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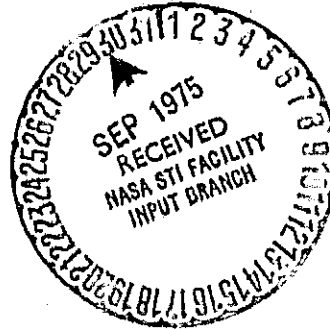
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SEARCH FOR SOLID CONDUCTORS OF Na$^+$ AND K$^+$ IONS: FIVE NEW CONDUCTORS

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ABSTRACT

Five conductors of three structure types have been discovered which, as solids, can transport Na^+ or K^+ ions with conductivities of $\sim 10^{-5}$ $(\Omega\,cm)^{-1}$ at 300 K. These compounds are: (1) the pyrochlores $NaTaWO_6$ and $NaTa_2O_5F$, both with an activation energy for conduction ΔE of 21 kJ/mole; (2) the body-centered cubic form of $NaSbO_3$, with $\Delta E = 42$ kJ/mole; (3) the niobates $2Na_2O \cdot 3Nb_2O_5$ and $2K_2O \cdot 3Nb_2O_5$, 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 $\sim 10^{-5}$ $(\Omega\,cm)^{-1}$ at 300 K. These compounds are: (1) the pyrochlores $NaTaWO_6$ and $NaTa_2O_5F$, both with an activation energy for conduction, ΔE, of 21 kJ/mole; (2) the body-centered cubic form of $NaSbO_3$, with $\Delta E = 42$ kJ/mole; and (3) the niobates $2Na_2O \cdot 3Nb_2O_5$ and $2K_2O \cdot 3Nb_2O_5$, 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 speci-
men strongly affects the measurement of its ionic conductivity and so
determines the techniques used. Because of its importance to this pro-
gram, 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 avail-
able single crystals of a good ionic conductor, internal polarization at de-
fects 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 avail-
able 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 (ϵ''). 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 ob-
serve polarization in powders. The relaxation time of this polarization,
although too small for the aforementioned "ordinary" methods of con-
ductivity 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 pro-
cedure, 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.

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[*]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" (β'') 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), $NaTa_2O_5F$, 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 $2K_2O \cdot 3Nb_2O_5$ 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_2O_5 and Ta_2O_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 "σ_{cc}", at each of several temperatures, allowing also the calculation of an activation energy ΔE 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 μamps/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 μseconds 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 μsec.

Reversible electrodes were of four types: (1) molten alkali metal, (2) alkali metal amalgam, (3) alkali hexafluorphosphate in 0.1-0.5 M solution in propylene carbonate, referred to later as "PC solution", and (4) Na_xWO_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 $NaSbO_3 \cdot 1/6$ NaF; (b) the Na pyrochlores $NaTaWO_6$

and $NaTa_2O_5F$; (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 $KSbO_3$ 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 $\mu amp/cm^2$ 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, σT, against $1/T$, the slopes yielding ΔE values. The measured conductivity of $NaSbO_3$ (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 ΔE, but a calculated conductivity, σ_{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 ϵ''. Figure 4 compares the two new planar conductors with β-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. ΔE for the two niobates is ~17 kJ/mole; for K-beta alumina it is ~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, 5×10^{-5} to 1×10^{-5} $(\Omega\,cm)^{-1}$, 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 $Li_xV_2O_5$ (β, 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 conductivity calculated from dielectric loss (curve 1) is shown for comparison. 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 $\sim 10^{-3}$ $(\Omega\,\text{cm})^{-1}$. All these data are considered self-consistent, and show that only a low level of transport at 300 K is likely, $\sim 10^{-7}$ $(\Omega\,\text{cm})^{-1}$, 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 composition $LiAlSi_2O_6$; this was a lower Li content than in the eucryptite reported in other work, $LiAlSiO_4$ (ref. 23), with which it has been compared in figure 7. This conductivity-reciprocal temperature plot shows a change in slope, or in ΔE, 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 calculated from the ΔE and the single datum point available. The ΔE 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 5×10^{-7} $(\Omega\,\text{cm})^{-1}$ 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 tantalates 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), $\sim 10^{-5}$ $(\Omega\,cm)^{-1}$ 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 alumina.

