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SEARCH FOR SOLID CONDUCTORS OF Na⁺ AND K⁺ IONS: FIVE NEW CONDUCTORS

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TECHNICAL PAPER presented at
American Ceramic Society
Washington, D.C., May 3-7, 1975
ABSTRACT

Five conductors of three structure types have been discovered which, as solids, can transport Na\(^+\) or K\(^+\) ions with conductivities of \(\approx 10^{-5} \, (\Omega \text{ cm})^{-1}\) at 300 K. These compounds are: (1) the pyrochlores NaTaWO\(_6\) and NaTa\(_2\)O\(_5\)F, both with an activation energy for conduction \(\Delta E\) of 21 kJ/mole; (2) the body-centered cubic form of NaSbO\(_3\), with \(\Delta E = 42\) kJ/mole; (3) the niobates 2Na\(_2\)O · 3Nb\(_2\)O\(_5\) and 2K\(_2\)O · 3Nb\(_2\)O\(_5\), with the alkali ions probably in open layers of the incompletely determined structure; \(\Delta E = 17\) kJ/mole. On the basis of approximately 40 structure types, some generalizations have been made regarding the relation between structure and ionic transport.
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SUMMARY

Five conductors of three structure types have been discovered which, as solids, can transport Na⁺ or K⁺ ions with conductivities of $\sim 10^{-5} (\Omega \text{ cm})^{-1}$ at 300 K. These compounds are: (1) the pyrochlores NaTaWO₆ and NaTa₂O₅F, both with an activation energy for conduction, $\Delta E$, of 21 kJ/mole; (2) the body-centered cubic form of NaSbO₃, with $\Delta E = 42$ kJ/mole; and (3) the niobates $2\text{Na}_2\text{O} \cdot 3\text{Nb}_2\text{O}_5$ and $2\text{K}_2\text{O} \cdot 3\text{Nb}_2\text{O}_5$, with the alkali ions probably in open layers of the incompletely determined structure, $\Delta E = 17$ kJ/mole. On the basis of approximately 40 structure types, some generalizations have been made regarding the relation between structure and ionic transport.

INTRODUCTION

The basis of the Ford high energy density secondary battery is the high Na⁺ ion conductivity of the crystalline ceramic separator, Na beta alumina, in the role of solid electrolyte (ref. 1). The discovery of this substance has stimulated search for other solid conductors of alkali metal ions. The LeRC program was initiated with in-house work and expanded to include some contractual work with LeRC performing the principal evaluations. About 40 structure types were evaluated; 5 new conductors (within 3 of the structure types) have been found. Relations between structure and ionic mobility are discussed. The present report encompasses the work of previous reports (refs. 2, 5) and additional work not reported elsewhere.
Program Approach

The search for solid ionic conductors comprised a sequence of four stages. These were: (A) literature search for compounds meeting certain criteria; (B) preparation of preliminary specimens suitable for screening; (C) a screening procedure designed to evaluate potentiality of ionic conduction in relatively crude preparations; (D) final specimen preparation and evaluation. These stages are the subject of the following brief discussion.

Stage (A) Literature search. - To summarize the crystal-chemical criteria described previously (ref. 2), structures are sought which exhibit loosely held cations within a rigid structural skeleton, the latter usually being oxygen polyhedra about a small metallic ion. In addition to loose cation bonding, it was desired to have: (a) chemical stability to possible electrochemical application; (b) stability to the pressures and temperatures needed for fabricating non-porous ceramic; (c) partial occupancy of the cation sites or the possibility of creating vacancies by aliovalent substitution; (d) no electronic contribution to the conduction. The greatest number of structures meeting the criteria were tunnel types, i.e., with the cation relatively loosely bonded within tunnels. It seemed advisable to sample a broad range of open structures. Several types of tunnel structures were included, such as non-intersecting as well as intersecting tunnel types. Examples of the former are the bronzes and bronze-related types, and the hollandites; examples of intersecting tunnel types are certain silicates, the pyrochlores, and a unique body-centered cubic (BCC) form of NaSbO$_3$. Only one layer type, i.e., with the cation in open layers, was found to meet the selection criteria; it was one of the successful candidates.

Stage (B) Preparation of preliminary specimens. - Some details of fabrication of test specimens are given in the EXPERIMENTAL Section; however, the preparative procedures for each material have necessarily been left to the references given in the Tables (RESULTS).
Stage (C) Screening procedure. - The perfection of a ceramic specimen strongly affects the measurement of its ionic conductivity and so determines the techniques used. Because of its importance to this program, this matter is reviewed here.

