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Electrical Properties of $K_2FeCl_5 \cdot H_2O$ and K_2AlF_5

J. SCHOONMAN,* E. E. HELLSTROM, AND R. A. HUGGINS

Center for Materials Research, Stanford University, Stanford, California 94305

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The electrical conductivity of nominally pure $K_2FeCl_5 \cdot H_2O$ and anhydrous K_2AlF_5 has been studied from 300 to 690°K. $K_2FeCl_5 \cdot H_2O$ exhibits mixed ionic and electronic conduction, whereas K_2AlF_5 is a pure ionic conductor. The mass and charge transport processes in $K_2FeCl_5 \cdot H_2O$ seem to be governed by deviations from both molecularity and stoichiometry. At elevated temperatures both potassium and chloride ions are mobile in $K_2FeCl_5 \cdot H_2O$.

1. Introduction

Ternary alkali fluoroaluminates of general compositions ABX_4, A_2BX_5, and A_3BX_6 crystallize in layer (ABX_4), channel (A_2BX_5), or framework (A_3BX_6) structures.

The electrical properties of nominally pure and doped potassium tetrafluoroaluminate were reported elsewhere (*1*). The present paper deals with electrical properties of two compounds of general composition $A_2BX_5 \cdot (xH_2O)$, which crystallize in channel structures.

Potassium pentachloroferrate (III) monohydrate (erythrosiderite), $K_2FeCl_5 \cdot H_2O$, has an orthorhombic structure with unit cell dimensions $a = 13.57$, $b = 9.92$, and $c = 6.93$ Å. It contains four molecules per unit cell (*2*) and does not dehydrate upon heating. The structure can be looked upon as containing a three-dimensional network of channels.

Potassium pentafluoroaluminate monohydrate, $K_2AlF_5 \cdot H_2O$, dehydrates at temperatures higher than 545 K (*3*). K_2AlF_5 has an orthorhombic structure and is isostructural with K_2FeF_5 (*4*). The unit cell has the dimensions $a = 7.10$, $b = 12.60$, and $c = 19.60$ Å and contains 16 formula units (*3, 4*).

$K_2FeCl_5 \cdot H_2O$ contains a reducible $3d$ ion, and therefore, it is expected that this material will exhibit both electronic and ionic conduction. In contrast, conduction in K_2AlF_5 is expected to be predominantly ionic, as it does not contain easily reducible species. This paper reports data on the nature of the electrical charge transport in both $K_2FeCl_5 \cdot H_2O$ and K_2AlF_5.

2. Experimental Aspects

2a. *Materials*

$K_2FeCl_5 \cdot H_2O$ was obtained commercially from the Research Organic/Inorganic Chemical Corporation. Pellets could easily be pressed at pressures of the order of 10^5 psi. $K_2AlF_5 \cdot H_2O$ was prepared from stoichiometric proportions of KHF_2 (made from KF and concentrated HF) and AlF_3. The latter was prepared from $Al(OH)_3$ dissolved in concentrated HF (*1*). The resulting suspension was dried and X-ray examination confirmed the presence of pure $K_2AlF_5 \cdot H_2O$. This was subsequently dehydrated to give K_2AlF_5 at about 625°K in a purified argon stream. Pellets of K_2AlF_5 were also obtained by hot-pressing $K_2AlF_5 \cdot H_2O$ at about 725°K, during which dehydration occurred.

2b. *Electrical Measurements*

Pressed pellets, provided with painted or sputtered Pt electrodes, were spring-loaded in

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* Present address: Solid State Department, State University of Utrecht, Sorbonnelaan 4, Utrecht–De Uithof, The Netherlands.

an evacuable conductivity cell. Alternating current conductivities were measured with an impedance bridge (G.R. 1608A). The frequency dependence of the admittance parameters was studied in the range 0.025–50 kHz with a capacitance bridge (G.R. 1615) using an external oscillator and an amplified null-detector.

Direct current polarization was measured with a Cary electrometer (model 401), using a dry cell as a constant voltage source. Transference numbers for $K_2FeCl_5 \cdot H_2O$ were measured using $BaCl_2$-doped KCl as protective electrolytes in an arrangement described elsewhere (*1*).

3. Experimental Results

Figure 1 shows the temperature dependence of the electrical conductivity at 1 kHz of pellets of nominally pure $K_2FeCl_5 \cdot H_2O$ and K_2AlF_5. Except for region I ($K_2FeCl_5 \cdot H_2O$), the conductivity results were independent of the frequency in the range measured.