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 $NaSbO_3$ · 1/6 NaF and $2K_2O$ · $3Nb_2O_5$. 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 un-
qualified; e.g., the hexagonal tungsten bronzes and other tunnel types
show a measurable AC conductivity due to ion carriers even where
σ_e is very small, but this ionic conductivity has a short relaxation
time and so is not applicable to appreciable ion transport. With nu-
merous "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 struc-
tures. 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 ΔE's
were about the same, suggesting that impedance to transport in hol-
landite 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 cagelike 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 pychlores $AB_1B_2X_6$,
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 pyrochlores $AB_1B_2X_7$ 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, $KSbO_3 \cdot 1/6$ 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 σ_{ion} near 10^{-5} $(\Omega \, cm)^{-1}$ at 300 K, with no appreciable electronic conductivity:

1. Body centered cubic $NaSbO_3$, with or without 1/6 mole NaF/mole used for stabilization; $\Delta E = 42$ kJ/mole; above 530 K its conductivity exceeds that of β-alumina.

2. Pyrochlores $NaB_1B_2X_6$, exemplified by $NaTaWO_6$ and $NaTa_2O_5F$; $\Delta E = 21$ kJ/mole for both compounds.

3. The niobates $2M_2O \cdot 3Nb_2O_5$ (M = Na or K), a layer type of as yet undetermined structure; ΔE = 17 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.

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TABLE I. - SUBSTANCES WITH $\sigma_{ion} \geq 10^{-5}$ $(\Omega\,cm)^{-1}$ AT 300 K, AND $\sigma_e = 0$

Formula	Structure; references	ΔE, kJ/mole	$\sigma_{300\,K}$, $(\Omega\,cm)^{-1}$	Comments
$NaSbO_3$, pure or $NaSbO_3 \cdot 1/6\ NaF$	BCC form, NaF for possible stabilization. Intersection tunnels (11, 12).	42 from ϵ'' and transport	10^{-5}; PC electrodes	May react with Na. Sinterability depends on success of Na stabilization, not yet established. Can be compacted to 95 percent density.
$NaTaWO_6$ and $NaTa_2O_5F$	Pyrochlore type, intersection tunnels (10, 11)	21 from ϵ''	10^{-5}; PC electrodes	Both unstable to sintering. Compacts to 93 percent density. Made only by ion-exchange. Oxyfluoride more stable to Na.
$2\ Na_2O \cdot 3\ Nb_2O_5$ and $2\ K_2O \cdot 3\ Nb_2O_5$	Structure incomplete. Alk. ion in layers, possibly as in beta alumina.	17 from ϵ'' and transport	10^{-5}; PC electrodes	Na cpd by ion exchange and not sinterable. K cpd stable and sinterable.

TABLE II. - SUBSTANCES WITH ION MOBILITY NOT APPLICABLE TO TRANSPORT

Formula	Structure; references (occ. = occupancy of site)	ΔE, kJ/mole	$\sigma_{300\ K}$, $(\Omega\ cm)^{-1}$	Comments
$K_2W_4O_{13}$	WO_3-type tunnels, K in 5/6 occ. (25)	16 from ϵ''	10^{-4}, from ϵ''	Large σ_e
β-$Li_{0.6}V_2O_5$	Li in part occ. in tunnels (26, 6)	9 to 25, 4-probe	10^{-3}, from transport	Large σ_e
$K_xMg_{x/2}Ti_{(8-x/2)}O_{16}$ x from 1.6 to 2.0	Hollandite type. K in 80 to 100 percent occ. in tunnels (17, 18)	21 to 25, from ϵ''	10^{-3} to 10^{-5}, from ϵ''	10^{-3} $(\Omega\ cm)^{-1}$ at 1 μsec; polarized rapidly in both crystal and ceramic.
$NaAlSi_2O_6$	β- Spodumene (27) ion-exchanged. Na in silica-type channels.	Not det'd.	10^{-5} at 1 μsec	Polarized rapidly. Li cpd conductivity too low to measure.
$LiAlSi_2O_3$	β-Eucryptite of low Li content. Li in silica-type channels. (20 to 22)	67, <670 K 96, >670 K	10^{-5} at 670 K by 2-probe AC	Ref. (23) reports higher σ for higher Li content ($LiAlSiO_4$).
$K_{0.3}Ta_{0.3}W_{0.7}O_3$	Hex. tungsten bronze (33). K in part occ. in tunnels	16 to 26 from ϵ''	10^{-4} to 10^{-6}, from ϵ''	More mobility than tetrag. and cubic bronzes. Much variability between samples. Some σ_e developed.

