft acids (cations) will preferably combine with soft bases (anions) forming the most covalent compounds whereas hard cations and hard anions will form the most ionic compounds. However, relative hardnesses may vary depending on the type of reaction in question. For the systems discussed here, the following series of “anions” and monovalent cations arranged according to increased hardness (here, ionicity) seem to be most adequate:  $I^- < Br^- < Cl^- < \text{polymer oxometallates (aluminates, titanates, niobates etc.)} < \text{oxoanions (nitrates, sulphates etc.)}$ ;



Position of the hydrogen ion in this series is less definite because it may easily transform from ionic  $H_3O^+$  or  $NH_4^+$  to covalent  $H^+$  (actually bound to the rigid oxide lattice as  $OH^-$  or volatilised as a hydrogen halide).

For alkali–alkali exchange, size effects are dominating because differences in bond character are small; however,

bond type differences become very important in systems including both soft and hard cations.

Roles of both factors (ion size and hardness) are illustrated by exchange equilibria between sodium  $\beta$ -alumina and molten nitrates (Fig. 2). It is evident that the polyaluminate crystals effectively absorb soft cations of intermediate size, close to that of  $\text{Na}^+$  or slightly larger, especially silver, whereas incorporation of too small or too large hard ions ( $\text{Li}^+$ ,  $\text{Rb}^+$  and especially  $\text{Cs}^+$ ) is unfavourable. The same is valid for all other known systems of the type “mixed oxide–oxosalt (nitrate or sulphate)”: Silver substitution for sodium or potassium in a mixed oxide is almost irreversible [2, 26, 35, 36, 41–43, 49–54]; preference for  $\text{Ti}^+$  over alkali ( $\text{K}^+$  and/or  $\text{Na}^+$ ), although less strong than that for  $\text{Ag}^+$ , was found not only in  $\beta$ -alumina (Fig. 2) but also in hollandite-type titanates [43] and  $\text{MSbO}_3$  series [53]. Of course,  $\text{Ti}^+$  or  $\text{K}^+$  substitution for  $\text{Na}^+$  in many structures may be restricted or even precluded [35, 36, 41, 50, 55] by the great differences in their radii.

There is thus no need in using great excess of silver nitrate and in repeated treatments with fresh portions of the salt, a typical practice of many previous works. Some excess of silver nitrate, however, may be necessary to maintain the mixed nitrate in molten state as discussed below.

In accordance with the HSAB principle, exchange equilibria may be shifted in the opposite direction when chloride or bromide melts are used instead of nitrates in systems comprising soft cations. Ion-exchange preparation of completely substituted lithium  $\beta$ -alumina, impossible in purely nitrate melts (see Fig. 2), becomes possible when silver  $\beta$ -alumina is treated with  $\text{LiCl}+\text{LiNO}_3$ , owing to effective combination of soft  $\text{Ag}^+$  with soft  $\text{Cl}^-$ . An alternative preparation route is the reaction of  $\text{NH}_4$ - $\beta$ -

alumina with  $\text{LiNO}_3$ . The decomposition of  $\text{NH}_4\text{NO}_3$  shifts the equilibrium to favour  $\text{Li}^+$  in the crystal [34].

In contrast, lithium  $\beta$ '-alumina could be prepared without using a silver or ammonium intermediate, by direct reaction of sodium  $\beta$ '-alumina with excess  $\text{LiCl}$  at  $675^\circ\text{C}$  [10]. This process is, obviously, favoured by the following factors:

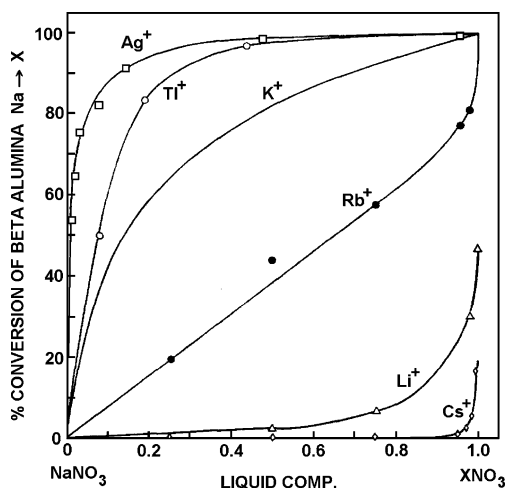
- Alkali coordination in the  $\beta'$ -phase is four-fold, more suitable for  $\text{Li}^+$  than the six-fold coordination in the  $\beta$ -phase.
- The entropic term is more significant here due to higher temperature.
- Volume relations in the chloride system favour the equilibrium shift toward formation of  $\text{NaCl}$ : The combination of small  $\text{Li}^+$  with large  $\text{Cl}^-$  is less stable than  $\text{NaCl}$  due to greater anion–anion repulsion in  $\text{LiCl}$ , which is illustrated by higher melting point of  $\text{NaCl}$  ( $801^\circ\text{C}$ ). The same reason is, probably, responsible for the fact that more  $\text{Li}$  enters the sodium  $\beta$ -alumina from an iodide melt than from a nitrate melt [34].

A different approach to exchange equilibria, with emphasis on aqueous systems rather than melts, may be found in the review by Clearfield [3].

For favourable kinetics, it is, of course, necessary to provide good contact between the solid and liquid phases and to maintain the salts in molten state in the course of exchange [2]. E.g. when a sodium- or potassium-containing mixed oxide reacts with a stoichiometric portion of  $\text{AgNO}_3$  or  $\text{TlNO}_3$  slightly above their melting points (say, at  $220^\circ\text{C}$ ), the liquid disappears by the end of the process due to formation of solid solutions based on  $\text{NaNO}_3$  or  $\text{KNO}_3$ , having higher melting temperatures, and complete substitution may be then kinetically hindered. It is therefore necessary to consult respective binary phase diagrams and either raise the temperature or, preferably, use a small excess of the starting nitrate.

England et al. [1] and Clearfield [3] discuss kinetic equations based on the interdiffusion coefficient and crystal size. However, the interdiffusion coefficient is expected to vary significantly in the course of exchange due to the mixed cation effect (see “Self-diffusion and chemical diffusion” section) which makes these equations hardly applicable. To reduce the effect, the exchanging ions should be similar in size, a condition coinciding with that recommended from the thermodynamic point of view.

With silver substitution for alkali, the main problem may be their different coordination preferences. In contrast to four to eight weak bonds typical of alkali cations, silver, as well as copper (I), tends to be the dumbbell coordination with two relatively strong bonds, and this may sometimes hinder diffusion. E.g. in  $\alpha$ - $\text{NaFeO}_2$ -related phases, alkali



**Fig. 2** Exchange equilibria between beta-alumina crystals and various binary nitrate melts containing  $\text{NaNO}_3$  and another metal nitrate at  $300$ – $350^\circ\text{C}$  (reproduced with permission from [34])

ions have six-fold coordination, but silver or copper substitution for alkali induces layer gliding to form delafossite-type structures with two-fold coordination of the coinage metal. Ion exchange in powders of this structural family is usually fast and complete, but with single-crystalline plates having ca. 1 mm in radius, only 50% exchange had been achieved within several days at room temperature and then remained unaltered for 6 months; according to the X-ray data, each crystal was a combination of the starting Na compound and the completely exchanged regions, with no signs of a solid solution. In two other structures, still unsolved, fast silver substitution for sodium resulted in poorly crystalline, nearly amorphous materials, presumably due to similar coordination changes [49].

It follows from the discussion in “[Self-diffusion and chemical diffusion](#)” section that ion-exchange testing of ionic mobility in mixed oxides should be performed at relatively low temperatures (preferably, below 300 °C) and within relatively short periods to avoid reconstructions and to select phases with highest cation diffusivities. On the other hand, using aqueous solutions may sometimes result in hydrolysis and/or sorption of water molecules blocking the cation diffusion paths; caustic substances (both alkaline and acidic) may destroy or dissolve some phases. Of course, acid treatment is necessary for the ion-exchange preparation of proton conductors, but it cannot be recommended as general procedure for testing cation mobility. Therefore, low-melting, relatively inert salts, especially nitrates or eutectics based on them, seem preferable.

