SELECTION AND PRELIMINARY EVALUATION OF THREE STRUCTURES AS POTENTIAL SOLID CONDUCTORS OF ALKALI IONS: TWO HOLLANDITES, A TITANATE, AND A TUNGSTATE

by Joseph Singer, Harold E. Kautz, William L. Fielder, and J. Stuart Fordyce

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Utilization of crystal-chemical criteria has suggested three structure types in which alkali ions may be mobile: (1) hollandites $\text{K}_x\text{Mg}_{x/2}\text{Ti}_{(8-x/2)}\text{O}_{16}$ and $\text{K}_x\text{Al}_{x}\text{Ti}_{(8-x)}\text{O}_{16}$ for $1.6 \leq x \leq 2.0$; (2) tungstate $\text{K}_2\text{W}_4\text{O}_{13}$; and (3) sodium hexatitanate $\text{Na}_2\text{T}_6\text{O}_{13}$. Each is a "tunnel" structure. An electrical screening procedure, previously tested on beta-alumina, has indicated high $\text{K}^+$ ion mobility in the hollandites and in the tungstate, but not in the hexatitanate. Specimens were polycrystalline disks near 90 percent of theoretical density. The ac conductivity calculated from dielectric and capacitance measurements has been attributed to ion mobility. This $\sigma_{ac}$ was up to $10^{-2}$ ($\text{Ocm})^{-1}$ for hollandites and about $10^{-4}$ ($\text{Ocm})^{-1}$ for the tungstate, with activation energies of ~21 to 25 and ~16 kJ/mole (~5 to 6 and ~4 kcal/mole), respectively. Electronic conduction and chemical reactivity have eliminated the tungstate from further consideration. The hollandites have been considered worthy of further development and evaluation.
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SUMMARY

Utilization of crystal-chemical criteria has suggested three structure types in which alkali ions may be mobile: (1) hollandites $K_x Mg_{(x/2)}Ti_{[8-(x/2)]}O_{16}$ and $K_x Al_{-x}Ti_{(8-x)}O_{16}$ for $1.6 \leq x \leq 2.0$; (2) the tungstate $K_2W_4O_{13}$; and (3) sodium hexatitanate $Na_2Ti_6O_{13}$. Each is a "tunnel" structure. An electrical screening procedure, previously tested on beta-alumina, has indicated high $K^+$ ion mobility in the hollandites and in the tungstate, but not in the hexatitanate. Specimens were polycrystalline disks near 90 percent of theoretical density. The ac conductivity calculated from dielectric and capacitance measurements has been attributed to ion mobility. This $\sigma_{ac}$ was up to $10^{-2}$ ohm-centimeter$^{-1}$ for hollandites and about $10^{-4}$ ohm-centimeter$^{-1}$ for the tungstate, with activation energies of ~21 to 25 and ~16 kilojoules per mole (~5 to 6 and ~4 kcal per mole), respectively. Electronic conduction and chemical reactivity have eliminated the tungstate from further consideration. The hollandites have been considered worthy of further development and evaluation.

INTRODUCTION

The discovery of the extraordinary alkali ion mobility in the beta-alumina structure (refs. 1 to 3) has stimulated research and development in solid electrolytes. This report deals with the selection and preliminary screening of new materials considered for the solid electrolyte role in secondary battery applications, with the hope that operating temperatures might be lower than the 573 K requirement of the ceramic beta-alumina types. Selection is based on crystal-chemical criteria. The electrical screening, fully described elsewhere (ref. 4) is designed to apply to specimens more readily made than
the type that would be required for a definitive evaluation by direct measurement of ion transport. An ac conductivity may be calculated by way of measurement of dielectric loss and capacitance. This $\sigma_{ac}$, calculated with the aid of Cole-Cole plots, may be provisionally attributed to ion mobility; its magnitude and that of the corresponding activation energy, along with directly measured electronic conductivity (ref. 4), are the major screening considerations in this work.

Selection of Candidate Materials

Selection of candidates was based on crystal-chemical features like the following: (1) chemical or mineralogical evidence of ready replacement of the cation; similarly, evidence of isomorphism with other groups in place of the anionic group; (2) long alkali-oxygen bond lengths; and (3) large fraction of cation sites unoccupied, these sites being in distinct layers - or tunnels - formed by a rigid framework of the large polyhedral anions.

Table I lists the relevant data, as far as has been reported from X-ray structure analysis, for the three structure types selected in this work. Views of the structures are given in the references noted in table I. All three happen to be "tunnel" structures, that is, the alkali ions are in tunnels.

