JOURNAL OF SOLID STATE CHEMISTRY **18**, 141–147 (1976)

Studies of Potassium Ferrite $K_{1+x}Fe_{11}O_{17}$. I. Electronic Conductivity and Defect Structure

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Received January 5, 1976

The electronic conductivity of the nonstoichiometric potassium ferrite phase (with the β-alumina structure) has been measured as a function of temperature and potassium ion concentration. The latter was varied by coulometric titration using the cell: K_{liq}/K–β-alumina/$K_{1+x}Fe_{11}O_{17}$. At 523°K the conductivity increased nearly linearly as x was increased from 0.09 to 0.65 while the activation energy for conduction decreased from 0.1 to 0.07 eV. The cell emf was completely reversible. The results are consistent with the view that the excess potassium ions are charge compensated by reduction of Fe^{3+} to Fe^{2+}, and a comparison with results in the literature for some iron-containing spinels suggests that a similar small polaron electron hopping mechanism operates.

Introduction

β- and β″-alumina are being extensively investigated because of their high ionic conductivity and chemical inertness which makes them attractive solid electrolytes for batteries. The isomorphous iron analogs on the other hand have received much less attention. The latter exhibit electronic as well as ionic conductivity and have been used, in the form of solid solutions with β-alumina, as alkali-metal-ion reversible electrodes in conjunction with β-alumina electrolyte (*1*, *2*). Hever (*1*) suggested that the electronic conductivity was due to the presence of Fe^{2+} as well as Fe^{3+} in the structure and moreover that alkali metal ions could pass from the electrolyte into the ferrite converting equal numbers of Fe^{3+} ions to Fe^{2+}:

$$Fe^{3+} + e + Na^{+} \rightleftharpoons Fe^{2+}Na^{+}.$$

The alkali ion excess could be accommodated in the loosely packed layers in the structure. This was supported by the fact that addition of Ti^{4+} ions increased the electronic conductivity by producing extra Fe^{2+} ions, while Roth (*3*) found that the electronic conductivity was greatest in samples with the largest Fe^{2+} content as found by analysis. On the other hand, Mössbauer measurements on a mixed ferrite–aluminate (*2*) cathode failed to show the presence of Fe^{2+} until a considerable charge has been passed and alternative reactions were suggested.

Most work to date has been on ferrites with many additives or over very small ranges of stoichiometry and it seemed that a study covering a wide range of stoichiometry on a relatively pure, well-defined phase would help to clarify the position.

In the present work the electronic conductivity of potasium ferrite in the form of a high-density polycrystalline ceramic has been measured as a function of temperature and potassium content changed by coulometric titration using the cell:

$$K_{liq}/K\text{–}\beta\text{-alumina}/K\text{-ferrite}.$$

Mössbauer measurements on samples with varying potassium contents are reported in Part II of our study (*4*).

Printed in Great Britain

Experimental

Preparation of Potassium Ferrite

For the coulometric titration experiments (sample A), Analar grade potassium carbonate and ferric oxide (from A. R. ferric ammonium sulphate heated to 1120°K for 2 days) were ground together in a 1:6.5 mole ratio and heated to 1170°K in oxygen for 22 hr. X-ray powder photographs showed the product to consist predominantly of the three-block phase with some two-block phase. Nothing else could be detected. The powder was cold pressed, sealed in platinum foil, and placed in a bed of alumina powder in an alumina hot press die. After heating under vacuum at 523°K to ensure removal of volatile materials, the sample was hot pressed in an oxygen atmosphere at 1400°K for 6 hr using a pressure of 7500 psi. The resulting pellets had a density of 4.19 $g \cdot cm^{-3}$ (98 % theoretical) and a potassium content of 6.27 ± 0.25 wt % (equivalent to the formula $K_{1.516}Fe_{11}O_{17}$ or K_2O 7.3 Fe_2O_3, depending on the defects present, to be discussed later). Potassium analysis was by flame emission after dissolution of the sample in concentrated hydrochloric acid followed by suitable dilution. X-ray photographs showed mainly two-block phase with some three-block, but again no other phases. The *d* spacings for the two-block phase agreed closely with those of Dyson and Johnson (*5*) while those for the three-block phase could be easily indexed by analogy with the three-block mixed ferrite–aluminate data reported by the same authors. The three-block to two-block conversion was first observed to occur by Rooymans et al. (*6*) above 1320°K. For the later low-temperature conductivity experiment the sample (B) was prepared in a slightly different manner that had been developed to give higher densities. This involved vacuum hot pressing of a similar platinum-sealed pellet in a graphite die for 6 min at 1470°K under a pressure of 4000 psi. The encapsulation and surrounding alumina powder successfully prevented reduction of the sample, or serious alkali loss. The pellet had a density of 4.31 $g \cdot cm^{-3}$ (ca. theoretical) and a potassium content of 6.84 ± 0.24 wt % (corresponding to the formula $K_{1.665}Fe_{11}O_{17}$ or K_2O. 6.6 Fe_2O_3). Again it contained mainly two-block phase with some three-block.