The ideal reagents for probing  $\text{Na}^+$  mobility in oxide structures are silver nitrate and its eutectic with potassium nitrate. With lithium and potassium salts, negative results are possible due to great radius differences, and this will not necessarily mean low  $\text{Na}^+$  mobility. The most suitable reagents for probing  $\text{K}^+$  mobility in oxides are silver nitrate and thallium nitrate (although the latter is poisonous!). Depending of the specific structure, either former or latter may be more effective. Thus, it is desirable to test both. Sodium salts may also be used with the same limitation as above. The ideal reagent to test  $\text{Rb}^+$  or  $\text{Cs}^+$  mobility is again thallium nitrate.

Unfortunately, it is difficult to find well-suitable reagents for testing lithium mobility in oxides. Of course, silver salts may be used and fast exchange will mean fast lithium diffusion; however, absence of exchange may merely mean that  $\text{Ag}^+$  is too large for this specific structure.  $\text{Cu}^+$  is ideal in size, but does not provide stable low-melting oxosalts like nitrate, and exchange between lithium-containing oxides and cuprous halides may be thermodynamically unfavourable. Of all available copper (I) salts,  $\text{CuCl}$  is, obviously, the most suitable due to lower melting point (430 °C), higher bond ionicity, and smaller anion compared

to those of  $\text{CuBr}$  and  $\text{CuI}$ . Indeed,  $\text{LiScO}_2$  reacts with excess  $\text{CuCl}$  at 650 °C to give  $\text{CuScO}_2$  [56]. Besides the high temperature, this reaction is favoured by formation of the delafossite-type phase with two-fold coordination of Cu, i.e. with essentially covalent bonding. It is worth noting that, due to the low electronegativity of Sc and high ionicity of Sc–O bonds, A–O bonds in  $\text{AScO}_2$  should be less ionic than similar bonds in aluminates, titanates or niobates. In any case, reactions with  $\text{CuCl}$  are of low use for screening lithium ion conductors because they cannot be performed at low temperatures.

Another possible approach to testing lithium mobility is, probably, treatment with acids, either aqueous or molten (e.g. benzoic acid is liquid between 122 °C and 249 °C). The process seems to be thermodynamically favourable although many mixed oxides are unstable in acidic media as mentioned above. Another limitation is the fact that diffusion mechanisms are entirely different for  $\text{Li}^+$  and protons, and proton diffusivity in some structures may be much lower, thus blocking the mobility of  $\text{Li}^+$ .

### Ionic conductivity, diffusion and exchange in non-intersecting channels

A very specific class of frameworks with wide non-intersecting channels, where high cation conductivities are either proved experimentally or anticipated, comprises a variety of structure types and deserves a special consideration. Eleven of these types, mostly titanates and gallates, together with three quasi-one-dimensional conductors, are discussed in our recent review [21], and four of them are represented in Fig. 1, but the class actually includes multiple (alumo)silicates, phosphates, borates etc., and the number will grow in the future.

Measuring ionic conductivity in such a material meets serious limitations mentioned in “[Overview of methods for selection of promising solid electrolytes](#)” section. In a ceramic sample, most crystallites are in orientations unfavourable for the ionic transport and effectively block transport through those in favourable orientation. Actually, this is a series connection of very low and very high resistances. As a result, ionic conductivity of such a ceramics is several orders of magnitude lower than that of a single crystal in “easy” direction.

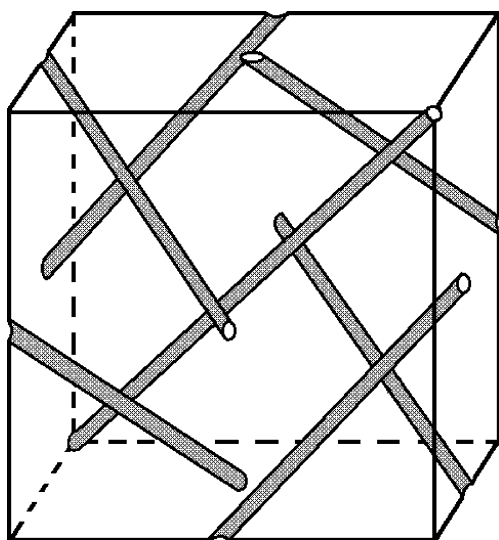
The situation may be clarified with single crystals. However, besides difficulties with growing crystals, there appears another problem: What direction should be chosen for the measurements? The classical tensor formalism [57] presumes that both conductivity and resistivity are second rank tensors, and consequently, the number of independent measurements is equal to the number of independent unit cell parameters, ranging from one to six for cubic and

triclinic crystals, respectively; the knowledge of all components of the tensor permits correct prediction of the resistivity value in any direction. This approach, however, fails to describe resistivity of crystals with *non-parallel and non-intersecting* channels of ion transport.

