JOURNAL OF SOLID STATE CHEMISTRY 22, 171–177 (1977)

# Ionic Conductivity in KCl-Doped Polycrystalline $SrCl_2$

C. C. LIANG, J. R. REA, A. V. JOSHI, AND D. L. FOSTER

*P. R. Mallory & Co. Inc., Laboratory for Physical Science, Northwest Industrial Park, Burlington, Massachusetts 01803*

Received February 19, 1977

Conductivity studies on polycrystalline $SrCl_2$ doped with KCl have been carried out. The results are in substantial agreement with published results for single crystal work on $SrCl_2$, the activation energies being 1.8 eV for the intrinsic region, 0.35 eV for the extrinsic region, and 0.45 eV for the regions in which association of defects occurs. Most significant was the discovery of metastable electrolytes (4–5 mole% KCl in $SrCl_2$) having a conductivity of $1 \times 10^{-6}$ ohm$^{-1}$ cm$^{-1}$ at room temperature. These supersaturated solutions could be heat cycled up to 72°C, and they retained their initial conductivity after storage for 6 months at room temperature. This indicates that the equilibrium solubility of a dopant is not necessarily the limiting factor for extrinsic conductance in a solid material.

## Introduction

Several studies dealing with ionic conductivity in single crystals of $SrCl_2$ have been reported recently (*1–3*). These studies have established that the conductivity is overwhelmingly anionic and that a vacancy mechanism is favored. It was found that doping $SrCl_2$ with monovalent cations ($K^+$, $Na^+$) increased the conductivity, but that doping with trivalent cations ($La^{3+}$, $Y^{3+}$) decreased the conductivity. Furthermore, doping with $K^+$ ions increased the conductivity more than doping with $Na^+$ ions. The $K^+$ ion concentrations studied were 0.43 and 3.06 mole% (*1*) and 0.02 and 0.04 mole% (*3*).

The different regions in the plots of log $(\sigma T)$ vs $(1/T)$ for the nominally pure single crystals of $SrCl_2$ were interpreted as follows. The range from ~500 to ~650°C was assigned (*1, 3*) as the intrinsic conductivity region, in which the conductivity is mostly due to thermally created defects of the Frenkel type:

$$SrCl_2 \rightarrow Sr_{Sr}^{\times} + 2Cl_i' + 2V_{Cl}^{\bullet}$$

The apparent activation energy calculated from the slope of the plot in this region was 1.25 eV (*1*) or 1.9 eV (*3*). For temperatures greater than 650°C the slope of the plot was greater (~ 3 eV). This increase was attributed (*1, 3*) to the onset of a second order transition in $SrCl_2$ (*4*) involving a randomization of ions in the structure (*5*).

The region of the plots in a narrow temperature range around 350°C was assigned as the extrinsic region, in which the conductivity is due to vacancies caused by monovalent impurities:

$$MCl \rightarrow M_{Sr}' + Cl_{Cl}^{\times} + V_{Cl}^{\bullet}$$

The reported activation energies are 0.34 eV (*1*) and 0.38 eV (*3*). For temperatures below about 300°C the slope of the plots increased again, giving apparent activation energies of 0.46 eV (*1*) and 0.48 eV (*3*). This increase was attributed to the association of oppositely charged defects into complexes or clusters. Evidence for the existence of such clusters in trivalently doped $CaF_2$, the crystal structure of

Printed in Great Britain

ISSN 0022-4596

which is identical to that of $SrCl_2$, has been presented (*6*). In the case of doping $SrCl_2$ with KCl the defects could form associations such as the following:

$$\begin{aligned} M'_{Sr} + V^{\bullet}_{Cl} &\rightarrow [M_{Sr} - V_{Cl}]^{\times}, \\ 2M'_{Sr} + V^{\bullet}_{Cl} &\rightarrow [2M_{Sr} - V_{Cl}]^{\bullet}, \\ M'_{Sr} + 2\,V^{\bullet}_{Cl} &\rightarrow [M_{Sr} - 2V_{Cl}]^{\bullet}, \end{aligned}$$

etc.