Experimental

Synthesis of materials. - Polycrystalline specimens, of densities ~90 percent of theoretical, were made of each of the compounds studied, by solid-state reactions employing usual ceramic procedures (ref. 5). The hollandites and the hexatitanate were made from commercial high purity carbonates and oxides by several successive firings and remixings until X-ray diffraction showed single phase. One firing at 1423 K for 6 hours, after the 1273 K decomposition, was sufficient for the hexatitanate. However, the hollandites required two reaction firings between which they were ground and repressed into balls or disks. The two firings were at 1373 K for 2 hours and then 1473 K for 2 hours in air within packing powder of the same composition. Other procedures appear in reference 6. It was necessary to prepare $K_2WO_4$ below the peritectic temperature of 1123 K (refs. 7 and 8). For high density, the preparation was from $K_2WO_4$ and $WO_3$ under hydrostatic pressure with the pressure applied before the heating to 1073 K had commenced. This apparently did succeed in inhibiting needle growth, a density of ~95 percent having been achieved.

Table II lists the specimens of the several compounds, with information on their physical form and texture, which were subjected to screening by electrical methods.
Samples 1 and 2 of Na beta-alumina are included from other work (ref. 4) for comparison.

**Electrical measurements.** Elsewhere (ref. 4), the electrical screening procedure has been tested on Na beta-alumina. In the appendix, the Cole-Cole analysis is illustrated by application to a hollandite sample 8. Initially, ac measurements were made of dielectric loss and capacitance over a range of frequency and temperature. From these data an ac conductivity was calculated, $\sigma_{ac}$, utilizing the Cole-Cole plot, this in turn yielding an activation energy $\Delta E$. Finally dc polarization was used to measure electronic conductivity (ref. 9). The procedure was designed to permit preliminary evaluation with specimens of only moderate density and purity without the need for intensive development of specimens suitable for direct ion transport measurements.

It should be noted here that this screening procedure (ref. 2) provides a necessary, but not sufficient, indication of ionic conduction. The calculation of $\sigma_{ac}$ (see appendix) attributes this conductivity to ion transport on the assumption that the relaxation time $\tau$ is that of a space charge polarization due to mobile ions. This assumption is fortified by the increase of $\tau$ values in specimens improved in the sense of single crystal character, as well as by the small electronic conductivity observed in most cases.

**RESULTS**

Table III summarizes the results of this investigation.

Figures 1 and 2 are typical plots of the experimentally determined dielectric constant $\varepsilon'$, and dielectric loss $\varepsilon''$, respectively, as functions of temperature. Specifically, the data of figures 1 and 2 comprise measured dielectric constants and losses, respectively, at four frequencies for the hollandite sample 8. The relaxation time $\tau$ at temperature $T$ of the sample, required by equation (A1) in the appendix, is obtained from the condition at the loss peak when $\omega\tau = 1$ at temperature $T$ where $\omega$ is $2\pi$ times the frequency $\nu$. The data points for $\nu = 10^4$ hertz are employed for figure 3, which is a typical Cole-Cole plot (ref. 10) as used to determine the polarization, $\varepsilon_s - \varepsilon_\infty$, needed for calculating $\sigma_{ac}$. A set of such plots of $\varepsilon''$ against $\varepsilon'$ was obtained for each sample, a separate plot for each frequency. The utilization of the information in figures 1 to 3 to obtain the desired $\sigma_{ac}$ function for each sample is illustrated in the appendix for sample 8.

Figures 4 to 7 present $\sigma_{ac}$ plotted as $\sigma T$ against $1/T$ for the indicated samples. The positions of the resonance peaks in one-decade increments from $10^2$ to $10^6$ hertz are indicated in these figures so that, employing the relation $\omega\tau = 1$, one may deduce the relative magnitude of the relaxation times of the samples. It is to be noted that resonant frequencies increase with increasing temperature.
The last column of table III presents the data of electronic conductivity in the form of its ratio to the total conductivity. The ratio is observed to be even smaller for the hollandites than for Na beta-alumina, and it is very large for the tungstate.

DISCUSSION

In figure 4, one notes that the $\sigma$ value at 298 K for the K-hollandite sample 8, $1.7 \times 10^{-2}$ ohm-centimeter$^{-1}$, is an order of magnitude higher than given for Na beta-alumina (table III); of course, this requires confirmation by direct measurement of K$^+$ ion transport.