To illustrate this, let us consider a group of closely related frameworks including aluminosilicates analcite and leucite and also many synthetic analogues. Their crystal structures are cubic or pseudocubic (tetragonal or monoclinic) with non-intersecting diffusion channels running along the four  $\langle 111 \rangle$  directions [58] (see Fig. 3). For a cubic crystal, the tensor approach predicts equal resistivity in all directions. However, if one takes two long samples of small cross section (a prerequisite for correct measurement of components of a resistivity tensor [57]), parallel and non-parallel to the direction of channels, their resistivities will be different in obvious contradiction with the classical approach.

Similarly, in cation conducting tetragonal  $A(UO_2)_4(VO_4)_3$ , where  $A=Na, Li$  [59], non-intersecting migration channels run alternatively along [100] and along [010]. Many other structures may exist with various arrangements of non-intersecting conduction paths. Thus, be the crystal structure unknown (or known but complicated: showing no obvious diffusion channels), it will be difficult to find proper directions for the resistivity measurements on single crystals, even when their point group is known.

In such instances, preliminary ion-exchange testing of the ionic mobility might be especially useful, but here we meet another problem, that of single-file diffusion (SFD), i.e. the case where the diffusing particles are not able to pass each other. This problem was analysed in a great



**Fig. 3** A schematic of non-intersecting sodium channels in analcite [58]

number of papers (e.g. [60–62] and references therein), mostly theoretical and/or considering transport of neutral molecules in empty channels of zeolites or ion transport in biological membranes where it may be assisted by electrical fields; however, nothing could be found there on the theory of *ionic* (chemical or isotope) exchange in single-file systems. The model for a neutral tracer exchange with total concentration fixed [60] seems to be the closest approximation. The SFD theory predicts that square mean displacement should be proportional to the square root of time and not to the first power of time, as in the classical diffusion theory.

The experimental data on ion and isotope exchange in non-intersecting channels are scarce and somewhat contradictory. Chandrashekar et al. [63] discovered very high one-dimensional sodium ion conductivity in single crystals of sodium titanogallate (NGT) depicted in Fig. 1c but failed to find any isotope exchange after 2-day treatments in molten  $NaNO_3$  containing  $^{22}Na$  tracer. On the other hand, single-crystalline sodium magnesiotitanates, depicted in Fig. 1a, b, have similar (or even lower) ionic conductivities but exchange their sodium for silver in few minutes at similar (or even lower) temperatures as discussed above; ion exchange in crystals of  $KTiOPO_4$  (KTP) is effectively used for creation of strictly one-dimensional optical waveguides [64] although its one-dimensional ionic conductivity [64, 65] is much lower than that for NGT. Moreover, the exchanged-ion concentration depth profile in KTP obeys the equations for classical diffusion rather than SFD [64, 66]. These apparent inconsistencies need explanations.

The explanation for KTP is that it is not strictly one-dimensional ion conductor. The bottleneck radii for potassium ion transfer along  $x$ - and  $y$ -axes are shorter by 0.39 and 0.57 Å, respectively, than that for transfer along  $z$  [66]. Hence, macroscopic ion transport in directions other than  $z$  is hardly possible. However, some limited transfer between the adjacent one-dimensional  $z$ -axis paths is still possible, at least, along  $x$ . The most direct proof of this is the ion exchange with  $RbNO_3$  sprinkled on *only one* (100) face of the KTP crystal [67]. This would be absolutely impossible in the case of true SFD.

For the strictly one-dimensional conductors depicted in Fig. 1, two different explanations are proposed. The first, most obvious and similar to that for KTP, is kinetic. The two structures in Fig. 1a, b contain double- and triple-barrelled channels, respectively; hence, they may permit counterdiffusion of ions (although bottlenecks between the barrels are considerably narrower than those within a given barrel), whereas the two structures in Fig. 1c, d are true single-file structures and counterdiffusion is impossible there.