As a part of our continuing investigations of solid state electrolyte materials, we have measured the conductivity as a function of temperature for polycrystalline $SrCl_2$ incorporated with up to 15 mole% KCl. The results of these measurements are reported here and are compared to the results of the single crystal studies described above. Discussion of the discovery of a relatively high conducting ($1 \times 10^{-6}$ $ohm^{-1}$ $cm^{-1}$ at 25°C) metastable mixture is included.

## Experimental

Strontium chloride was obtained from two sources. Cerac/Pure $SrCl_2$ (99.5%) was used as received. Fisher Certified ACS-grade $SrCl_2 \cdot 6\ H_2O$ was heated at 130°C under vacuum for several hours to obtain anhydrous $SrCl_2$, which was used without further treatment. Fisher Certified ACS-grade KCl was dried before use. The trivalent dopants $LaCl_3$ and $CrCl_3$ were obtained anhydrous from Ventron (Alfa Products) and used as received. All material preparations and conductivity measurements were carried out in an argon-filled Vacuum Atmospheres dry box.

All KCl–$SrCl_2$ mixtures containing 1 mole% or greater concentrations of KCl were prepared using the pure materials. Mixtures containing less than 1 mole% KCl were prepared by diluting a previously made 2.5 mole% mixture. All preparations were carried out as follows. Appropriate amounts of material were weighed (usually to total about 10 g) and put into an alumina crucible, which was then placed in a furnace at 1000–1100°C. The contents of the crucible were soaked for <10 min after becoming molten and then quenched by pouring into a stainless steel pan. After the material had cooled, it was ground for at least 1 hr using an alumina mortar and pestle on a Fisher mechanical grinder.

Conductivity cells were typically made by pressing 500 mg of electrolyte to 4000 psi in a 0.60 in. diameter steel die and then pressing on graphite electrodes at 50,000 psi. The thickness of the electrolyte layer in a cell was determined by measuring the thickness of an equal amount of the same electrolyte pressed to 50,000 psi without the electrodes. The use of electrode materials other than graphite did not result in significantly different measurements.

The conductivity measurements were carried out at various temperatures with the cells held in lava sample holders in a thermostatted Blue M furnace. The cell resistance was determined using a General Radio conductance bridge at 1000 Hz, or for resistances greater than $2 \times 10^5$ ohms, a Keithly electrometer. The conductivity was calculated from the cell's resistance and area and the thickness of the electrolyte.

## Results

A plot of the conductivity ($\sigma$) of $SrCl_2$ vs concentration of KCl for the freshly prepared electrolytes at room temperature is shown in Fig. 1. The maximum conductivity was $1 \times 10^{-6}$ $ohm^{-1}$ $cm^{-1}$ and occurred at the 4–5 mole% compositions. The low concentration region is expanded in the upper right-hand portion of the figure to emphasize that the incorporation of only 0.1 mole% KCl increased the conductivity of $SrCl_2$ by two orders of magnitude to $3 \times 10^{-8}$ $ohm^{-1}$ $cm^{-1}$.

Measured conductivities at room temperature for nominally pure $SrCl_2$ ranged from $1 \times 10^{-11}$ to $3 \times 10^{-10}$ $ohm^{-1}$ $cm^{-1}$, depending largely on the compressibility of the material, the least compressible giving the lowest conductivity, as expected. The densities of the pressed pellets of $SrCl_2$ ranged from 65 to 90% of the theoretical densities. The lower-densities seemed more characteristic of the Fisher $SrCl_2$

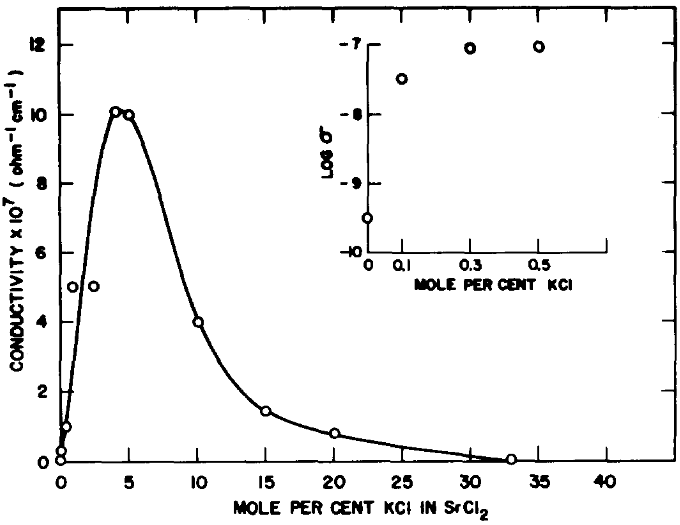

FIG. 1. Conductivity of $SrCl_2$ as a function of KCl concentration.

and may be related to low impurity concentrations, since all pellets of doped $SrCl_2$ had densities in the 91–96% range.

