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# Ionic Conductivity of Some Alkaline Earth Halides

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The ionic conductivity above and below the melting temperature has been measured for the fluorides, chlorides, and bromides of calcium, strontium, and barium and for magnesium chloride. The observed behavior is of three types: *I* ($MgCl_2$, $CaCl_2$, $CaBr_2$, $BaBr_2$), there is an increase in conductivity of several orders of magnitude on melting; *II* ($BaCl_2$, $SrBr_2$), there is a solid–solid transition accompanied by a large increase in conductivity with little subsequent change on melting; and *III* ($CaF_2$, $SrF_2$, $BaF_2$, $SrCl_2$), the conductivity of the solid is continuous and changes only slightly on melting.

## Introduction

In marked constrast to the situation for the alkali halides, the ionic conductivity of the alkaline earth halides has not been very thoroughly explored. As part of a program of surveying the ionic conductivity behavior of different types of ionic crystal, we have examined a number of alkaline earth halides. In some instances, striking differences from the alkali halides are found. We have been concerned largely with high-temperature conductivity and have examined materials up to and just beyond the melting temperature. The emphasis is on the order of magnitude of the conductivity over wide temperature ranges rather than on precision measurements. Therefore, we have adopted techniques that permit easy measurement with a wide variety of materials. As a result, we have accepted as relatively unimportant errors such as that in the geometrical factor relating conductance to conductivity.

## Experimental Methods

For all the new data reported here, measurements have been made on samples obtained by freezing the molten salts in conductivity cells. For the fluorides, these cells were closed boron nitride crucibles maintained in flowing purified argon. The other salts were sealed (after drying) under vacuum in fused quartz conductivity cells. Cell constants were determined by measuring the conductivities of potassium chloride solutions in the same or similar cells. For salts other than the fluorides, a check on the cell constant was available by comparing the conductivities of the molten salts with the very accurate data of Bockris et al. (*1*). Uncertainties of as much as 10–20% remain because of such effects as lead resistance corrections, volume changes on freezing, etc. Platinum electrodes were used almost exclusively. These proved generally satisfactory except for $BaF_2$ where corrosion was apparent (possibly due to oxygen contamination).

Conductance measurements were made with a Wayne–Kerr universal impedance bridge operated at 1–10 kHz. Normally, there was only a small dispersion in conductivity in this range and data at 10 kHz were taken, as extrapolation to infinite frequency would result in a change much smaller than the uncertainty in cell constant. Occasionally, usually at the beginning of an experiment, a larger frequency dispersion of the conductivity was observed, almost certainly due to electrode effects. Such data were generally discarded.

Additional experimental details are provided under the discussion of individual salts or groups of salts below.

## The Alkaline Earth Fluorides

Data for $CaF_2$ have been reported earlier (*2*) and were obtained mainly in experiments with single crystals. These are shown in Fig. 1, in which newer data, taken just above and below the melting temperature, are included. Here and throughout, we plot log (conductivity) as a function of reciprocal temperature, for convenience and because it provides almost linear plots for many of the data; however, we attach no special significance to this method of plotting.

$SrF_2$ (Merck, "Suprapur") was studied exclusively as melt and solid obtained by freezing the melt. The data are also shown in Fig. 1. As for $CaF_2$ there is no measurable change in conductivity on melting. The results were reproducible for several samples and are in good accord at lower temperatures with those reported by others for single crystals (*3*, *4*).

$BaF_2$ (Merck, "Suprapur"), by way of contrast, presented problems. Platinum electrodes suffer attrition in molten $BaF_2$. Tungsten electrodes were also tried, with some success. However, we did not get sufficiently reproducible results to merit reporting them. Those we obtained showed, however, that the conductivity of melt was close to that of molten $SrF_2$ and, most significantly, there was again very little change in conductivity on freezing.