Conductivity Cell

The experimental arrangement is shown in Fig. 1. A 0.7 mm thick disk of sodium β-alumina (Electricity Council) was exchanged for potassium by immersion in mixtures of molten sodium and potassium nitrates containing progressively higher concentrations of potassium nitrate over a period of 10 days. This was sealed to the end of an α-alumina tube, to the other (cold) end of which was glued a Pyrex capillary tube carrying through it a tungsten wire which pressed on a pad of carbon felt above the β-alumina. The assembly was evacuated through the capillary tube and flame sealed around the tungsten wire. Potassium was electrochemically pumped in from a bath of molten potassium in a dry box. This potassium half-cell was pressed on one face of the ferrite sample which had been machined from the

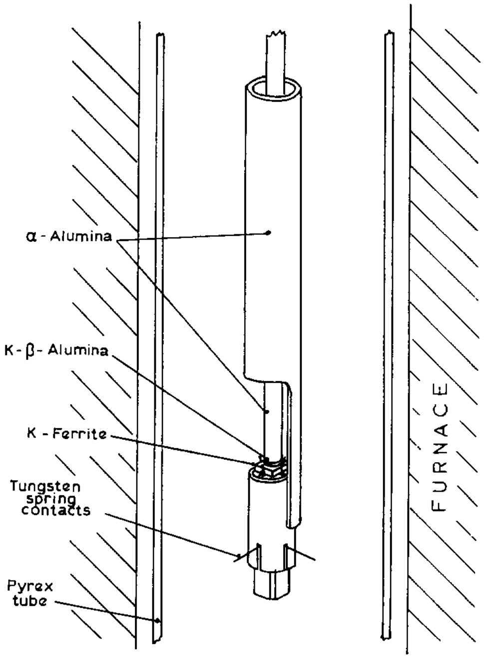

FIG. 1. Cell and conductivity jig.

hot-pressed pellet (A) into a square, side 4.7 mm, thickness 0.7 mm, by means of precision annular diamond saw using kerosine as lubricant. The sample was in turn supported on a jig constructed from alumina which carried four tungsten spring contacts that pressed symmetrically on the four sides allowing the resistivity to be measured by the Van de Pauw technique (7). The whole assembly was mounted in a Pyrex enclosure which was evacuated and then filled with pure argon which had been dried and passed through a titanium furnace. The gas leaving the apparatus passed through a small electrochemical oxygen meter, which indicated a partial pressure of less than 10^{-9} atm.

Coulometric titrations were carried out at between 523 and 573°K by passing constant currents (ca 10 μA) for measured times between the potassium half-cell and the four resistivity contacts. After turning the current off the emf was monitored until a steady value was reached (2–10 hr). Resistivity measurements were then made as a function of temperature between 323 and 573°K, the potassium half-cell being electrically disconnected and a constant current passed through adjacent four-point contacts such that the emf between them did not exceed 300 mV. Under these conditions, electrolysis at the current contacts should not occur and they should be completely blocking to ions. The voltage across the remaining two contacts (in the region of 2 mV) was measured on a high impedence ($>10^9$ Ω) digital voltmeter. Stray thermoelectric emf's were eliminated by repeating with the current direction reversed. The cell assembly was heated by means of a conventional tube resistance furnace and temperatures were measured by means of a chromel–alumel thermocouple in contact with the sample.

For the low-temperature experiment the same apparatus was used but without the potassium half-cell. The Pyrex container was immersed in a Dewar flask containing liquid nitrogen and the temperature was controlled by varying the gas pressure in the tube. A measurement was also made with the sample (B) directly immersed in liquid nitrogen.

Results and Discussion

Equilibrium Cell emfs

Figure 2 shows the equilibrium emf of the cell at 523°K (i.e., the potassium activity in the ferrite(A)) as a function of composition (x) calculated from the charge passed during each titration and the mass of the specimen, assuming the formulas $K_{1+x}Fe_{11}O_{17}$, together with chemical analyses of samples at the starting and final compositions. It can be seen that almost one complete cycle was followed without significant hysteresis, showing that equilibrium had been obtained and that the processes were completely reversible. Difficulty was found, however, in maintaining a good ionic contact between the potassium half-cell and the ferrite; this limited the currents usable without undue polarization to a few microamps. At a later stage this contact was improved by wetting the interface with a trace of $KAlCl_4$–$AlCl_3$ eutectic which is a good electrolyte melting at 423°K.

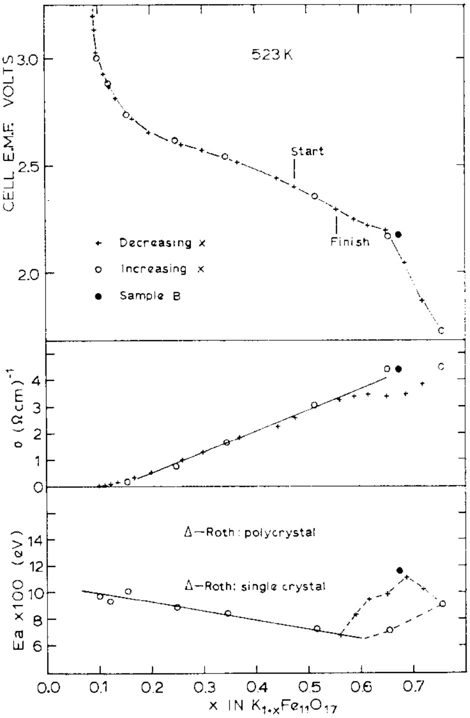

FIG. 2. Cell emf, electronic conductivity, and activation energy as a function of x in $K_{1+x}Fe_{11}O_{17}$.