TABLE III. – SUBSTANCES WITH $\sigma_{ION} < 10^{-6}$ $(\Omega\,cm)^{-1}$ BY DIELECTRIC LOSS MEASUREMENTS

Formula	Structure; reference	Comments
$6\,Li_2O \cdot 17\,TiO_2$	Ramsdellite-related, open structure as in manganese oxides (28)	No ϵ'' peaks
$\left.\begin{array}{c} Ag \\ K \end{array}\right\}\,WTaO_6$	Pyrochlore; Ag, K in different sites (8b) than in Na cpd (10).	No ϵ'' peaks, occupancy of 8b blocks ion motion
$Na_2O \cdot 2\,Sb_2O_4$	Pyrochlore, "lone electrons" of Sb postulated in 8b (29, 12).	Like preceding entry, but blocked by "lone pairs" (29, 12)
$KMgTi_{3.2}O_8$	Hollandite-related orthorhombic (34).	$\epsilon'' - \Delta E$ 65 kJ/mole, and σ $3 \cdot 10^{-8}$ $(\Omega\,cm)^{-1}$
$KAlO_2$, and $K_{0.8}Al_{0.8}Si_{0.2}O_2$	β-cristobalite non-defect, and with defects. Silicate tunnel type (30).	No ϵ'' peaks.
$K_{6.6}Al_{1.5}Mg_{2.5}Si_4O_{16}$	Carnegieite, with defects. Silicate tunnel type (31).	No ϵ'' peaks.
Linde A · $LiNO_3$	Zeolite-like; with small cage structure (32, 0)	No ϵ'' peaks, Li-NMR positive.
$Mg_2Al_4Si_5O_{18}$ with some Na substitution	Cordierite-type with Na defects (14).	No ϵ'' peaks. Poor indications in pulsed AC.

The following entries are more or less closely related to the "tetragonal-tungsten-bronze" structure type according to X-ray diffraction (15) although precise structures have not been elucidated. None show resolved ϵ'' peaks

$1\,K_2O \cdot 5\,Ta_2O_5$	Tetragonal (15)	
$1\,K_2O \cdot 4\,Ta_2O_5$	Hex. tungsten bronze (15)	$\sigma \sim 10^{-12}$ to direct measurement with PC electrodes.
$21\,Na_2O \cdot 79\,Ta_2O_5$	Tetrag. tungsten bronze related (15)	K analogue, which is hexagonal, shows some loss.
$5\,Li_2O \cdot 95\,Ta_2O_5$	Orthorhombic (15)	
$11\,K_2O \cdot 89\,Nb_2O_5$		Variable losses with moisture content.
$1\,Li_2O \cdot 14\,Nb_2O_5$	Monoclinic (15)	
$3\,K_2O \cdot 13\,Nb_2O_5$	Tetragonal (15)	
$7\,K_2O \cdot 13\,Nb_2O_5$	Tetragonal (15)	Some ϵ'' loss.
$34\,K_2O \cdot 66\,Ta_2O_5$	Tetragonal (15)	Some ϵ'' loss.
$Na_2O \cdot 13\,Nb_2O_5$	Monoclinic (15)	
$K_4Nb_6O_{17} \cdot xH_2O$		
$NaNb_3O_8$	Orthorhombic (15)	
KNb_3O_8	Orthorhombic (15)	

Most of the remaining entries have structures which have very few, or no, counterparts; no ϵ'' peaks.