The second explanation is thermodynamic and emphasizes the difference between silver ion exchange and

isotope exchange. The former is driven by the decrease in enthalpy, while the latter is only by increase in entropy. However, in the case of SFD, there is practically no entropy change because ions do not mix: The partially exchanged channel would contain a long sequence of  $^{22}\text{Na}$  followed by long sequence of  $^{23}\text{Na}$ . To understand the difference on the microscopic (mechanistic) level, assume that the first foreign ion ( $^{22}\text{Na}^+$  or  $\text{Ag}^+$ ) has entered the channel. What's the next? In the case of isotope exchange, the most probable next event will be moving the foreign ion backward into the liquid because entering the second foreign ion requires concerted movement of a great number of ions in a channel which needs substantially high energy. In the case of chemical exchange, the foreign ion (here,  $\text{Ag}^+$ ) is bound much stronger and its backward movement is of little probability. The most probable (energetically favourable) event will be entering the second  $\text{Ag}^+$  whose tight binding will provide the energy necessary for concerted move of several next ions in the channel.

Indeed, ion exchange in true single-file structures is also possible, although slow. This was shown many years ago [43, 44] for powders and ceramics of the hollandite type (Fig. 1d) in molten  $\text{AgNO}_3$ ,  $\text{TlNO}_3$  or  $\text{Ti}_2\text{SO}_4$  and, more recently [55], for those of NGT (Fig. 1c) in molten  $\text{LiNO}_3$ . Therefore, both the above explanations seem to be valid, and one-dimensional channels may represent a unique case where chemical diffusion is possible in the absence of self-diffusion.

More experimental data are necessary to elucidate ion-transport mechanisms in one-dimensional channels, and the work is in progress. Our preliminary results for  $\text{Na}_x\text{Mg}_{x/2}\text{Ti}_{2-x/2}\text{O}_4$  with double-barrelled channels (Fig. 1a) indicate that the kinetics of silver exchange in powders represents a combination of the classical model and SFD; the exchange rate decreases drastically with  $x$  changing from 0.8 to 0.95 due to lowering concentration of sodium vacancies. On the other hand, the ionic conductivity increases significantly with  $x$  [68] because it is a single-file process, probably of the soliton type, and does not need vacancies.

## Conclusions

Ion-exchange reactions in molten or aqueous media are very useful not only for preparing new, often metastable, materials with valuable properties (e.g. solid electrolytes and electrode materials) but also for preliminary testing of various materials for their cation mobility, as suggested initially by England and co-workers [1]. However, quantitative estimations of ionic conductivities from the ion-exchange kinetic data are hardly possible due to the mixed alkali effect. Many new examples are reviewed illustrating various aspects of the method. Empirical principles of

shifting ion-exchange equilibria and rational principles of the ion-exchange testing are formulated. Special attention is paid to problems of the mass transport in one-dimensional channels.

**Acknowledgement** The author thanks D.N. Solodovnikova for her help with ion-exchange experiments mentioned in the last paragraph before “Conclusions” section (to be published elsewhere).