The $\Delta E$ values for all the hollandite isomorphs fall within a narrow range; however, sample preparation parameters have not yet been controlled to the point where quantitative significance can be given to the $\Delta E$ values in table III. Within the same limitations, it should be noted that the activation energy for the hollandite conductivity is about the same as for Na beta-alumina.

The appendix treats the data of sample 8 in detail, but attention may be called at this point to a special aspect of the Cole-Cole treatment which bears upon the comparison between K-Mg-hollandite and Na beta-alumina.

A single relaxation time in a dielectric would produce the "ideal" Cole-Cole plot, $\epsilon''$ against $\epsilon'$, as a semicircle with radius of $\epsilon''_{\text{max}}$ and diameter of $\epsilon_s - \epsilon_{\infty}$ (refs. 4 and 10); or,

$$\frac{\epsilon''_{\text{max}}}{\epsilon_s - \epsilon_{\infty}} = 0.5$$

Usually, there is a distribution of relaxation times which attenuates $\epsilon''_{\text{max}}$ but not $\epsilon_s - \epsilon_{\infty}$, resulting in the ratio being <0.5. For Na beta-alumina sample 2, the ratio was 0.42 (ref. 4); for the hollandite sample 8, it was 0.125.

Figure 5 discloses close agreement in conductivity among the three compacted Ba-hollandites, including the D.W. crystal aggregate; the powder, sample 3, as expected, diverges from the group. The relaxation times of the three samples prepared in the present work are similar, as shown by the resonance positions; the 10$^3$-hertz peak was unfortunately not available for the D.W. sample. The magnitude of $\sigma$ at 298 K, $4.2 \times 10^{-5}$ ohm-centimeter$^{-1}$, for Ba-hollandite sample 5 prepared here, is much lower than for the K analog and about the same as for the potassium aluminum isomorphs (table III).

Figure 6 again suggests that sample preparation variables may affect relaxation time and yet permit a relatively unaffected value of conductivity to be calculated by the
present method. Sample 11 had been made with a better K-retention technique than had sample 10; their conductivity values were substantially the same, yet the relaxation time at 298 K (as extrapolated) for sample 11 was $6.3 \times 10^{-6}$ seconds, and for sample 10, $2.5 \times 10^{-9}$ seconds. Comparing conductivities of the K-Mg-hollandites to those of the K-Mg and Ba-Mg isomorphs, it appears that specimen improvement will not bring the values of the latter two up to that of the best K-Mg sample 8. It is perhaps not surprising the Ba$^{++}$ ion is less mobile than K$^+$, but there appears to be no ready explanation for K$^+$ ion to be less mobile in the Al-hollandite than in the Mg isomorph. Theory appears not to provide a model of relaxation time which can be used to distinguish between a number of plausible mechanisms; therefore, no attempt has been made in this work to employ the concept of relaxation time other than in the above qualitative way.

The tungstate $K_2W_4O_{13}$ (fig. 7) has the lowest activation energy of all the materials discussed here, although its conductivity is of the order of that of the more poorly conducting hollandite isomorphs, that is, the Ba-Mg and K-Al types. No further work has been planned upon the tungstate because it was found to react with potential anolytes and catholytes, and also because of its large electronic conductivity. However, it is interesting that the experimental results support the use of the crystal-chemical criteria which had predicted a mobile ion in this structure.

The selection criteria appear to have failed in the case of $Na_2Ti_6O_{13}$. No data are shown for it because no loss peak was obtained. However, further work on this compound appears warranted in view of the extraordinarily interesting kind of Na$^+$ sites in this structure and the residual uncertainties about the absolute validity of the dielectric loss peak requirement.

**SUMMARY OF RESULTS**

The ac screening method, based on measurement with the known Na-ion conductor, Na beta-alumina, has been applied to substances of three types of structure and has eliminated two, as summarized below:

1. Three structure types have been selected by crystal-chemical criteria, synthesized as polycrystalline compacts and aggregates, and investigated by electrical methods for alkali ion mobility. Mobility of the alkali ion, within the limits of interpretation of ac methods, has been observed in: (1) K-Mg-hollandites, $K_xMg_{x/2}Ti[8-(x/2)]O_{16}$ for $1.6 \leq x \leq 2.0$ and (2) $K_2W_4O_{13}$. The findings in the hollandites extends the prior work of Dryden and Wadsley on the hollandite $BaMgTi_7O_{16}$. The tungstate had not been investigated previously. The alkali-aluminum-hollandites show effects analogous to those in the Mg isomorphs.