$LiTa_3O_8$ and $Li_{1.8}Ta_{5.8}W_{0.2}O_{16}$	$LiTa_6O_{15}F$ type (15)	
Li_5GaO_4	(36)	
$CsAlSi_2O_6$	Pollucite; a "layer" structure, no vacancies (33).	
$Na_2Ti_6O_{13}$	K cpd is isomorphous (2); "dual" tunnel with vacancies.	Structure suggests mobility; none observed.
$LiAl_5O_8$	Inverse spinel-type (6); (i.e., $Al_2(LiAl_3)O_8)$. Layers similar to β-Al_2O_3.	
$Li_{1.2}Nb_{5.6}Ti_{0.4}O_{14.8}F_{1.2}$	$LiNb_6O_{15}F$-type (6), with defects.	Some ϵ'' and positive NMR.
$Ca_5(PO_4)_3F_3$, made to be deficient in CaF_2	Apatite-type; chem. anal. does not confirm defect CaF_2.	Some ϵ'' peaking probably due to F^-.
Na_2BeF_4	K_2SO_4-type (6).	NMR also negative.
K_2TiF_6	A_2BF_6-type (6).	NMR also negative.
$NaLnF_4$, with $Ln = Nd$ or Y.	Both hexagonal and cubic forms (6).	Some ϵ'' loss.
$Li_{0.1}Y_{0.2}(Ta_{0.69}W_{0.31})O_3$	Perovskite-type, with defects (7).	
$Li_2Ge_7O_{15}$, $Li_{1.7}Ge_{6.7}Ta_{0.3}O_{15}$, and $LiNaGe_4O_9$	Similar, but not identical inter-woven tunnel structures.	Positive NMR, but low σ_{AC} to direct measurement.
$K_{0.15}Ta_{0.5}W_{0.5}O_3$	Tetrag. tungsten bronze-type (33).	No ϵ'' peaks.

* Crystals grown by R. Mazelsky, Westinghouse Research Laboratory, Pittsburgh, Pa.