The low, varying densities caused nonreproducible results for conductivity measurements as a function of increasing temperature for pure $SrCl_2$ and low dopant concentrations ($\leqslant$0.5 mole% KCl). These measurements tended not to fall on smooth curves until temperatures of 400–500°C were reached. All subsequent measurements as a function of decreasing temperature were higher than the corresponding measurements made for increasing temperature. Also, the decreasing temperature plots formed smooth curves which were reproducible depending on the starting material. These results indicate a sintering reaction at temperatures above 500°C.

Doping with trivalent metal ions did not significantly alter the room temperature conductivity of pure $SrCl_2$, as shown below.

| Dopant | Conc. (mole%) | Conductivity ($ohm^{-1}$ $cm^{-1}$) |
|---|---|---|
| $LaCl_3$ | 0.5 | $5.8 \times 10^{-11}$ |
| $LaCl_3$ | 1 | $4.1 \times 10^{-11}$ |
| $LaCl_3$ | 3 | $3.6 \times 10^{-11}$ |
| $CrCl_3$ | 1 | $3.6 \times 10^{-11}$ |

The $SrCl_2$ used here (Fisher) had a conductivity of 3–4 × $10^{-11}$ $ohm^{-1}$ $cm^{-1}$ at room temperature.

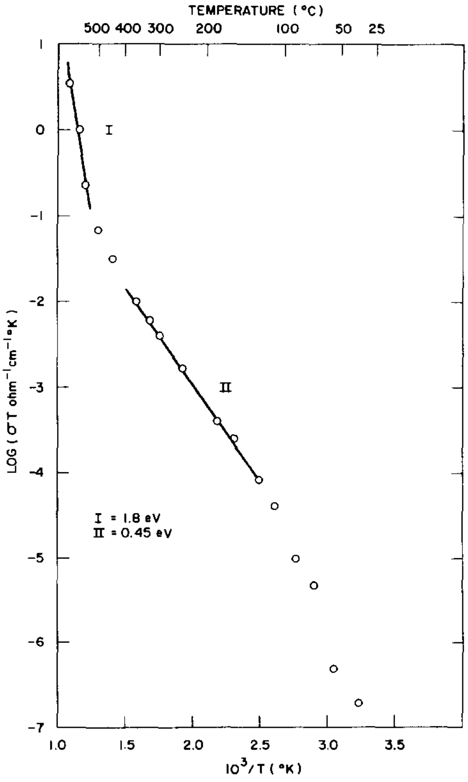

FIG. 2. log ($\sigma T$) vs $1/T$ for nominally pure $SrCl_2$.

TABLE I

COMPARISON OF ACTIVATION ENERGIES MEASURED IN SINGLE CRYSTALS AND IN THE PRESENT WORK

| | Barsis and Taylor (*1*) (eV) | Hood and Morrison (*2*) (eV) | Pailloux *et al.* (*3*) (eV) | Present work (eV) |
|---|---|---|---|---|
| $T > 650°C$ | 3 | 3.2 | — | — |
| $500 < T < 650°C$ (intrinsic) | 1.25 | — | 1.9 | 1.8 |
| Extrinsic | 0.34 | 0.4 ± 0.1 | 0.38 | 0.35 |
| Association | 0.46 | | 0.48 | 0.48 |
| Precipitation | — | — | — | 0.56 |

The effect of temperature on the conductivity of (sintered) nominally pure $SrCl_2$ is shown in Fig. 2, in which log ($\sigma T$) is plotted against reciprocal temperature. Although only three measurements were taken for $T > 500°C$ (Region I in Fig. 2), the calculated activation energy (1.8 eV) is in the range reported in the single crystal studies for intrinsic conductivity (see Table I). Region II in Fig. 2 has a slope corresponding to an activation energy of 0.45 eV. The slope for the region $T < 125°C$ was not calculated since there were large errors involved in measuring the very high resistances by the method employed.