2. The activation energy for alkali mobility $\Delta E$, given by the temperature dependence of the calculated ac conductivity, is no more than 22 kJoules per mole (5.3 kcal/
mole) for the K-Mg-hollandites. For $K_2W_4O_{13}$ $\Delta E$ is 16 kilojoules per mole (3.9 kcal/mole). The highest calculated ac conductivities at 298 K are: (a) $1.7 \times 10^{-2}$ ohm-centimeter$^{-1}$ for K-Mg-hollandites; (b) $4.7 \times 10^{-5}$ ohm-centimeter$^{-1}$ for "saturated" Ba-Mg-hollandite; and (c) $8.3 \times 10^{-5}$ ohm-centimeter$^{-1}$ for $K_2W_4O_{13}$. For comparison, a partially oriented compact of beta-alumina had been measured yielding $\Delta E = 18$ kilojoules per mole (4.4 kcal/mole) and $\sigma_{ac} (298 \text{ K}) = 1.2 \times 10^{-3}$ ohm-centimeter$^{-1}$. No electronic contribution is included in the foregoing ac conductivities since they are calculated from loss resonances, nor can they be taken to represent true ionic transport until so directly proven. Direct determination of the electronic contribution by measurements with blocking electrodes places the upper limit of the electronic conductivity $\sigma_{\text{electronic}}$ fraction of the total well under $10^{-3}$ for the hollandites. For $K_2W_4O_{13}$, however, the $\sigma_{\text{electronic}}$ is a major part.

Lewis Research Center,
National Aeronautics and Space Administration,
Cleveland, Ohio, July 24, 1972,
120-34.
APPENDIX - ILLUSTRATION OF $\sigma_{ac}$ CALCULATION FOR HOLLANDITE SAMPLE 8

The data of figures 1, 2, and 3 are employed here to determine $\sigma_{ac}$ for sample 8:

$$\sigma_{ac} = \frac{\varepsilon_s - \varepsilon_\infty}{\tau} \quad \text{(A1)}$$

where for $\nu = 10^4$ hertz $\tau = 1/\omega_{\text{resonance}} = (2\pi\times10^4)^{-1}$ second, $\tau$ being the relaxation time involved in the absorption process.

From the position of the $10^4$-hertz resonance (fig. 2), we observe the $(2\pi\times10^4)^{-1}$ second is the magnitude of the relaxation time of sample 8 at the temperature given by $1/T = 7.4\times10^{-3}$ K$^{-1}$.

From figure 3 we estimate according to the analysis given in reference 10

$$\varepsilon_s - \varepsilon_\infty = 175$$

This is a pure number in the units employed in this report. In order to obtain $\sigma_{ac}$ in units of ohm-centimeter$^{-1}$, this must be multiplied by the permittivity of free space $\varepsilon_0 = 8.85\times10^{-14}$ coulomb/volt-centimeter. Then, equation (1) becomes

$$\sigma_{ac} = \frac{(175)(8.85\times10^{-14})}{(2\pi\times10^4)^{-1}} \frac{C}{\text{sec-V-cm}} = 9.74\times10^{-7} \text{ (}\Omega\text{cm)}^{-1}$$

This number is then the calculated $\sigma_{ac}$ for sample 8 at $1/T = 7.4\times10^{-3}$ K$^{-1}$. Similarly, $\sigma_{ac}$ values were calculated at each of the other resonance peaks. From these four data points, figure 4 was obtained by a least squares calculation, assuming a temperature dependence of the following form:

$$\sigma_{ac}T = Ae^{-\Delta E/RT} \quad \text{(A2)}$$

thus also obtaining the parameters $\Delta E$ and $A$.

The precisions given in table III for $\Delta E$ are governed by the determination of the temperature at resonance. The dominant effects upon the $\sigma_{ac}$ precision are (1) the reading of the $\varepsilon_s - \varepsilon_\infty$ values from the Cole-Cole plots, and (2) the measurement of sample dimensions to furnish the value of geometrical capacitance; the former is estimated to be $\pm10$ percent, but the latter varies with sample configuration.
REFERENCES


<table>
<thead>
<tr>
<th>Candidate</th>
<th>Alkali-oxygen bond lengths, Å</th>
<th>Alkali site occupancy</th>
<th>Other structural information</th>
<th>Structure reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hollandite</td>
<td>3.0</td>
<td>8/10 to 1.0</td>
<td>Extensive isomorphism</td>
<td>12 and 13</td>
</tr>
<tr>
<td>$K_2W_4O_{13}$</td>
<td>(b)</td>
<td>5/6</td>
<td>WO$_3$-tunnel type</td>
<td>14</td>
</tr>
<tr>
<td>$Na_2Ti_6O_{13}$</td>
<td>2.58, 3.02</td>
<td>2/3</td>
<td>K, Rb isomorphs</td>
<td>15</td>
</tr>
</tbody>
</table>

*Ref. 11.