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.
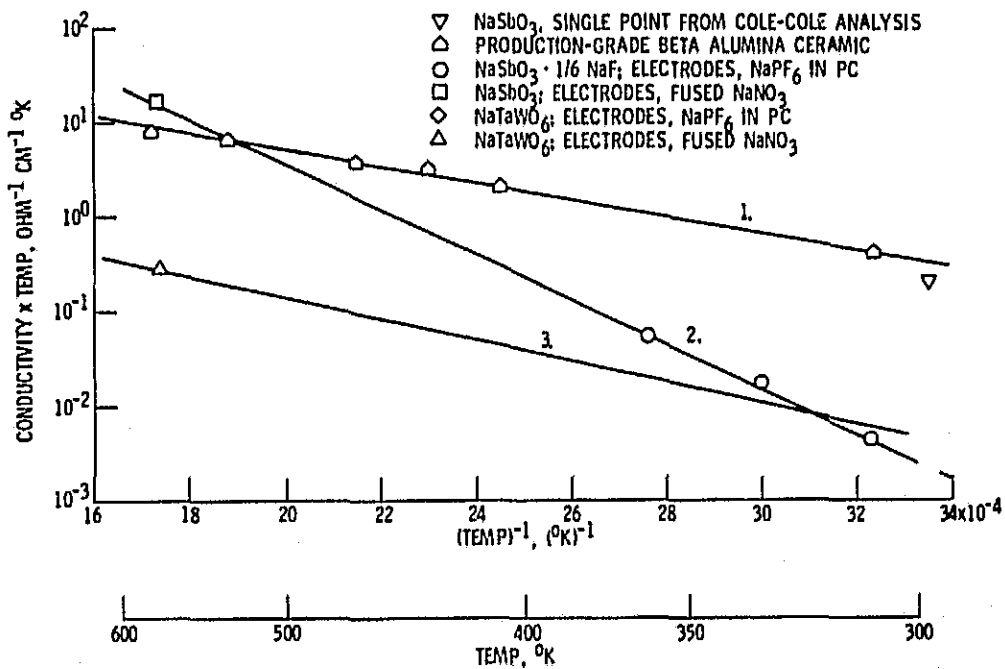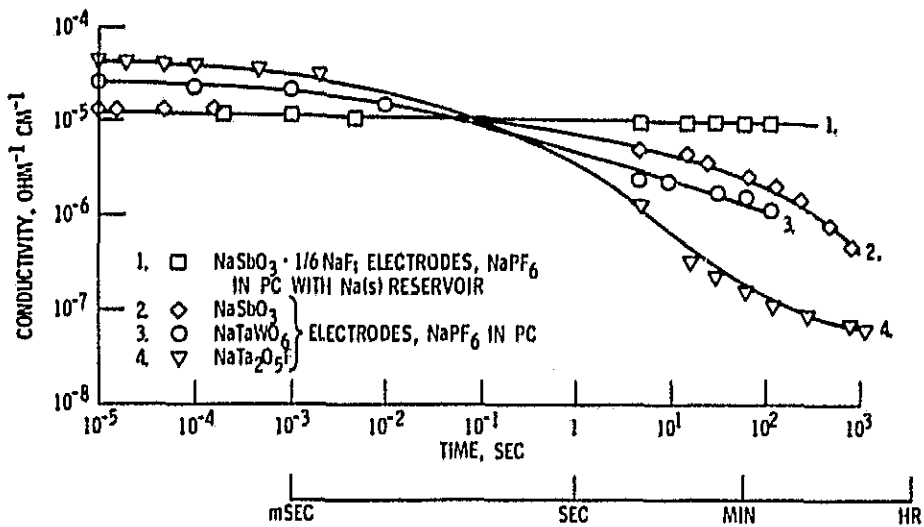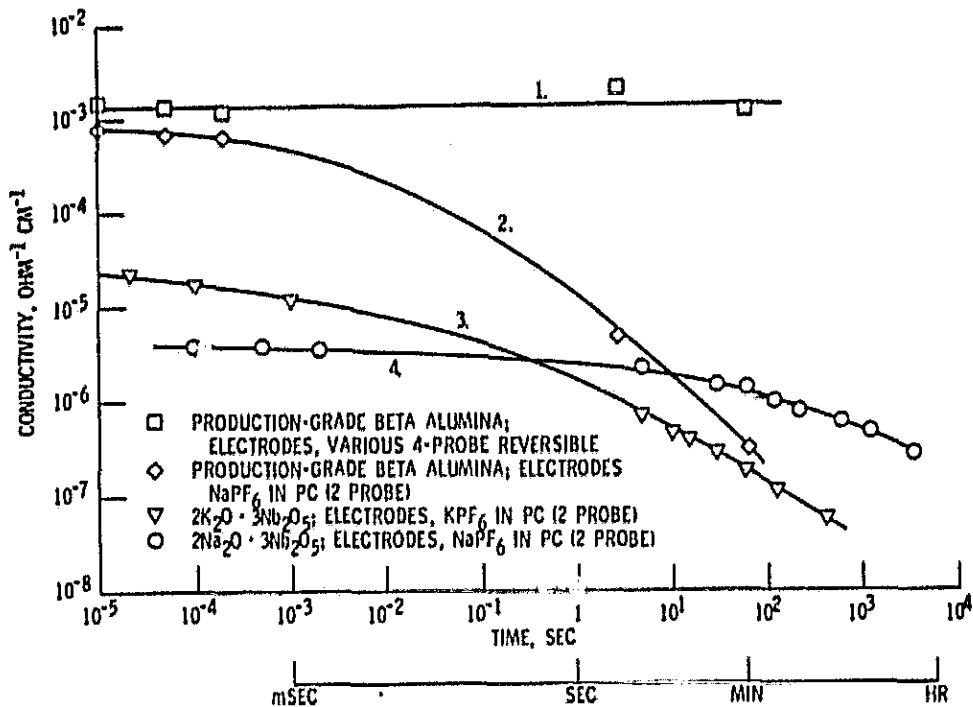
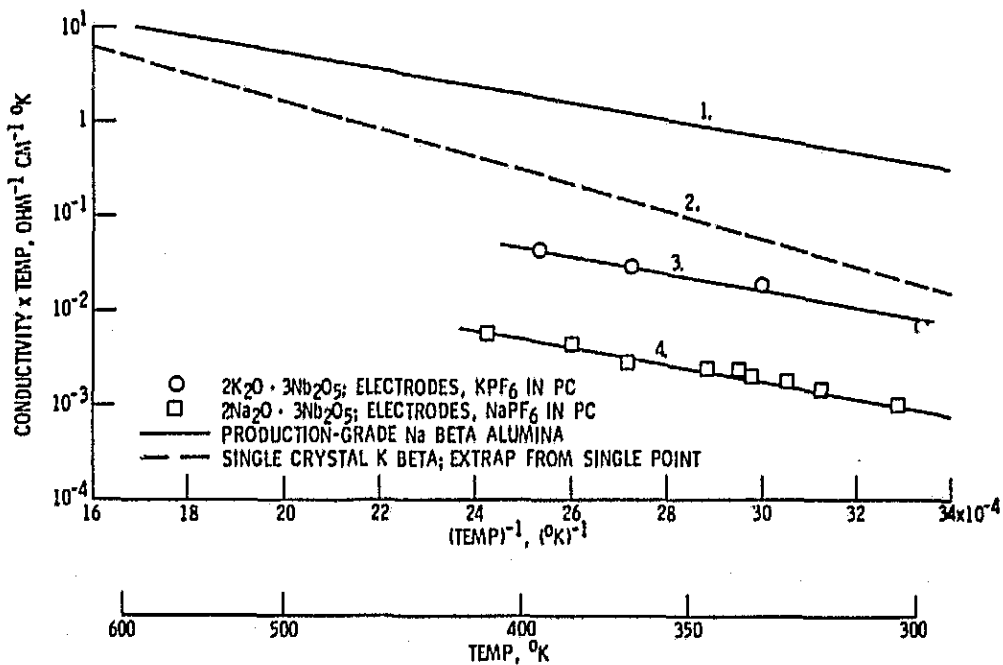**Figure 3. – DC conductivity of planar materials with time (300° K).**