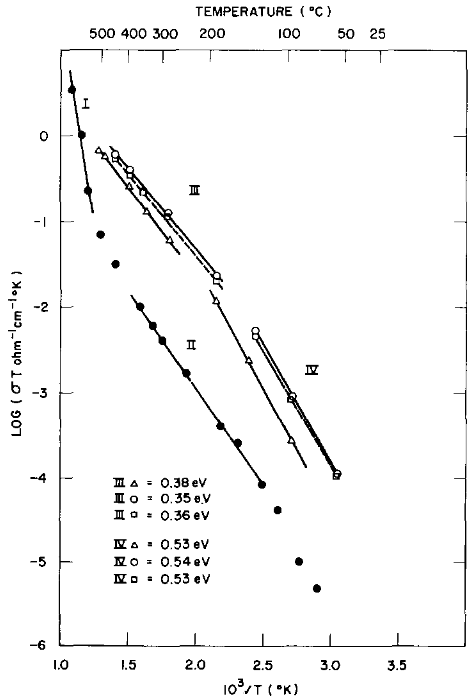

FIG. 3. log ($\sigma T$) vs $1/T$ for 0.1, 0.3, and 0.5 mole% KCl in $SrCl_2$. △ = 0.1 mole% KCl, ○ = 0.3 mole% KCl, ■ = 0.5 mole% KCl (● = nominally pure $SrCl_2$).

The effect of temperature on the conductivity of 0.1, 0.3, and 0.5 mole% KCl in $SrCl_2$ is shown in Fig. 3. Although the positions of the curves for these low concentrations vary somewhat, possibly due to dilution errors, the slopes in the regions indicated are reproducible within error. The activation energies calculated for these regions are as follows:

| | Region | |
|---|---|---|
| Conc. (mole%) | III (eV) | IV (eV) |
| 0.1 | 0.38 | 0.53 |
| 0.3 | 0.35 | 0.54 |
| 0.5 | 0.36 | 0.53 |
| Average | 0.36 | 0.53 |

Figures 4, 5, and 6 show log ($\sigma T$) vs ($1/T$) curves for 1, 5, and 15 mole% KCl incorporated in $SrCl_2$, respectively. The curve for nominally pure $SrCl_2$ is shown for comparison. In contrast to the observed behavior for

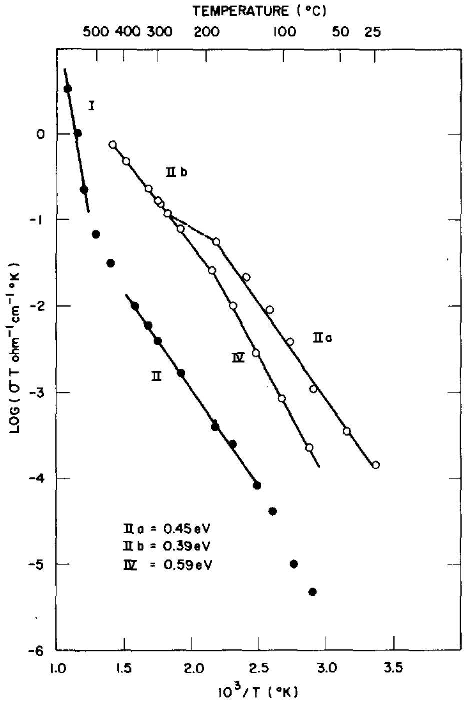

FIG. 4. log ($\sigma T$) vs $1/T$ for 1 mole% KCl in $SrCl_2$. Lower plot with closed circles shows nominally pure $SrCl_2$ for comparison.