With a perfect crystal, the principal polarization of ions which occurs upon application of a field is at the electrodes. Also, with typically available single crystals of a good ionic conductor, internal polarization at defects should not seriously interfere with the measurement of conductivity by ordinary methods (ref. 3). However, of principal importance to the present purpose is the specimen of poor texture* which is usually available for screening; it is likely to be fairly low density (<90 percent), of undetermined grain structure, and of only moderate purity. The work of Radzilowski, et al. (ref. 4) bears on this matter. They demonstrated how the Na+ ion conductivity in powdered beta alumina may be manifested as dielectric loss ($\varepsilon''$). Whereas they were employing beta alumina to test loss theory for anisotropic materials, the value of their work to the present program lay in the general application of dielectric loss to observe polarization in powders. The relaxation time of this polarization, although too small for the aforementioned "ordinary" methods of conductivity measurement, is obtainable from dielectric loss. Previous publications (ref. 5) have discussed this adaptation of loss methods to the screening of ionic conductor candidates in the form of preliminary specimens of variable perfection. During the course of the program, various validations (see below) were performed on this screening procedure, including comparison with independent methods developed under contract (refs. 6 and 7), such as NMR line-narrowing as caused by ion motion in powders. Also, the low temperature direct AC data obtained in dielectric loss measurements were useful with the better conducting materials; the low temperatures brought the longer relaxation times of these specimens into the detection range of the frequencies employed, $10^2$ - $10^6$ Hz, thus readily allowing AC conductivities to be measured which would have required very high frequencies at room temperature.

*containing myriad inter- and intra-crystalline imperfections.
Stage (D) Final specimen preparation and evaluation. - In the cases where screening tests made it advisable to prepare better specimens for advanced evaluation, their fabrication had to be individually tailored to the substance. The advanced evaluations were largely concerned with obtaining direct conductivity data with AC and DC methods and with several types of electrodes.

Incidental to this main program, some work was done on several special forms of Na beta alumina: (1) Single crystal tubing was attempted under contract and has been separately reported (ref. 8); (2) Large single crystal ingots were informally supplied by L. Rothrock of Union Carbide for evaluation, reported elsewhere (ref. 9); (3) Hot pressed ceramic specimens were informally submitted for measurement by W. McDonough of the Naval Research Laboratory; these data are to be reported by him; (4) Production grade "beta-double-prime" ($\beta''$) tubes were purchased from the British Railways Laboratory; it is referred to in this report as "production beta".

The present work has made use of the ingot single crystal and the production beta as reference materials.

EXPERIMENTAL

Specimen Preparation

As indicated earlier, only general remarks on synthesis can be made here; the references in the Tables (RESULTS) should be consulted for specific details.

Wherever possible, test specimens were fabricated by reaction sintering directly as discs 15 mm diameter and 2-3 mm thick. Component oxides were generally reacted in at least two steps: (1) decomposition from suitable compounds mixed in the required ratios, frequently with excess alkali metal component to compensate for volatilization; (2) grinding, sieving, compacting, and reaction sintering the mixed oxides, usually in more than one cycle to produce a single phase material as determined by X-ray diffraction. In some cases, packing the
compacted powder in loose powder was desirable to minimize volatilization at the sinter temperature.

High density and low porosity were required for specimens undergoing advanced evaluation, especially where liquid electrodes were to be used. Densities were determined directly upon the specimen disc and referred to the theoretical X-ray density wherever that could be ascertained. Porosity was considered adequately low if a 0.1 mm vacuum could be maintained on one side of the disc for 1 minute with air pressure of 10 N/cm$^2$ on the other side. In some cases the unstable Na analogue of a structure type was desired and it could be produced only by ion exchanging the stable K or Rb compounds. This was accomplished by stirring the stable analogue as a powder in molten NaNO$_3$, usually more than once and maintaining a large excess of Na$^+$ over the total quantity of the alkali ion to be replaced. Ion exchange had to be used to make the sodium pyrochlores NaTaWO$_6$ (refs. 10 and 11), NaTa$_2$O$_5$F, and the BCC NaSbO$_3$ phase (ref. 12). Work is continuing to determine if the latter can be made without resorting to ion exchange if NaF is included with the starting oxides (refs. 13 and 14). Ion exchange was also used to make some of the silicates (see Tables) and the sodium analogue from the stable 2K$_2$O·3Nb$_2$O$_5$ compound.

Czochralski-type growth was attempted by L. Rothrock, Union Carbide Co., with a hollandite of composition K$_{1.7}$Mg$_{0.85}$Ti$_{7.15}$O$_{16}$. The best coarse-grained sections were excised and used as the "nearly single crystal" hollandite of this work.

Several kinds of Na beta alumina were employed as reference material: (a) discs were synthesized by reaction sintering and also by hot pressing pure beta, providing specimens which could be taken as crude samples of a very good conductor; (b) discs were cut from the best ingot crystals supplied to us, to act as nearly perfect specimens of a very good conductor; and (c) sections were cut from the production beta tubes.

About 20 phases in the 6 binary systems of Li, Na, and K oxides with Nb$_2$O$_5$ and Ta$_2$O$_5$ were prepared as discs under contract (ref. 15), as an outgrowth of on-going work on those systems at the National
Bureau of Standards. These binary oxides promised opportunities for "open structures" to occur, with the Nb-O and Ta-O coordination polyhedra providing the skeletal rigidity. The promise was indeed realized, principally as tunnel structures with one notable layer type exception.