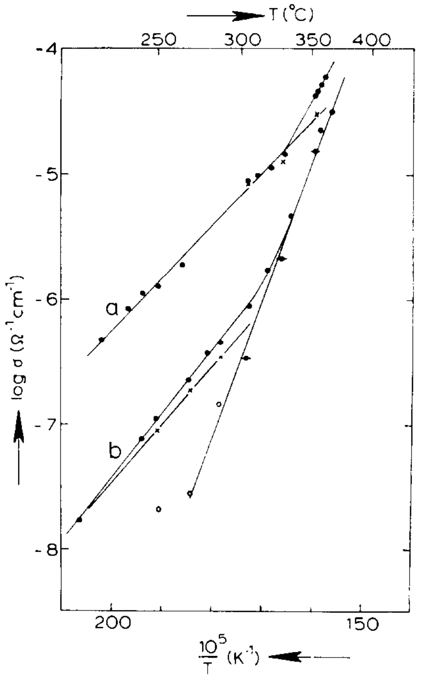

FIG. 2. Ionic (⊖, ○) and electronic (×) contributions to the total conductivity (·) for two different pellets of $K_2FeCl_5 \cdot H_2O$. ⊖, ionic contribution to curve a, and ○ to curve b.

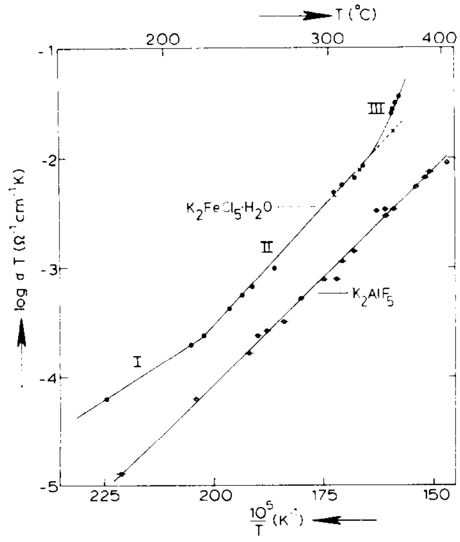

FIG. 1. The temperature dependence of the electrical conductivity of $K_2FeCl_5 \cdot H_2O$(· ·) and of K_2AlF_5 (⊖⊖) at 1 kHz. × = steady-state dc conductivity values.

The electrical conductivity of $K_2FeCl_5 \cdot H_2O$ was found to vary from sample to sample. Two examples are presented in Fig. 2. In this figure the total conductivity, as well as the ionic and electronic contributions, are plotted as functions of the reciprocal temperature. The electronic contribution was deduced from steady-state values obtained by dc polarization measurements using ionically blocking electrodes. Conductivities calculated from initial transient dc currents were comparable to those obtained by ac measurements. Linear current-voltage characteristics were observed for the initial as well as the steady-state currents over the voltage range 0–0.8 V.

The electrical conductivity of K_2AlF_5 is reproducible upon heating and cooling in the region 445–690°K.

The majority of the pellets of $K_2FeCl_5 \cdot H_2O$ exhibited conductivities close to the conductivities expressed by curve b in Fig. 2. The conductivity of these samples above 585°K is reproducible upon heating and cooling. This is demonstrated in Fig. 3.

Transference number measurements were performed at temperatures where $K_2FeCl_5 \cdot$

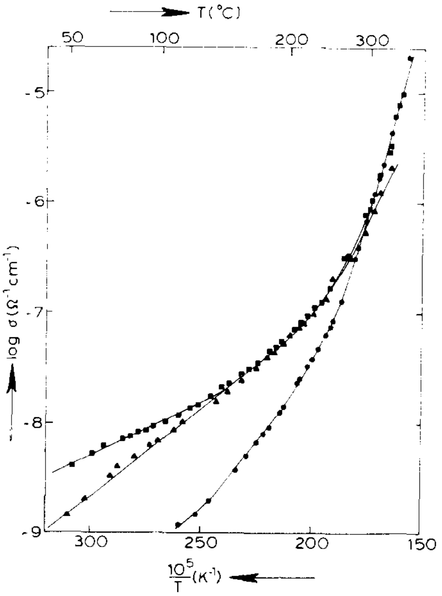

FIG. 3. The temperature dependence of the electrical conductivity of $K_2FeCl_5 \cdot H_2O$ (··) at 1 kHz. After cooling to room temperature the same sample was reheated: ■■, ac conductivity; ▲▲, steady-state dc conductivity.

H_2O samples exhibited predominately ionic conductivity. Assuming negligible proton conductivity, and $t_{K^+} + t_{Cl^-} = 1$, we obtained 0.43 for the transference number of the potassium ions at 640°K. At $T = 686°K$, $t_{K^+} = 0.75$.

For nominally pure K_2AlF_5 the dc steady-state current is negligibly small compared to the initial transient current, indicating a very small electronic contribution to the conductivity.

Conductivity activation enthalpies are gathered in Table I. The subscripts *e* and *i* denote electronic and ionic conductivity, respectively. The low-temperature activation enthalpy for the total conductivity is not included in the table, since conductivities are frequency-dependent up to about 490°K.