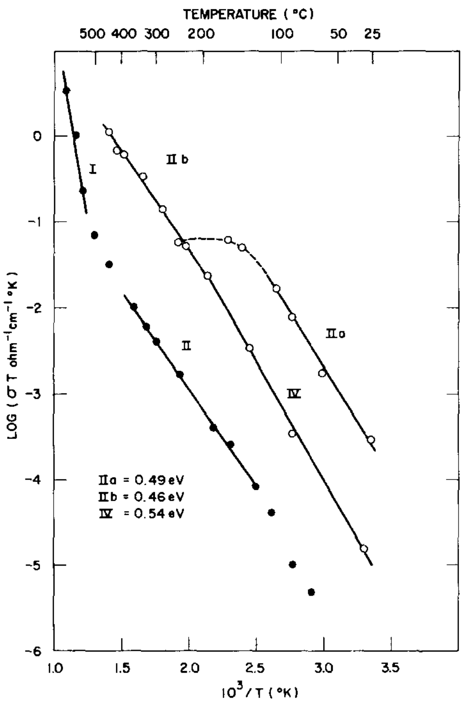

FIG. 5. log ($\sigma T$) vs $1/T$ for 5 mole% KCl in $SrCl_2$. Lower plot with closed circles shows nominally pure $SrCl_2$ for comparison.

the lower concentrations, the initial increasing temperature curves were higher than the decreasing temperature curves up to about 180°C. At higher temperatures the increasing and decreasing temperature curves were the same. If the temperature were increased again after one complete heating cycle for a given sample, the lower curve was followed. Thus the upper curve for these concentrations was unattainable after once raising the temperature above 150°C. Heat cycling should be carried out on the upper curves for temperatures lower than 72°C. Cells stored at room temperature for 6 months retained their initially high conductivity. The decreasing temperature plots in Fig. 4 and 5 for 1 and 5 mole% KCl, respectively, are practically identical and agree well with the plot obtained by Barsis and Taylor (*1*) for 3 mole% KCl in a single crystal of $SrCl_2$. The activation energies calculated from the linear regions of the plots in Figs. 4, 5, and 6 are as follows:

| | Region | | |
|---|---|---|---|
| Conc. (mole%) | IIa (eV) | IIb (eV) | IV (eV) |
| 1 | 0.45 | 0.39 | 0.59 |
| 5 | 0.49 | 0.46 | 0.54 |
| 15 | 0.47 | 0.48 | 0.59 |
| Average | 0.47 | 0.44 | 0.57 |

Table II summarizes the activation energies taken from Figs. 2–6. The values of 0.45 eV for Region II (Fig. 2) for nominally pure $SrCl_2$, 0.47 eV for Regions IIa (Figs. 4–6) for 1, 5, and 15 mole% KCl, and 0.44 eV for Regions IIb (Figs. 4–6) for 1, 5, and 15 mole%

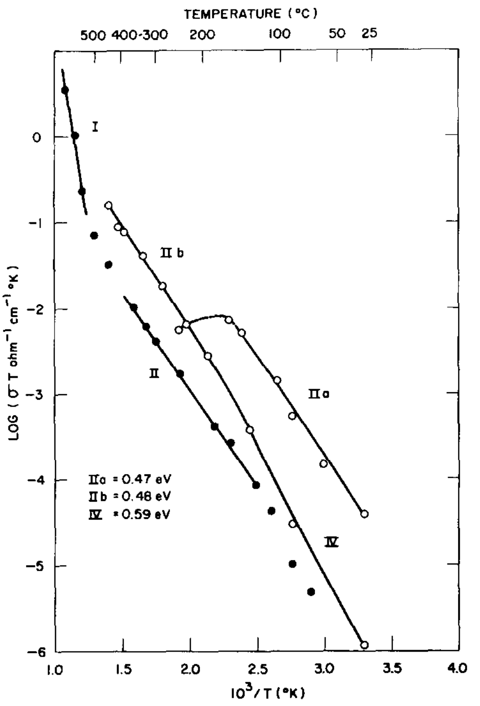

FIG. 6. log ($\sigma T$) vs $1/T$ for 15 mole% KCl in $SrCl_2$. Lower plot with closed circles shows nominally pure $SrCl_2$ for comparison.

KCl are essentially the same with an overall average of 0.46 eV. The average value of 0.36 eV for Region III (Fig. 3) for 0.1, 0.3, and 0.5 mole% KCl is significantly lower. The activation energies for all of the KCl mixtures in the 25–150°C range (Regions IV, Figs. 3–6) can probably be considered to be the same within error with an average of 0.55 eV.