Electrical Measurements

1. The principal screening tool was the dielectric loss and associated AC conductivity technique discussed above and described in detail in earlier reports. The Cole-Cole analysis (ref. 2) of loss yields a calculated AC conductivity, referred to below as \( \sigma_{cc} \), at each of several temperatures, allowing also the calculation of an activation energy \( \Delta E \) for the relaxation process involved in the polarization. Further, the AC conductivity directly observed at the low temperatures permitted estimation of the conductivity to be expected with improved specimens. Thus, a range of specimen quality was accounted for: if loss peaks were poorly resolved and also the estimated AC conductivity were low, the candidate was considered a poor conductor; the Tables of RESULTS show the quantitative criteria employed.

2. A technique for direct measurement of the ionic conductivity in polycrystalline or single crystal specimens was developed in contract work on a materials survey (ref. 7). It may be described as a very fast DC pulse 2-probe method which is hardly affected by polarization. For comparison, both it and the loss method were applied to the same hollandite coarse-grained material.

3. Improved samples of screened-in candidates were measured by 2-probe and 4-probe AC and DC methods, using blocking or reversible electrodes as appropriate; currents of 10-100 \( \mu \)amps/cm\(^2\) were commonly employed. With blocking electrodes, of sputtered-on Pt or painted-on C, AC conductivities over a range of frequencies were obtained, and DC conductivities were observed for times from \( \mu \)seconds after application of field; the long time DC conductivity was taken as
electronic. The effect of interfacial resistance in the 2-probe AC measurement was relatively small for frequencies \(>10^4\) Hz; it was similarly small in the DC measurement for times less than 10–50 \(\mu\)sec.

Reversible electrodes were of four types: (1) molten alkali metal, (2) alkali metal amalgam, (3) alkali hexafluorophosphate in 0.1-0.5 M solution in propylene carbonate, referred to later as "PC solution", and (4) \(\text{Na}_x\text{WO}_3\) in the composition range for single phase tetragonal tungsten bronze. This phase was suitable for limited measurements as an AC reversible solid electrode (ref. 16); for this purpose, a special method was developed to synthesize these electrodes on the surface of the specimen (ref. 17).

Porosity low enough to prevent electrical shorting is required for the use of liquid electrodes. Where adequate density could not be achieved, liquid electrodes could be used with polymer-filled specimens employing a commercial epoxy drawn into the sample under suction and, after setting of the polymer, sanding the surfaces.

RESULTS

Tables I to III list the substances which were synthesized and measured, the parameters obtained, and references for structure and/or synthesis. About 40 structure types were screened. A number of these were represented by specimens of a range of composition to provide for maximal mobility, but not all such sub-variants have been listed. The Tables indicate several Na compounds as having been made by ion-exchange; it may be expected that the directly measured conductivities of these compounds are probably too low, because of their non-sinterability.

Table I. - Most of the substances which passed the first screening appear in Tables I and II. Table I contains the three structure types which may be considered capable of "fast ion transport". These are: (a) the Na antimonate in its BCC polymorph, stabilized with NaF at the composition \(\text{NaSbO}_3 \cdot 1/6\) NaF; (b) the Na pyrochlores \(\text{NaTaWO}_6\)
and NaTa$_2$O$_5$F; (c) the niobates of Na and K of composition $2M_2O \cdot 3Nb_2O_5$, of undetermined structure but presumed to have the $M^+$ (alkali) ions in layers, according to R. S. Roth of the National Bureau of Standards. The K niobate was the only one which could be sintered to a non-porous ceramic. The Na pyrochlores and the Na niobate were exchange products and formed porous discs; some were plugged with polymer for measurement with the PC electrodes. The BCC Na-antimonate with NaF has given conflicting results regarding stability to sintering, and is still being investigated. The highest compaction, ~95 percent of theoretical density, could be reproducibly achieved only with the Na-exchanged KF-stabilized K$_3$SbO$_3$ analogue, under the conditions 3500 N/cm$^2$ and 670 K.

Figures 1 to 4 contain the conductivity data for the best conductors found in this work. The criterion for true ionic transport, as applied here, was the observation of negligible polarization with time, within the limitations of the electrode reversibility, in 10-100 µamp/cm$^2$ DC measurements. The criterion is regarded to have been met in the measurements shown in Figures 1 and 3; validation for the curves obtained with PC electrodes is provided by comparisons with the experiments which employed the more completely reversible electrodes, represented by the antimonate data of curve 1 of Figure 1 and the beta alumina data of curves 1 and 2 of Figure 3. Curve 1 of Figure 3 is actually an overlap of 3 sets of data made with different 4-probe reversible electrodes: (a) of tetragonal-I sodium tungsten bronze (ref. 17); (b) of strips of paper wet with PC solution; and (c) of solid Na.