## References

- England WA, Goodenough JB, Wiseman PJ (1983) Ion-exchange reactions of mixed oxides. *J Solid State Chem* 49:289–299
- Belyaev IN, Nalbandyan VB, Lupeiko TG (1986) Salt melts in the chemistry and technology of mixed oxides: 1. Exchange reactions of salt melts with mixed oxides. In: Delimarskii YK (ed) *Ionnye Rasplavy i Tverdye Elektrolity*, issue 1. Naukova Dumka, Kiev, pp 1–13 (in Russian)
- Clearfield A (1988) Role of ion exchange in solid-state chemistry. *Chem Rev* 88:125–148
- Gopalakrishnan J (1995) Chimie douce approaches to the synthesis of metastable oxide materials. *Chem Mater* 7:1265–1275
- Yaroslavtsev AB (1997) Ion exchange on inorganic sorbents. *Russ Chem Rev* 66:579–596
- Sebastian L, Gopalakrishnan J (2003) Lithium ion mobility in metal oxides: a materials chemistry perspective. *J Mater Chem* 13:433–441
- Singer J, Fielder WL, Kautz HE, Fordyce JS (1976) New solid conductors of  $\text{Na}^+$  and  $\text{K}^+$  ions. *J Electrochem Soc* 123:614–617
- Goodenough JB, Hong HUP, Kafalas JA (1976) Fast  $\text{Na}^+$ -ion transport in skeleton structures. *Mater Res Bull* 11:203–220
- Farrington GC, Briant JL (1978) Hydronium beta" alumina: a fast proton conductor. *Mater Res Bull* 13:763–773
- Briant JL, Farrington GC (1981) Ionic conductivity in  $\text{Li}^+$ - $\text{Na}^+$  beta and beta" alumina. *Solid State Ionics* 5:207–210
- Seevers R, Denuzzio J, Farrington GC (1983) Ion transport in  $\text{Ca}^{2+}$ ,  $\text{Sr}^{2+}$ ,  $\text{Ba}^{2+}$ , and  $\text{Pb}^{2+}$  beta" aluminas. *J Solid State Chem* 50:146–152
- Nalbandyan VB, Trubnikov IL, Bukun NG, Medvedev BS (1986) Proton conductivity of ceramic niobic and tantalac acids with the pyrochlore structure. *Inorg Mater* 22:736–740
- Brunner DG, Tomandl G (1987) A new proton-conducting ceramics: part II, preparation of proton-conducting  $\text{NH}_4\text{NbWO}_6$  and  $\text{NH}_4\text{TaWO}_6$ . *Adv Ceram Mater* 2:794–797
- Nalbandyan VB, Medvedeva LI, Medvedev BS (2004) Two new types of intermediate temperature (200–500°C) proton conductors. In: *Future hydrogen energy and platinum group metals in new independent states*. Pt. 2, Moscow, pp 24–29 (in Russian)
- Doeff MM, Anapolsky A, Edman L, Richardson TJ, De Jonghe LC (2001) A high-rate manganese oxide for rechargeable lithium battery applications. *J Electrochem Soc* 148:A230–A236
- Whittingham MS (2004) Lithium batteries and cathode materials. *Chem Rev* 104:4271–4301
- Yang WS, Li XM, Yang L, Evans DG, Duan X (2006) Synthesis and electrochemical characterization of pillared layered  $\text{Li}_{1-2x}\text{Ca}_x\text{CoO}_2$ . *J Phys Chem Solids* 67:1343–1346
- Becht GA, Vaughey JT, Britt RL, Eagle CT, Hwu SJ (2008) Ion exchange and electrochemical evaluation of the microporous phosphate  $\text{Li}_9\text{Fe}_7(\text{PO}_4)_{10}$ . *Mater Res Bull* 43:3389–3396
- Ellis BL, Lee KT, Nazar LF (2010) Positive electrode materials for Li-ion and Li-batteries. *Chem Mater* 22:691–714