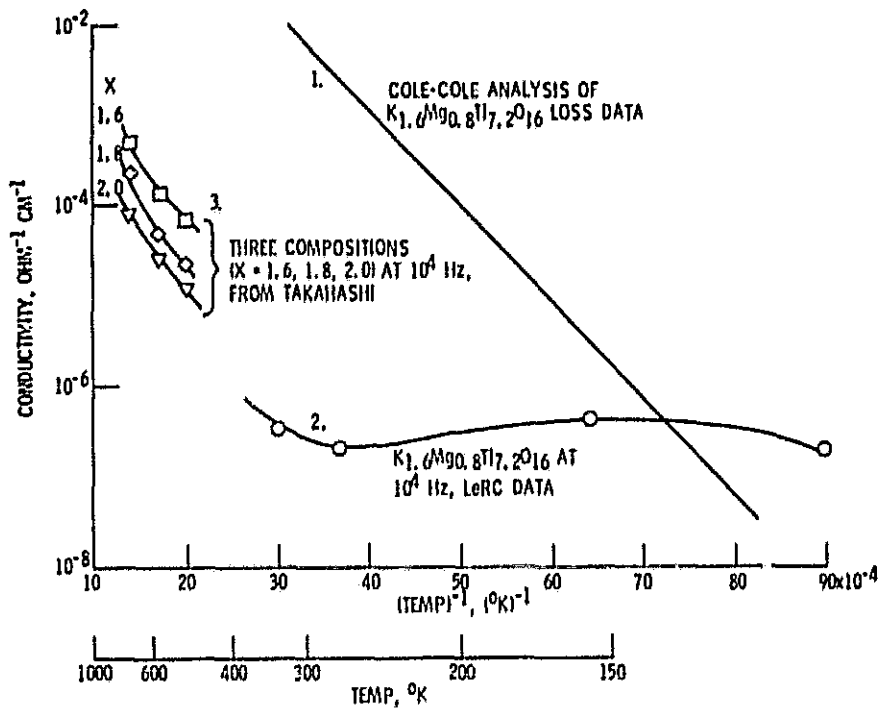**Figure 4. – Conductivity of planar materials with temperature; comparison with beta aluminas.**