Figures 2 and 4 are plots of conductivity × temperature, $\sigma T$, against $1/T$, the slopes yielding $\Delta E$ values. The measured conductivity of NaSb$_3$O$_3$ (which is the same with or without NaF) extrapolates to an intersection with the production beta alumina ceramic at about 520 K. Cole-Cole analysis of dielectric loss of the antimonate (data not reported in detail) gave the same $\Delta E$, but a calculated conductivity, $\sigma_{CC}$, about two orders larger than that directly measured. The NaTaWO$_6$ data, curve 3 of figure 2, exhibit an internal consistency between two independent
reversible electrode measurements and the slope obtained from Cole-Cole analysis of $\varepsilon''$. Figure 4 compares the two new planar conductors with $\beta$-alumina. Comparison of the K niobate conductivity with K-beta alumina would require ceramic of both; however, only single crystal K-beta alumina data are available (ref. 1) from which the extrapolation of curve 2, Figure 4, was made. $\Delta E$ for the two niobates is $\sim 17$ kJ/mole; for K-beta alumina it is $\sim 29$ kJ/mole. It appears likely that this K niobate has a larger conductivity than a ceramic K-beta might have vic. 300-370 K.

The directly measured (reversible electrodes) conductivities of the two niobates, the two pyrochlores, and the antimonate are all about the same, $5 \times 10^{-5}$ to $1 \times 10^{-5} (\Omega \text{ cm})^{-1}$, vic. 300 K.

**Table II.** - This table contains those substances which showed ionic transport with limitations which disqualify them as potential battery separators. Several tunnel types are tabulated, showing either mixed conduction or conductivities of too low a magnitude. Mixed conductors were considered to be of low interest, and only dielectric loss data are given for them. However, some effort was directed to the separation of the two contributions to conduction in the case of $\text{Li}_x\text{V}_2\text{O}_5$ ($\beta$, monoclinic phase). The method developed (ref. 6) may be useful in similar problems; here it was adequate for determining the value of $x$, about 0.6, for which the electronic part was lowest.

Conductivity in the hollandite structure has long been speculated upon; some indirect measurements, namely by dielectric loss, had been made which suggested the possibility of fast ion transport (refs. 18 and 2). Recently, direct measurements have been reported (ref. 19): The latter, curves 3, Figure 5, are compared with dielectric loss results obtained in this program (curves 1 and 2). Further, direct measurements have been made on the same large-grained material, effectively single crystal, by two independent methods: PC electrodes (fig. 6), and very fast-pulsed DC (not shown; data from W. L. Roth, GE Research Lab.). As shown in Figure 5, the directly measured AC conductivity (curve 2) appears to extrapolate to fair agreement
with the higher temperature data of Takahashi (curve 3); the conduc-
tivity calculated from dielectric loss (curve 1) is shown for compari-
son. The data obtained even with nearly single crystal material
(Fig. 6) show the rapid onset of internal polarization after the first
µsec conductivity value of $\sim 10^{-3}$ (Ω cm)$^{-1}$. All these data are con-
sidered self-consistent, and show that only a low level of transport
at 300 K is likely, $\sim 10^{-7}$ (Ω cm)$^{-1}$, after the rapid polarization.

β-Eucryptite and β-spodumene were selected as representatives
of the numerous open structure types known as "stuffed derivative
quartz" structures (ref. 20). The β-eucryptite offered, in addition,
an opportunity to observe how Li mobility might be affected by the
disordering reported to occur either at 670 K (ref. 21) or 710 K
(ref. 22). The β-eucryptite made in this program had the composi-
tion LiAlSi$_2$O$_6$; this was a lower Li content than in the eucryptite re-
ported in other work, LiAlSiO$_4$ (ref. 23), with which it has been com-
pared in figure 7. This conductivity-reciprocal temperature plot shows
a change in slope, or in $\Delta E$, for the LeRC composition at no higher a
temperature than 670 K, from $\Delta E = 66$ kJ/mole to 96 kJ/mole. The
higher Li-containing eucryptite data is shown as a broken line calcu-
lated from the $\Delta E$ and the single datum point available. The $\Delta E$
values appear to be the same for the two independent experiments up to
the transition.

A direct conductivity measurement (not shown) made at LeRC on a
disc of Na-exchanged β-spodumene yielded a value of $5 \times 10^{-7}$ (Ω cm)$^{-1}$
at 300 K; this was a 0.1 msec reading, after which rapid polarization
was observed. Neither these, nor any other silicates measured so far,
are considered capable of appreciable ion transport.

Table III. - Listed here are substances eliminated by the dielectric
loss screening criteria, i.e., no loss peaking and/or little or no low
temperature AC conductivity. About one-third of the entries in this
table came from the six phase diagram studies of the alkali metal tan-
talates and niobates; almost all of these are one-dimensional tunnel
structures related to the bronze structures (ref. 15). The other entries
represent a variety of open structures. Many of the compounds in Table III show some indication of ion mobility, either by ε", or by NMR in the form of line narrowing (ref. 6).