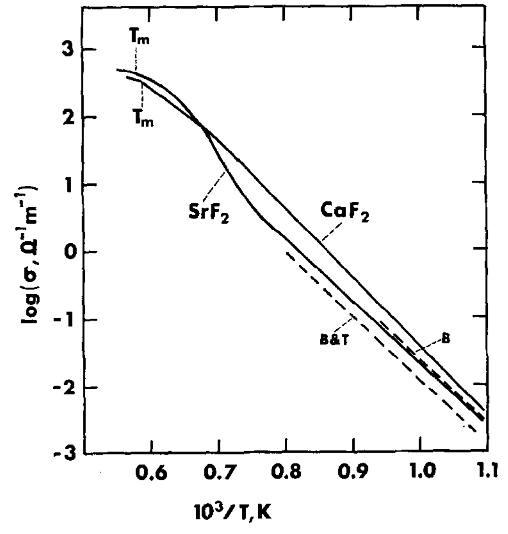

FIG. 1. The logarithm of the conductivity $\sigma$ as a function of reciprocal temperature for $CaF_2$ and $SrF_2$. Dashed lines are previous work on single crystals by Barsis and Taylor (*3*) and Bollman and his co-workers (B) (*4*). $T_m$ is the melting temperature.

## Barium Chloride and Strontium Bromide

Data for these two salts have been reported earlier (*5*). They are characterized by a solid state transition in which the conductivity increases by several orders of magnitude to a value characteristic of molten salts, and indeed there is only a small further increase in conductivity on melting.

## Strontium Chloride

Strontium chloride (from Research Organic Chemicals/Research Inorganic Chemicals) was thoroughly dehydrated by prolonged heating before sealing under vacuum in quartz conductivity cells with platinum electrodes. Conductivity measurements were made on the melt and on the solid sample obtained by freezing the melt. At lower temperatures, the results agreed quite well with previous measurements on single crystals (*3*, *6*). As with $SrBr_2$ and $BaCl_2$, at high conductivities we found some frequency dispersion of the conductivity,

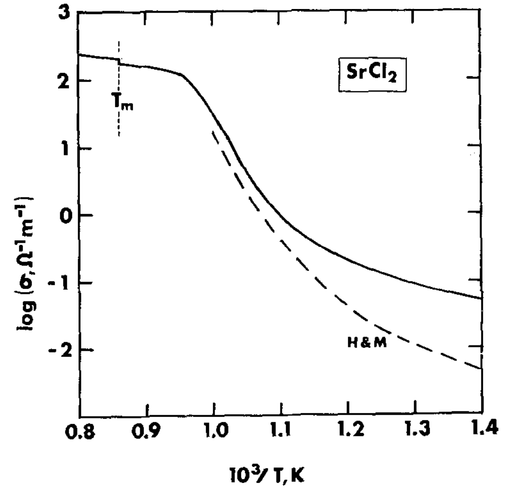

FIG. 2. The logarithm of the conductivity $\sigma$ as a function of reciprocal temperature for $SrCl_2$. The dashed line is from Hood and Morrison (*6*). $T_m$ is the melting temperature.

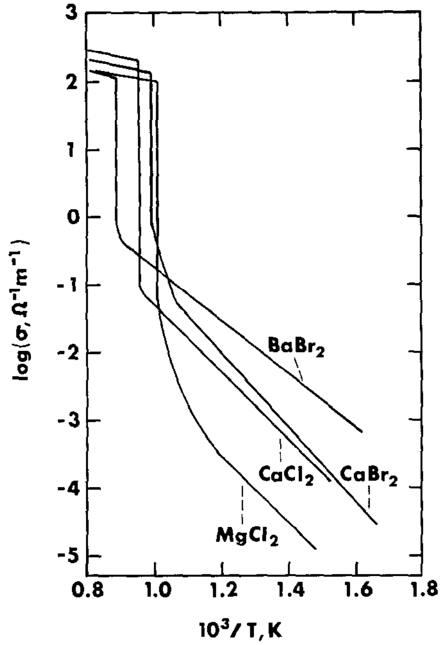

FIG. 3. The logarithm of the conductivity $\sigma$ as a function of reciprocal temperature for $MgCl_2$, $CaCl_2$, $CaBr_2$, and $BaBr_2$. The vertical portion of the curves corresponds to the melting temperature.

presumably due to electrode polarization. The measured resistance was plotted against the inverse square root of frequency and extrapolated to infinite frequency (7). The results are shown in Fig. 2. As with the fluorides the most striking feature is the high conductivity of the high-temperature solid and the small change on melting.

## Magnesium Chloride and Bromide, Calcium Chloride and Bromide, and Barium Bromide

Samples of $MgCl_2$, $6H_2O$, and $CaCl_2$ from Mallinckrodt Chemical Company (Analytical Reagent Grade) and of $MgBr_2$, $CaBr_2$ and $BaBr_2$ from Research Organic Chemicals/ Research Inorganic Chemicals were thoroughly dehydrated and sealed in quartz conductivity cells as for $SrCl_2$.