20. Ren Z, Wang Y, Liu S, Wang J, Xu Z, Cao G (2005) Synthesis of cobalt oxyhydrate superconductor through a disproportionation reaction route. *Chem Mater* 17:1501–1504
21. Avdeev M, Nalbandyan VB, Shukaev IL (2009) Alkali metal cation and proton conductors: relationships between composition, crystal structure, and properties. In: Kharton VV (ed) *Solid state electrochemistry I*. Wiley-VCH, Weinheim, pp 227–278
22. McDonald JR (1987) Impedance spectroscopy and its use in analyzing the steady-state ac response of solid and liquid electrolytes. *J Electroanal Chem* 223:25–50
23. Boukamp BA (2004) Electrochemical impedance spectroscopy in solid state ionics: recent advances. *Solid State Ionics* 169:65–73
24. Macdonald JR, Tuncer E (2007) Deconvolution of immittance data: some old and new methods. *J Electroanal Chem* 602:255–262
25. Tesler AB, Lewin DR, Baltianski S, Tsur Y (2010) Analyzing results of impedance spectroscopy using novel evolutionary programming techniques. *J Electroceram* 24:245–260
26. Nalbandyan VB, Medvedeva LI, Sudorgin NG, Medvedev BS (1993) Determination of the specific resistivity of ceramic cation conductors on sodium rare-earth silicates: comparison of methods and identification of error sources. *Russ J Electrochem* 29:1207–1214
27. Yoshikado S, Ohachi T, Taniguchi I, Onoda Y, Watanabe M, Fujiki Y (1983) Frequency-independent ionic conductivity of hollandite type compounds. *Solid State Ionics* 9(10):1305–1309
28. Yoshikado S, Ohachi T, Taniguchi I, Watanabe M, Fujiki Y, Onoda Y (1989) Ion conduction in one-dimensional ionic conductors  $A_{1-x}Ti_{2+x}B_{5-x}O_{12}$  (ATBO, A=Na or K and B=Al or Ga,  $x < 1$ ). *Solid State Ionics* 35:377–385
29. Riess I (1996) Review of the limitations of the Hebb–Wagner polarization method for measuring partial conductivities in mixed ionic electronic conductors. *Solid State Ionics* 91:221–232
30. Yaroslavtsev AB (1997) The investigation of ion diffusion in solids with the help of ion exchange. *Solid State Ionics* 97:281–284
31. Chebotin VN, Perfil'ev MV (1978) *Elektrokimiya Tverdykh Electrolytov* (Electrochemistry of solid electrolytes). Khimiya, Moscow, p 107, in Russian
32. Hughes K, Isard JO (1972) Ionic transport in glasses. In: Hladik J (ed) *Physics of electrolytes*, vol 1. Academic, London, p 387
33. Dyre JC, Maass P, Roling B, Sidebottom DL (2009) Fundamental questions relating to ion conduction in disordered solids. *Rep Prog Phys* 72:046501
34. Yao YFY, Kummer JT (1967) Ion exchange properties of and rates of ionic diffusion in beta-alumina. *J Inorg Nucl Chem* 29:2453–2475
35. Nalbandyan VB, Belyaev IN, Mezghorina NV (1979) Ion-exchange reactions of sodium ferrititanates and related compounds with salt melts. *Zh Neorg Khim* 24:3207–3212 (in Russian)
36. Nalbandyan VB (1999) A family of nonstoichiometric titanates with one-dimensional triple channels. *Russ J Inorg Chem* 44:511–519
37. Kummer JT (1972) Beta-alumina electrolytes. *Prog Solid State Chem* 7:141–175
38. Foster LM, Campbell DR, Chandrashekar GV (1978) Self-diffusion and Na-K exchange in  $\beta$ - and  $\beta'$ -gallate fast ion conductors. *J Electrochem Soc* 125:1689–1695
39. Hervieu M, Michel C, Raveau B (1971) Propriétés d'échange d'ions de quelques oxydes ternaires de type pyrochlore: les pyrochlores  $H_{1+x}(H_2O)Ta_{1+x}W_{1-x}O_6$  et  $NH_4TaWO_6$ . *Bull Soc Chim France* 3939–3943
40. Michel C, Guyomar'h A, Raveau B (1977) Nouveaux échangeurs cationiques avec une structure a tunnels entrecroisées: les oxydes  $A_{12}M_{33}O_{90}$  et  $A_{12}M_{33}O_{90} \cdot 12H_2O$ . *J Solid State Chem* 22:393–403
41. Masquelier C, d'Yvoire F, Bretey E, Berthet P, Peytour-Chansac C (1994) A new family of sodium ion conductors: the diphosphates and diarsenates  $Na_7M_3(X_2O_7)_4$ ; (M=Al, Ga, Cr, Fe; X=P, As). *Solid State Ionics* 67:183–189
42. Quarez E, Mentre O, Oumellal Y, Masquelier C (2009) Crystal structures of new silver ion conductors  $Ag_7Fe_3(X_2O_7)_4$  (X=P, As). *New J Chem* 33:998–1005