DISCUSSION

The results of this survey are indicative of the rarity of alkali ion conductivity in solids of the magnitude of that in Na beta alumina. The even higher conductivity by Cu⁺ and Ag⁺ ions in many solids is a special case (ref. 24) which appears to have little bearing on alkali ion transport. However, the conductivities found for the three structure types in the present work (Table I), \( \sim 10^{-5} \, (\Omega \text{ cm})^{-1} \) at \(-300 \, K\), with activation energies of 16 to 42 kJ/mole, are higher by orders of magnitude than found previously for alkali metal ions except for beta aluminas.

It was beyond the scope of the program to intensively develop any of the more successful candidates to its ultimate conductivity, and some improvement may lie in this direction. If a choice were to be made for this purpose, it would be limited to those with the prospect of sinterability to suitably low porosity, i.e., only NaSbO₃ · 1/6 NaF and 2K₂O · 3Nb₂O₅. However, if these were to be considered for use with alkali metal positive electrodes, the first question would concern reactivity at the interface. The quality of the ceramic may affect this matter, so that the indications of reactivity found with even the best preparations made here may not apply to a more perfect specimen. In any case, there may be applications employing positive electrodes other than alkali metals.

The entries in Table I come closest to the program's goal of new solid electrolytes. This survey may, further, assist in future work on the subject of the relation between structure and ion mobility.

These results should aid clarification of use of the term "fast ion conductor"; in the present context, at least, this term might well be reserved for substances performing no worse than those in Table I.
Further, even the term "ion conductor" could be misleading if unqualified; e.g., the hexagonal tungsten bronzes and other tunnel types show a measurable AC conductivity due to ion carriers even where $\sigma_e$ is very small, but this ionic conductivity has a short relaxation time and so is not applicable to appreciable ion transport. With numerous "open" structures incapable of appreciable ion transport, what can be said about the structural requirements for transport? The following, based on the present results, is addressed to this question.

The alkali ion paths in two of the good conductors of Table I, the antimonate and the pyrochlores, are channels which intersect within the unit cell, a structural feature which is absent in the tunnel structures. The latter may be typified by hollandite; Figure 6 illustrates the rapid polarization even in nearly single crystal material of this substance, although conductivity was about two orders higher than in the ceramic preparations. The frequency dependences and $\Delta E$'s were about the same, suggesting that impedance to transport in hollandite is both inter- and intra-granular. These observations should classify hollandite as a very poor conductor; in general, the same may be said for other non-intersecting tunnel structures.

Reference should be made to the X-ray structure publications on the pyrochlore (refs. 10 and 11) and BCC antimonate (refs. 12, 13, and 14) structures for detailed study of factors which may contribute to the high ion mobility in them. A few points may be brought out here, however. The key to mobility in the pyrochlore is the site "8b", which is at the center of a cage-like opening formed by the intersection of the six [110] tunnels, geometrically able to contain an atom of radius 1.80 Å. K$^+$ and the larger alkali ions are firmly held in 8b, but Na$^+$ is free to move through this site if nothing else is there. In pycholes $AB_1B_2X_6$, where $B_1$, $B_2$ represent the small transition ions inside the skeletal polyhedra, $BX_6$, ($X$ can be $O^-$, $F^-$, $OH^-$), the 8b sites may be empty; but in pyroclines $AB_1B_2X_7$ or $AB_1B_2X_6Y$, where $Y$ is an anion like $X$ (as in the mineral) 8b is occupied by $Y$ or by the seventh $X$. Another
occupant of 8b may be a "lone pair" of electrons (ref. 29), such as provided by Sb$^{+5}$ in the pyrochlore phase of sodium antimonate; it is to be noted that the latter appears in Table III among the non-conductors.

The structural aspects of mobility in the BCC antimonate are somewhat similar. A cage is also formed at the intersection of three tunnels. It is large enough to contain the F$^-$ of the added KF or NaF (typical composition, K$_3$SbO$_3$·1/6 KF) used for stabilization (refs. 13 and 34). In both the pure and the NaF-added antimonate, Na$^+$ ion is freer than K$^+$ ion; further, it is able to move through alternate channel paths despite the presence of F$^-$ ion. The added alkali does fill some of the crystallographic sites that are 30 percent unoccupied in the pure compound, yet the conductivity is hardly affected.

Although the structure of the 2:3 alkali niobate has not been determined, the single crystal X-ray diffraction data point to a layer structure, according to R. S. Roth of the National Bureau of Standards. It should be of considerable interest, when the analysis shall have been done, to compare the alkali ion environment in this niobate with that in beta-alumina.

Condensation

A. About 40 structure types were selected, and representatives synthesized and evaluated as solid conductors of Li$^+$, Na$^+$, or K$^+$ ions for use as solid electrolytes.