The $MgBr_2$ showed serious signs of decomposition on melting and data for this salt will not be reported. All the other salts showed sharp melting points in good agreement with literature values and no signs of discoloration, and gave reproducible conductivity results. The results, shown in Fig. 3, are remarkably similar for all four salts The conductivity of the solids is in the range typical of salts such as the alkali halides and, in contrast to the other materials described in this paper, the conductivity change on melting is several orders of magnitude.

## Discussion

In all of these salts it is extremely likely that the anion transport number is close to unity. Direct measurements of cation and anion mobilities have been made in some instances and transport numbers of the cations of the order of $10^{-6}$ or less have been found in the fluorides (*8*) and in $SrCl_2$ (*6*). Indeed, it is generally observed (*9*) that mobilities of the lower-charged ion in binary compounds are larger than those of the high-charged ions.

The possibility of electronic conductivity can be discounted (*10*). These are all transparent ionic crystals with band gaps greater than 5 eV.

In this paper, we wish to discuss only the magnitude of the conductivity and of conductivity changes and will not discuss activation energies or speculate about conduction mechanisms.

Elsewhere (*11*), simple salts, such as those under discussion have been divided into three classes. Class *I* comprises "normal" salts such as the alkali halides for which there is a large increase in ionic conductivity on melting. Salts in this class have an entropy of fusion that is about 10 $JK^{-1}$ per g ion (about 30 $JK^{-1}$ $mole^{-1}$ for the salts of this paper). $MgCl_2$, $CaCl_2$, $CaBr_2$, and $BaBr_2$ obviously fall into this class. Note that although three different structure types are represented here, the general features of the conductivity curves are remarkably similar (Fig. 3).

Class *II* salts have a first-order solid-state transition at which the conductivity increases by several orders of magnitude and in which there is an entropy increase comparable to the entropy of fusion (which in turn is correspondingly lower). AgI is a well-known example of this class, and clearly $BaCl_2$ and $SrBr_2$ are others.

TABLE I

CLASSIFICATION OF HALIDES BY TRANSITION TYPE AND ENTROPIES OF TRANSITION (IN $JK^{-1}mole^{-1}$)[a]

| | F | Cl | Br |
|---|---|---|---|
| Ca | *III*<br>17.6(*m*)[b] | *I*<br>27.2(*m*) | *I*<br>28.7(*m*) |
| Sr | *III* | *III*<br>14.2(*m*) | *II*<br>13.3(*s*) 11.3(*m*) |
| Ba | *III* | *II*<br>14.4(*s*) 13.3(*m*) | *I*<br>28.2(*m*) |

[a] From Ref. (*14*) except as noted. (*s*), solid–solid transition; (*m*) melting.

[b] From Ref. (*15*).

In Class *III* compounds, there is again a solid state transition, but it is now diffuse. It is clearly manifest in the thermodynamic properties of, e.g., $CaF_2$ and $SrCl_2$ (*12*). In these salts, there is a continuous increase in the conductivity of the salt from a value typical for "normal" crystals (such as the alkali halides) to a value typical of ionic melts. This is clearly shown in the data for $CaF_2$, $SrF_2$, and $SrCl_2$ and in the data for $PbF_2$ reported earlier (*13*). The entropy of fusion for salts in this class is anomalously low. All the dihalides in this class have the fluorite structure. Indeed, it is likely that all salts with the fluorite structure belong to this class.

In Table I we summarize the classification of the Ca, Sr, and Ba halides and collect literature values of entropies of fusion (and for $BaCl_2$ and $SrBr_2$ entropies of the solid–solid transition). Note that for class *I* halides the entropy of fusion is approximately 28 $JK^{-1}$ $mole^{-1}$, and about half this value for the others. Further, for the class *II* halides, the sum of the entropies of the solid state transition and of fusion is again about 28 $JK^{-1}$ $mole^{-1}$.

These data clearly support the notion (*2, 11*) that in Class *II* and *III* transitions, one ionic "sublattice" (in this instance, the anion one) disorders to a state analogous to that of a liquid. Certainly, the entropy change involved in the transition is comparable to the entropy of fusion and the conductivities of the solids are little further changed on melting.

## Acknowledgment

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