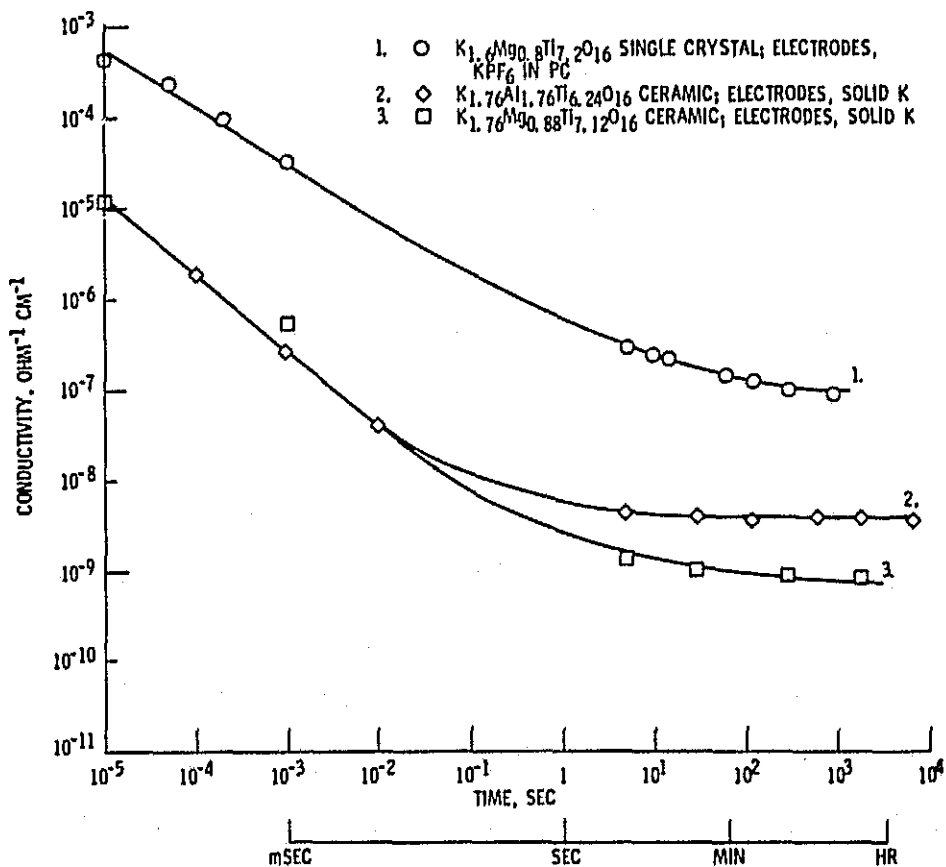Figure 5. - Comparison of AC conductivities of hollandites, $K_x Mg_{x/2} Ti_{(8-x/2)} O_{16}$.

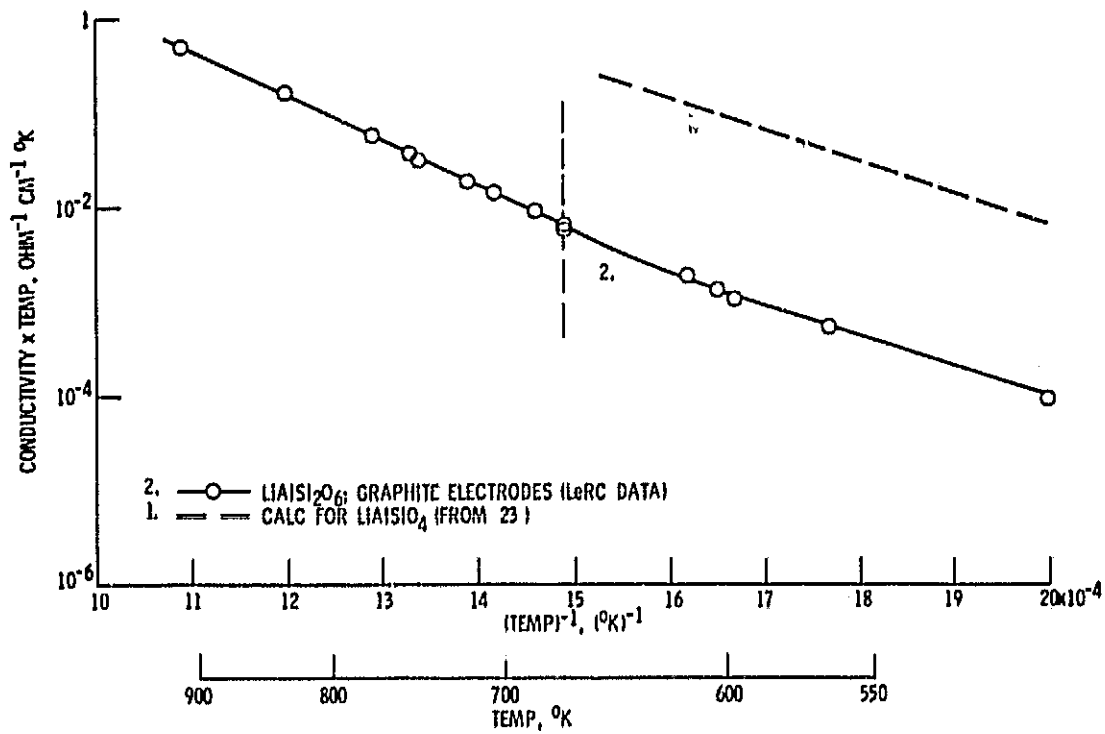Figure 6. - DC conductivity of Hollandites with time (300° K).

Figure 7. - AC conductivity of the silicate, β-eucryptite, with temperature; 2 compositions.