B. Three structure types were discovered to be capable of ionic transport, all with $\sigma_{\text{ion}}$ near 10$^{-5}$ (\text{S cm})$^{-1}$ at 300 K, with no appreciable electronic conductivity:

1. Body centered cubic Na$_3$SbO$_3$, with or without 1/6 mole NaF/mole used for stabilization; $\Delta E = 42$ kJ/mole; above 530 K its conductivity exceeds that of $\beta$-alumina.

2. Pyrochlores Na$_3$B$_4$B$_2$X$_6$, exemplified by NaTaWO$_6$ and NaTa$_2$O$_5$F; $\Delta E = 21$ kJ/mole for both compounds.
3. The niobates $2M_2O \cdot 3Nb_2O_5 (M = Na \text{ or } K)$, a layer type of as yet undetermined structure; $\Delta E = 17 \text{ kJ/mole}$; the K compound has at least the same conductivity at 300 K as a K-beta alumina ceramic may be estimated to have, and might be improved with ceramic development due to its sinterability.

C. The above new Na$^+$ conductors must at present be made by ion exchange from their K analogues, although the NaSbO$_3$ shows some indications of stabilization with addition of NaF. The K niobate presently is the only one of these new conductors which can be made directly and is stable to sintering.

D. Fast alkali ion transport is apparently likely only in structures with the ions in layers or in intersecting tunnels. Distinction has been made between high frequency AC ionic conductivity not applicable to transport, as exhibited by many open structures, and true transport of alkali metal ions, which occurs in very few structures. The likelihood of finding such alkali ion transporting structures appears to be small and to diminish in the sequence Na$^+$, K$^+$, Li$^+$. The beta aluminas continue to reign supreme.

E. New techniques have been developed for evaluating potential ionic conductors.

REFERENCES


21. H. Schulz and V. Tscherry; "Structural Relations Between the Low- and High-Temperature Forms of β-Eucryptite (LiAlSiO₄) and Low and High Quartz. II. High-Temperature Form of β-Eucryptite and High Quartz," Acta Cryst., B28, pp. 2174-2177 (1972).


34. R. S. Roth, H. S. Parker, and W. S. Brower; "Crystal Chemistry of Lithium in Octohedrally Coordinated Structures III. A New Structure-Type in the System K\textsubscript{2}O:Li\textsubscript{2}O:TiO\textsubscript{2} (K\textsubscript{x}Li\textsubscript{4-x/2}Ti\textsubscript{4-x/2}O\textsubscript{8})," Mat. Res. Bull., 8, pp. 327-332 (1973).


<table>
<thead>
<tr>
<th>Formula</th>
<th>Structure; references</th>
<th>$\Delta E$, kJ/mole</th>
<th>$\sigma_{300 K}$, $(\Omega \text{ cm})^{-1}$</th>
<th>Comments</th>
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</thead>
<tbody>
<tr>
<td>NaSbO$_3$, pure or NaSbO$_3 \cdot 1/6$ NaF</td>
<td>BCC form, NaF for possible stabilization. Intersection tunnels (11, 12).</td>
<td>42 from $\varepsilon''$ and transport</td>
<td>$10^{-5}$; PC electrodes</td>
<td>May react with Na. Sinterability depends on success of Na stabilization, not yet established. Can be compacted to 95 percent density.</td>
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<tr>
<td>NaTaWO$_6$ and NaTa$_2$O$_5$F</td>
<td>Pyrochlore type, intersection tunnels (10, 11)</td>
<td>21 from $\varepsilon''$</td>
<td>$10^{-5}$; PC electrodes</td>
<td>Both unstable to sintering. Compacts to 93 percent density. Made only by ion-exchange. Oxyfluoride more stable to Na.</td>
</tr>
<tr>
<td>$2 \text{Na}_2\text{O} \cdot 3 \text{Nb}_2\text{O}_5$ and $2 \text{K}_2\text{O} \cdot 3 \text{Nb}_2\text{O}_5$</td>
<td>Structure incomplete. Alk. ion in layers, possibly as in beta alumina.</td>
<td>17 from $\varepsilon''$ and transport</td>
<td>$10^{-5}$; PC electrodes</td>
<td>Na cpd by ion exchange and not sinterable. K cpd stable and sinterable.</td>
</tr>
<tr>
<td>Formula</td>
<td>Structure; references (occ. = occupancy of site)</td>
<td>( \Delta E ), kJ/mole</td>
<td>( \sigma ) 300 K, ((\Omega \text{cm})^{-1})</td>
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<td>( K_2W_4O_{13} )</td>
<td>WO₃-type tunnels, K in 5/6 occ. (25)</td>
<td>16 from ( c'' )</td>
<td>( 10^{-4} ), from ( c'' )</td>
<td>Large ( \sigma_e )</td>
</tr>
<tr>
<td>( \beta-Li_0.6V_2O_5 )</td>
<td>Li in part occ., in tunnels (26, 6)</td>
<td>9 to 25, 4-probe</td>
<td>( 10^{-3} ), from transport</td>
<td>Large ( \sigma_e )</td>
</tr>
<tr>
<td>( K_xMg_{x/2}Tl_{(8-x/2)}O_{16} ) for ( x ) from 1.6 to 2.0</td>
<td>Hollandite type, K in 80 to 100 percent occ. in tunnels (17, 18)</td>
<td>21 to 25, from ( c'' )</td>
<td>( 10^{-3} ) to ( 10^{-5} ), from ( c'' )</td>
<td>( 10^{-3} ) ((\Omega \text{cm})^{-1}) at 1 ( \mu \text{sec} ); polarized rapidly in both crystal and ceramic.</td>
</tr>
<tr>
<td>NaAlSi₂O₆</td>
<td>( \beta )-Spodumene (27) Ion-exchanged. Na in silica-type channels.</td>
<td>Not det'd.</td>
<td>( 10^{-5} ) at 1 ( \mu \text{sec} )</td>
<td>Polartted rapidly. Li cpd conductivity too low to measure.</td>
</tr>
<tr>
<td>LiAlSi₂O₃</td>
<td>( \beta )-Eucryptite of low Li content. Li in silica-type channels. (20 to 22)</td>
<td>67, ( \sim )670 K</td>
<td>( 10^{-6} ) at 670 K by 2-probe AC</td>
<td>Ref. (23) reports higher ( \sigma ) for higher Li content (LiAlSiO₄).</td>
</tr>
<tr>
<td>( K_{0.3}Ta_{0.3}W_{0.7}O_{3} )</td>
<td>Hex. tungsten bronze (33). K in part occ. in tunnels</td>
<td>16 to 26, from ( c'' )</td>
<td>( 10^{-4} ) to ( 10^{-6} ), from ( c'' )</td>
<td>More mobility than tetr. and cubic bronzes. Much variability between samples. Some ( \sigma_e ) developed.</td>
</tr>
</tbody>
</table>
TABLE III. - SUBSTANCES WITH $\rho_{E} \times 10^{-6}$ [ohm cm] BY DIELECTRIC LOSS MEASUREMENTS