*bNot available.

**TABLE I. - CRYSTAL STRUCTURE DATA USED IN SELECTION**
TABLE II. - IDENTIFICATION OF SAMPLES

<table>
<thead>
<tr>
<th>Sample</th>
<th>Compound</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Na beta-alumina</td>
<td>Powder ground from firebrick&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td>2</td>
<td>Na beta-alumina</td>
<td>~95 Percent dense polycrystalline compacted and partially oriented in synthesis, measured in &quot;easy&quot; direction</td>
</tr>
<tr>
<td>3</td>
<td>BaMgTi&lt;sub&gt;7&lt;/sub&gt;O&lt;sub&gt;16&lt;/sub&gt; (hollandite)</td>
<td>Powder ground from 1473 K solid-state reaction product</td>
</tr>
<tr>
<td>4</td>
<td>BaMgTi&lt;sub&gt;7&lt;/sub&gt;O&lt;sub&gt;16&lt;/sub&gt; (hollandite)</td>
<td>~90% Percent dense compact synthesized as disk by solid-state reactions</td>
</tr>
<tr>
<td>5</td>
<td>BaMgTi&lt;sub&gt;7&lt;/sub&gt;O&lt;sub&gt;16&lt;/sub&gt; (hollandite)</td>
<td>Partially oriented coarse-grained ingot</td>
</tr>
<tr>
<td>D. W.</td>
<td>BaMgTi&lt;sub&gt;7&lt;/sub&gt;O&lt;sub&gt;16&lt;/sub&gt;</td>
<td>D. W. utilizing the data of Dryden and Wadsley (ref. 12) obtained on oriented aggregate of BaMgTi&lt;sub&gt;7&lt;/sub&gt;O&lt;sub&gt;16&lt;/sub&gt;</td>
</tr>
<tr>
<td>6</td>
<td>K&lt;sub&gt;1.6&lt;/sub&gt;Mg&lt;sub&gt;0.8&lt;/sub&gt;Ti&lt;sub&gt;7.2&lt;/sub&gt;O&lt;sub&gt;16&lt;/sub&gt; (hollandite)</td>
<td>Powder ground from 1473 K solid-state reaction product</td>
</tr>
<tr>
<td>7</td>
<td>K&lt;sub&gt;1.6&lt;/sub&gt;Mg&lt;sub&gt;0.8&lt;/sub&gt;Ti&lt;sub&gt;7.2&lt;/sub&gt;O&lt;sub&gt;16&lt;/sub&gt; (hollandite)</td>
<td>~90% Percent dense disk</td>
</tr>
<tr>
<td>8</td>
<td>K&lt;sub&gt;1.6&lt;/sub&gt;Mg&lt;sub&gt;0.8&lt;/sub&gt;Ti&lt;sub&gt;7.2&lt;/sub&gt;O&lt;sub&gt;16&lt;/sub&gt; (hollandite)</td>
<td>Partially oriented coarse-grained ingot</td>
</tr>
<tr>
<td>9</td>
<td>K&lt;sub&gt;2&lt;/sub&gt;W&lt;sub&gt;4&lt;/sub&gt;O&lt;sub&gt;13&lt;/sub&gt;</td>
<td>~95% Percent dense compact</td>
</tr>
<tr>
<td>10</td>
<td>K&lt;sub&gt;2&lt;/sub&gt;Al&lt;sub&gt;2&lt;/sub&gt;Ti&lt;sub&gt;6&lt;/sub&gt;O&lt;sub&gt;16&lt;/sub&gt;</td>
<td>~90% Percent dense compact</td>
</tr>
<tr>
<td>11</td>
<td>K&lt;sub&gt;1.76&lt;/sub&gt;Al&lt;sub&gt;1.76&lt;/sub&gt;Ti&lt;sub&gt;6.24&lt;/sub&gt;O&lt;sub&gt;16&lt;/sub&gt;</td>
<td>Like sample 10 except for improved retention of K in sintering</td>
</tr>
<tr>
<td>12</td>
<td>Na&lt;sub&gt;2&lt;/sub&gt;Ti&lt;sub&gt;6&lt;/sub&gt;O&lt;sub&gt;13&lt;/sub&gt;</td>
<td>Coarse-grained ingot</td>
</tr>
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<sup>a</sup>Monofrax H, Harbison Carborundum, Falconer, New York.
TABLE III. - ELECTRICAL DATA AND CALCULATED PARAMETERS