TABLE I

CONDUCTIVITY ACTIVATION ENTHALPIES FOR $K_2FeCl_5 \cdot H_2O$ AND K_2AlF_5

	$K_2FeCl_5 \cdot H_2O$	K_2AlF_5
ΔH_e (eV)	0.31, 0.83	
ΔH_i (eV)	2.30	0.79

4. Discussion

The electrical conductivity of $K_2FeCl_5 \cdot H_2O$ is of mixed character: Both ionic and electronic species contribute to the conductivity. For $T < 490°K$ and $T > 585°K$ mixed ionic and electronic conduction is measured, whereas at intermediate temperatures electronic conduction prevails. From the results presented in Figs. 2 and 3 we arrive at the conclusion that the mobile electronic species are minority carriers as they can be expected to have higher mobilities than the ionic point defects.

In Figs. 2 and 3 it is seen that different $K_2FeCl_5 \cdot H_2O$ samples exhibit equal ionic contributions at high temperatures, but different electronic contributions to the total conductivity, whereas at temperatures lower than about 570°K ionic as well as electronic contribution show differences. This indicates a deviation from stoichiometry. The transference number measurements show that chloride ions are mobile at low temperatures, whereas at high temperatures potassium conduction takes over. In view of the temperature-cycling experiment (Fig. 3) we ascribe, therefore, the deviation from stoichiometry to the reaction

$$Cl_{Cl}^{\times} \rightarrow V_{Cl}^{\cdot} + e' + \tfrac{1}{2}Cl_2(g), \qquad (1)$$

whereby

$$Fe_{Fe}^{\times} + e' \rightleftharpoons Fe_{Fe}' \qquad (2)$$

may be of influence as well. Thermoelectric power measurements at 503°K revealed that the hot electrode was positive, indicating *n*-type conduction (*5*). The activation enthalpy of 0.31 eV can then be related to conduction of electrons in $K_2FeCl_5 \cdot H_2O$. Evidence for the combined presence of Fe(II) and Fe(III) in $K_2FeCl_5 \cdot H_2O$ stems from the presence of a broad absorption in the spectral region 210–700 μm. Since both potassium and chloride ions are mobile at high temperatures (region III) a deviation from molecularity (*6*) seems to be present as well. It may be represented by

$$(K_K^{\times})_{2-\delta}(V_K')_{\delta}(Fe_{Fe}^{\times})(Cl_{Cl}^{\times})_{5-\delta}(V_{Cl}^{\cdot})_{\delta} \cdot H_2O \qquad (3)$$

since simultaneous presence of mobile interstitial potassium as well as interstitial chloride ions in the channels of the structure seems unlikely.

The electrical conductivity of K_2AlF_5 is predominately ionic over the temperature range 440 to 690°K. In the case of $KAlF_4$, it was shown (*1*) that samples could be prepared easily with deviations from molecularity and that the ionic species dominating the conductivity could be varied. Either fluoride ions (large deviation from molecularity), or potassium ions are mobile, depending on composition. For K_2AlF_5 a similar preparation method was employed. Although X-ray examination of the hydrated compound confirmed the presence of pure $K_2AlF_5 \cdot H_2O$, the poor sensitivity of this technique excludes any firm conclusion about compositional influences on conductivities. A recent mass-spectrometric study of the thermodynamic properties of the KF–AlF_3 system (*7*) shows at 838°K the partial pressures over the condensed phase $2KF \cdot AlF_3$ to be $P(KAlF_4) \simeq P(KF) > P(AlF_3)$. This means that both potassium ion vacancies and fluoride ion vacancies can be present in K_2AlF_5, with an overall composition similar to the one, except for the water molecule, given above for $K_2FeCl_5 \cdot H_2O$, or generally $(A_{2(1-x)}B_x)X_{2+x}$ with $x > \frac{1}{2}$.

The deviations from the ideal composition do not allow at present a quantitative interpretation of the conduction activation enthalpies of both compounds. Nevertheless, quantitative data on $KAlF_4$ (*1*) and cryolite (Na_3AlF_6) (*8*, *9*) suggest that the stable compounds in the system $KF\text{-}AlF_3 : K_jAlF_{3+j}$ with $j = 1$, 2, and 3 are potential potassium conductors. From room temperature up to 700°K $\sigma(K_3AlF_6) \simeq \sigma(K_2AlF_5) > \sigma(KAlF_4)$ (*10*), the former two compounds exhibiting at 700°K conductivities of the order of 2×10^{-5} Ω^{-1} cm^{-1}. Such conductivities are well above the conductivities of classical electrolytes such as the potassium halides, but about three orders of magnitude less than the superionic conductor potassium-β-alumina.

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