43. Nalbandyan VB, Belyaev IN, Lupeiko TG, Mezghorina NV (1979) Ion-exchange reactions of hollandite-type compounds. *Zh Neorg Khim* 24:1546–1552 (in Russian)
44. Nalbandyan VB, Belyaev IN (1984) Ionic conductivity of phases of the hollandite type with different single-charge cations. *Zh Neorg Khim* 29:817–819 (in Russian)
45. Nalbandyan VB, Dugin VE, Belyaev IN (1983) Growth of crystals and cationic conductivity of non-stoichiometric sodium magnesium titanium oxyfluoride. *Inorg Mater* 19:283–286
46. Shilov GV, Atovmyan LO, Volochaev VA, Nalbandyan VB (1999) Crystal structure and ionic conductivity of a new sodium magnesium titanium oxide. *Crystallogr Rep* 44:960–964
47. Nalbandyan VB (1991) Ionic conductivity of sodium titanates, magnetitanates, and zincotitanates. *Inorg Mater* 27:838–842
48. Nalbandyan VB (2000) Interaction of titanium dioxide with sodium fluoride and sodium carbonate. *Russ J Inorg Chem* 45:510–514
49. Nalbandyan VB (2000) Six NaCl-type trigonal superstructures based on sodium titanates. *Russ J Inorg Chem* 45:1652–1658
50. Nalbandyan VB (1999) On the structure type of  $Na_{10}MgTi_{10}O_{26}$ . *Crystallogr Rep* 44:965–971
51. Nalbandyan VB, Politaev VV (2009) Subsolidus phase relations, crystal chemistry and cation-transport properties of sodium iron antimony oxides. *Solid State Sci* 11:144–150
52. Nalbandyan VB, Medvedeva LI, Ivleva TI (1995) Synthesis of sodium-yttrium and silver-yttrium silicates. *Russ J Inorg Chem* 40:719–723
53. Nalbandyan VB, Avdeev M, Pospelov AA (2006) Ion exchange reactions of  $NaSbO_3$  and morphotropic series  $MSbO_3$ . *Solid State Sci* 8:1430–1437
54. Politaev VV, Nalbandyan VB, Petrenko AA, Shukaev IL, Volochaev VA, Medvedev BS (2010) Mixed oxides of sodium, antimony (5+) and divalent metals (Ni, Co, Zn or Mg). *J Solid State Chem* 183:684–691
55. Edwards DD, Empie NH, Meethong N, Amoroso JW (2006) Synthesis and transport studies of one-dimensional ion conductors:  $A_xGa_{4+x}Ti_{1-x}O_8$  (A=Li, Na, K). *Solid State Ionics* 177:1897–1900
56. Li J, Yokochi AFT, Sleight AW (2004) Oxygen intercalation of two polymorphs of  $CuScO_2$ . *Solid State Sci* 6:831–839
57. Vainshtein BK, Chernov AA, Shuvalov LA (eds) (1981) *Sovremennaya Kristallografiya* (Modern crystallography), vol 4, chapter 6. Nauka, Moscow (in Russian)
58. Breck DW (1974) *Zeolite molecular sieves*. Wiley, New York
59. Obbade S, Dion C, Rivenet M, Saadi M, Abraham F (2004) A novel open-framework with non-crossing channels in the uranyl vanadates  $A(UO_2)_4(VO_4)_3$  (A=Li, Na). *J Solid State Chem* 177:2058–2067
60. Rödenbeck C, Kärger J, Hahn K (1995) Tracer exchange and catalytic reactions in single-file systems. *J Catal* 157:656–664
61. MacKinnon R (2004) Potassium channels and the atomic basis of selective ion conduction (Nobel lecture). *Angew Chem Int Ed* 43:4265–4277
62. Eab CH, Lim SC (2010) Fractional generalized Langevin equation approach to single-file diffusion. *Physica A* 389:2510–2521
63. Chandrashekar GV, Bednowitz A, La Placa SJ (1979) A one dimensional sodium ion conductor. In: Vashista P, Mundy JN, Shenoy GK (eds) *Fast ion transport in solids*. Elsevier, Amsterdam
64. Bierlein JD, Vanherzeele H (1989) Potassium titanyl phosphate: properties and new applications. *J Opt Soc Am B* 6:622–633

65. Dahaoui S, Hansen NK, Protas J, Krane H-G, Fischer K, Mamier G (1999) Electric properties of  $\text{KTiOPO}_4$  and  $\text{NaTiOPO}_4$  from temperature-dependent X-ray diffraction. *J Appl Crystallogr* 32:1–10
66. Wellendorf R, Kaps C, Kriegel R (1996) On the  $\text{Rb}^+$  and  $\text{K}^+$  counterdiffusion in single crystals of  $\text{K}(\text{TiO})\text{PO}_4$ —a quasi-one-dimensional superionic conductor. *Ionics* 2:222–230
67. Bierlein JD, Brixner LH, Ferretti A, Hsu, WY (1988) Process for producing an optical waveguide and the product therefrom. US Patent 4,740,265.
68. Nalbandyan VB, Medvedev BS, Rykalova SI, Isakova SY (1988) Preparation and properties of the ceramic electrolytes of the sodium ferritanate type. *Neorg Mater* 24:1030–1034 (In Russian)