## Discussion

The activation energy of 0.36 eV for Region III ($525 > T > 275$°C) for 0.1, 0.3, and 0.5 mole% KCl (Fig. 3) agrees well with the value of the activation energy given for extrinsic conductivity in nominally pure single crystals of $SrCl_2$ (see Table I). Interestingly, a region having this low a slope was not observed for the single crystal $SrCl_2$ containing 0.43 mole% KCl (*1*).

The plots for the corresponding temperature regions for the higher concentrations of KCl as well as the plots for the metastable regions have steeper slopes, the apparent activation energy being 0.46 eV. This agrees well with values for the slopes in the 200–300°C range for the single crystal work (see Table I), in which the steeper slopes are attributed to the association of defects. Similar effects must also obtain in the present work for nominally pure $SrCl_2$, which has an apparent activation energy of 0.45 eV in the 125–350°C range. The absence of a purely extrinsic conductivity range for nominally pure $SrCl_2$ can be attributed to the onset of intrinsic conductivity at a temperature lower than that necessary to dissociate entirely the associated defects. The purely extrinsic region for the single crystals of $SrCl_2$ of Barsis and Taylor is very narrow, apparently less than 50°.

The still greater apparent activation energy, 0.55 eV, for all of the doped samples in the range 25–150°C can be attributed to precipitation of KCl, which results in a lower

TABLE II

SUMMARY OF ACTIVATION ENERGIES TAKEN FROM FIGS. 1–6[a]

| Conc. KCl (mole%) | Temperature Regions (Figs. 1–6) I | II | IIa | IIb | III | IV |
|---|---|---|---|---|---|---|
| 0 | 1.8 | 0.45 | | | | |
| 0.1, 0.3, 0.5 | | | | | 0.36 | 0.53 |
| 1, 5, 15 | | | 0.47 | 0.44 | | 0.57 |
| Average | 1.8 | | 0.46 | | 0.36 | 0.55 |

[a] All values are given in electron volts.

concentration of charge carriers. If this is the case, however, the solubility of KCl in $SrCl_2$ must be less than 0.1 mole% at room temperature, since the greater slope does appear in the 0.1 mole% KCl plot. If this analysis is correct, the question arises as to why metastable regions are not observed for the 0.1, 0.3, and 0.5 mole% mixtures. One possibility is that the low dopant concentrations do not allow for a sufficiently high compressibility for the supersaturation effect to be observed. In other words the gaps at the grain boundaries may be the limiting factor for conductivity in the freshly prepared low concentration materials. As was noted in the Results section, pure $SrCl_2$ was the least compressible material.

The most significant results of this study are the initially high conductivity curves for the 1, 5, and 15 mole% KCl mixtures exhibited in Figs. 4, 5, and 6, respectively. The curves are indicative of metastable supersaturated solid solutions of KCl in $SrCl_2$ formed by quenching the molten solutions. The metastable solid solutions are stable up to about 180°C, where precipitation of the excess KCl takes place. They seem to be indefinitely stable at room temperature. The shift of the 15 mole% curves to lower conductivities are indicative of the effectively reduced cross sectional area of the cell due to KCl inclusions. These results are significant in that they indicate that the equilibrium ionic conductivity of a material as determined by single crystal studies is not necessarily the highest ionic conductivity which can be attained.

## References

1. E. BARSIS AND A. TAYLOR, *J. Chem. Phys.* **45**, 1154–1162 (1966).
2. G. M. HOOD AND J. A. MORRISON, *J. Appl. Phys.* **38**, 4796–4802 (1967).
3. M. PAILLOUX, A. GERVAIS, M. JACQUET, AND M. BATHIER, *C.R. Acad. Sci. Paris Ser. B*, **274**, 991–994 (1972).
4. A. S. DWORKIN AND M. A. BREDIG, *J. Chem. Phys.* **67**, 697–698 (1963).
5. V. CROATTO AND M. BRUNO, *Gazz. Chim. Ital.* **76**, 246–254 (1946).
6. A. K. CHEETHAM, B. E. F. FENDER, AND M. J. COOPER, *J. Phys. C.* **4**, 3107–3121 (1971).