<table>
<thead>
<tr>
<th>Formula</th>
<th>Structure reference</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>$6 Li_2O \cdot 17 TiO_2$</td>
<td>Rutile-like related, open structure as in manganate oxides (18)</td>
<td>No $\epsilon''$ peaks</td>
</tr>
<tr>
<td>$Ag_2WO_6$</td>
<td>Pyrochlore, $Ag$ in different sites (18)</td>
<td>No $\epsilon''$ peaks, occupancy of $Ag$ blocks the motion</td>
</tr>
<tr>
<td>$KJ$</td>
<td>$WO_6$ octahedrons blocked by $Ag$ ions (18)</td>
<td></td>
</tr>
<tr>
<td>$Na_2O \cdot 3 Na_2O_4$</td>
<td>Pyrochlore, &quot;low electron&quot; of $Na$</td>
<td>$\epsilon'' = 5.5 \times 10^{-5}$, and $\sigma = 3 \times 10^{-8}$ [ohm cm$^{-1}$]</td>
</tr>
<tr>
<td>$KNaNO_2 \cdot 2NO_3$</td>
<td>Holmium-related orthorhombic (17)</td>
<td>$\epsilon''$ peaks</td>
</tr>
<tr>
<td>$KAlO_3$ and $NaAlO_3$</td>
<td>-translatable mono-defect, and with defects. Silicate tunnel type (10).</td>
<td></td>
</tr>
<tr>
<td>$K_2Al_{2}O_7 \cdot 8H_2O$</td>
<td>Cermcrite, with defects. Silicate tunnel type (11).</td>
<td>$\epsilon''$ peaks</td>
</tr>
<tr>
<td>$LiNO_3^+$</td>
<td>Zeolite-like, with small cage structure (11, 16).</td>
<td>$\epsilon''$ peaks, Li-NMR positive</td>
</tr>
<tr>
<td>LiAl$_2$Si$<em>2$O$</em>{10}$ with some Na substitution</td>
<td>Cordierite-like with Na defects (11).</td>
<td>$\epsilon''$ peaks Poor orientation to or AC.</td>
</tr>
</tbody>
</table>

The following entries are more or less closely related to the "tetragonal-tungsten-bronze" structure type according to X-ray diffraction (11) although precise structures have not been elucidated. None show resolved $\epsilon''$ peaks:

<table>
<thead>
<tr>
<th>Formula</th>
<th>Structure reference</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>$Na_2O \cdot 5 TaO_2$</td>
<td>Tetragonal (18)</td>
<td>$\epsilon'' = 10^{-12}$ by direct measurement with AC.</td>
</tr>
<tr>
<td>$K_2O \cdot 4 TaO_2$</td>
<td>Hex. tungsten bronze (18)</td>
<td>$\epsilon'' = 10^{-12}$ by direct measurement with AC.</td>
</tr>
<tr>
<td>$Na_2O \cdot 10 TaO_2$</td>
<td>Tetragonal (18)</td>
<td>$\epsilon'' = 10^{-12}$ by direct measurement with AC.</td>
</tr>
<tr>
<td>$Li_2O \cdot 5 TaO_2$</td>
<td>Orthorhombic (18)</td>
<td>$\epsilon'' = 10^{-12}$ by direct measurement with AC.</td>
</tr>
<tr>
<td>$K_2O \cdot 13 TaO_2$</td>
<td>Tetragonal (18)</td>
<td>$\epsilon'' = 10^{-12}$ by direct measurement with AC.</td>
</tr>
<tr>
<td>$Na_2O \cdot 13 TaO_2$</td>
<td>Tetragonal (18)</td>
<td>$\epsilon'' = 10^{-12}$ by direct measurement with AC.</td>
</tr>
<tr>
<td>$Na_2O \cdot 0.5 TaO_2$</td>
<td>Monoclinic (18)</td>
<td>$\epsilon'' = 10^{-12}$ by direct measurement with AC.</td>
</tr>
<tr>
<td>$Na_2O \cdot 0.5 TaO_2$</td>
<td>Tetragonal (18)</td>
<td>$\epsilon'' = 10^{-12}$ by direct measurement with AC.</td>
</tr>
<tr>
<td>$Li_2O \cdot 0.5 TaO_2$</td>
<td>Orthorhombic (18)</td>
<td>$\epsilon'' = 10^{-12}$ by direct measurement with AC.</td>
</tr>
</tbody>
</table>

Most of the remaining entries have structures which have very few, or no, counterparts, no $\epsilon''$ peaks.

<table>
<thead>
<tr>
<th>Formula</th>
<th>Structure reference</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>$LiTaO_3$ and $Li_2TaO_3$</td>
<td>$LiTaO_3$-type (19)</td>
<td></td>
</tr>
<tr>
<td>$Li_2O_2$</td>
<td>(10)</td>
<td></td>
</tr>
<tr>
<td>$CaAl_2SiO_6$</td>
<td>Polllite, a &quot;layer&quot; structure, no vacancies (13).</td>
<td></td>
</tr>
<tr>
<td>$Na_2TiO_3$</td>
<td>K cephaloanhydrase (13); &quot;dual&quot; tunnel with vacancies.</td>
<td></td>
</tr>
<tr>
<td>$Na_2O_2 \cdot 2H_2O$</td>
<td>Inverse spinel-like (20), i.e., $Al_2(OH)_2Cl_2$.</td>
<td></td>
</tr>
<tr>
<td>$Li_2O \cdot 2H_2O$</td>
<td>$Li_2O$-type (18), $\epsilon''$ positive.</td>
<td></td>
</tr>
<tr>
<td>$Ca(OH)_2 \cdot 2H_2O$</td>
<td>$Ca(OH)_2$-type (18), $\epsilon''$ positive.</td>
<td></td>
</tr>
<tr>
<td>$Na_2O$</td>
<td>$Na_2O$, with low $\rho_{E}$ and $\sigma$, or $\epsilon''$ loss.</td>
<td></td>
</tr>
<tr>
<td>$La_2O_3$</td>
<td>Both hexagonal and cubic forms (10).</td>
<td></td>
</tr>
<tr>
<td>$La_2O_3 \cdot 2H_2O$</td>
<td>$La_2O_3$-type, with defects (17).</td>
<td></td>
</tr>
<tr>
<td>$La_2O_3 \cdot H_2O$</td>
<td>Similar, but not identical intergrown tunnel structures.</td>
<td></td>
</tr>
<tr>
<td>$K_2O \cdot 15Na_2O$</td>
<td>Tetrac. tungsten bronze-type (13).</td>
<td>No $\epsilon''$ peaks.</td>
</tr>
</tbody>
</table>
Figure 1. - DC conductivity of cubic materials with time (300 K).

Figure 2. - Conductivity of cubic materials with temperature; comparison with "production" beta alumina ceramic.
Figure 3. DC conductivity of planar materials with time (300° K).

Figure 4. Conductivity of planar materials with temperature; comparison with beta aluminas.
COLE-COLE ANALYSIS OF
$K_1.0MnO.8Si$_7$2O$_{16}$ LOSS DATA

THREE COMPOSITIONS
$Kx.0MnO.8Si$_7$2O$_{16}$ AT $10^4$ Hz,
FROM TAKAHASHI

Figure 5. - Comparison of AC conductivities of hollandites, $K_xMnO.8Si$_7$2O$_{16}$

DC conductivity of hollandites with time $300^\circ$ K.

Figure 6. - DC conductivity of hollandites with time ($300^\circ$ K).
Figure 7. AC conductivity of the silicate, β-eucryptite, with temperature; 2 compositions.