<table>
<thead>
<tr>
<th>Sample</th>
<th>Activation energy for alkali mobility, $\Delta E$ (kJ/mole)</th>
<th>Calculated ac conductivity (at 298 K), $\sigma_{ac}$ $(\Omega \cdot cm)^{-1}$</th>
<th>$\sigma_{electronic}$</th>
<th>$\sigma_{electronic} + \sigma_{ac}$</th>
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<tbody>
<tr>
<td></td>
<td>kJ/mole</td>
<td>kcal/mole</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Na beta-aluminas $^a$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>22±2</td>
<td>5.3±0.4</td>
<td>3.7±0.7x10$^{-4}$</td>
<td>~0.01 to 0.001</td>
</tr>
<tr>
<td>2</td>
<td>20</td>
<td>4.9</td>
<td>1.2±0.2x10$^{-3}$</td>
<td></td>
</tr>
<tr>
<td>Ba-Mg-hollandites</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>26±2</td>
<td>6.3±0.4</td>
<td>1.9±0.3x10$^{-6}$</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>23</td>
<td>5.7</td>
<td>4.7±0.8x10$^{-5}$</td>
<td>&lt;2x10$^{-5}$</td>
</tr>
<tr>
<td>5</td>
<td>22</td>
<td>5.3</td>
<td>4.2±0.8x10$^{-5}$</td>
<td>&lt;5x10$^{-5}$</td>
</tr>
<tr>
<td>D. W.</td>
<td>20</td>
<td>4.8</td>
<td>9.3±0.5x10$^{-5}$</td>
<td></td>
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<tr>
<td>K-Mg-hollandites</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>22±2</td>
<td>5.3±0.4</td>
<td>4.2±0.7x10$^{-7}$</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>20</td>
<td>4.8</td>
<td>5.9±0.8x10$^{-4}$</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>21</td>
<td>5.1</td>
<td>1.7±0.3x10$^{-2}$</td>
<td>&lt;5x10$^{-4}$</td>
</tr>
<tr>
<td>K$_2$W$<em>4$O$</em>{13}$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>16±2</td>
<td>3.9±0.4</td>
<td>8.3±1.0x10$^{-5}$</td>
<td>&gt;0.99</td>
</tr>
<tr>
<td>K-Al-hollandites</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>25±2</td>
<td>6.1±0.4</td>
<td>7.0±0.9x10$^{-5}$</td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>23</td>
<td>5.6</td>
<td>3.5±0.6x10$^{-5}$</td>
<td>&lt;2.5x10$^{-6}$</td>
</tr>
<tr>
<td>Na$_2$Ti$<em>6$O$</em>{13}$</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>12</td>
<td>No dielectric loss peaks observed</td>
<td></td>
<td></td>
<td></td>
</tr>
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</table>

$^a$Samples 1 and 2 were measured and analyzed in ref. 2 and data are repeated here for comparison.
Figure 1. - Dielectric constant $\varepsilon'$ plotted against $1/T$ for hollandite sample 8.

Figure 2. - Dielectric loss $\varepsilon''$ plotted against $1/T$ for hollandite sample 8.
Figure 3. - Cole-Cole plot for sample 8, illustrating derivation of $\varepsilon_s - \varepsilon_{\infty}$.
(Data at frequency of $10^3$ Hz.)

Figure 4. - Calculated ac conductivity as $\sigma T$ plotted against $1/T$ for K-Mg-hollandites.
Figure 5. - Calculated ac conductivity as $\sigma T$ plotted against $1/T$ for Ba-Mg-hollandites.

Figure 6. - Calculated ac conductivity as $\sigma T$ plotted against $1/T$ for K-Al-hollandites.

Figure 7. - Calculated ac conductivity as $\sigma T$ plotted against $1/T$ for K$_2$W$_4$O$_{13}$. Sample 9.
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—NATIONAL AERONAUTICS AND SPACE ACT OF 1958

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