Taking available thermodynamic data for the $AlCl_3$–NaCl (*8*) and $AlCl_3$–KCl–NaCl (*9*) systems as a guide, it might be expected to be stable from above 4 V to below 2.3 V with respect to pure potassium. It is just possible therefore that the portion of the curve below 2.3 V might have been influenced by this.

The emf of the cell was also measured as a function of temperature, allowing enthalpy and entropy changes to be calculated. These results will be reported elsewhere. The cell voltage obtained with sample B is also shown in Fig. 2.

Electronic Conductivity

The electronic conductivity at 523°K measured concurrently with the cell emfs and shown as a function of composition in Fig. 2 increases approximately linearly with the potassium content up to $x = 0.55$. Such results imply that the mobile species are produced because of the addition of potassium to the lattice. Moreover, the conductivity vanishes at the same composition to which the potassium activity decreases asymptotically, suggesting that no further charge compensation is possible beyond this point, preventing removal of more potassium ions.

At low x values it was necessary to maintain the current through the sample for up to 30 min before the initial ionic contribution to the conductivity died away as an ionic space charge was built up. The effect was similar to that found by Roth and Romanczuk (*3*).

Figure 3 shows the electronic conductivity as a function of temperature. Measurements above room temperature are given at several compositions arrived at during the coulometric titrations, and some results of Roth are given for comparison (dashed lines). The low-temperature measurements made on sample B are of lower precision. Activation energies derived from the relation $\sigma = \sigma_0 \exp(-E_a/RT)$ are shown in the bottom part of Fig. 2. It can be seen that E_a decreases slightly as x is increased from 0.1 to 0.65 but then there is an abrupt increase. When the composition was coulometrically titrated back to $x < 0.65$ the former activation energies and conductivities could not be reproduced, although the cell emf was completely reversible. It appeared, however, that the activation energy and conductivity were returning to the former values by the time x had reached 0.55. This hysteresis could be due to microstructural changes in the ceramic due to lattice

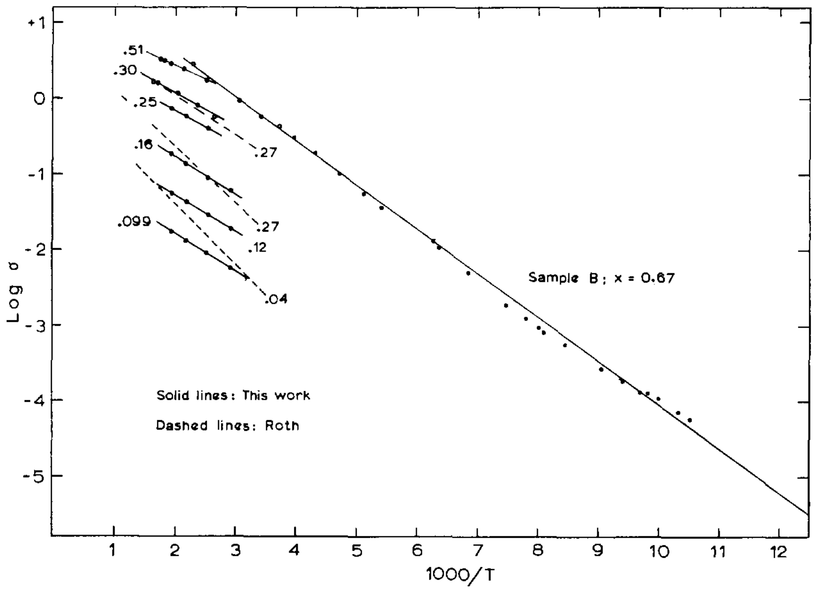

FIG. 3. Electronic conductivity of $K_{1+x}Fe_{11}O_{17}$ as a function of temperature. (x values given alongside the lines.)

strains set up by the extra potassium ions in the layers. However, sample B, which had a potassium content corresponding to that giving the highest activation energy for sample A, but had not been subject to coulometric titrations, gave an E_a value in close agreement. The apparent discontinuity in slope in the cell voltage versus x plot at this composition may indicate a minor phase change occurring here. Clearly, this region needs further study. X-ray Guinier powder photographs of B-type samples coulometrically titrated to x values of 0.35 and 0.86 showed no qualitative differences. The likely importance of grain boundary effects is seen when the present results are compared with those of Roth and Romanczuk. There is good agreement in σ and E_a for the single crystals grown from ferrite bars, but much higher activation energies were observed in his sintered polycrystalline samples. The latter had a considerably lower density than the hot pressed samples of the present work. The fluoride–flux grown crystals, however, also showed a much higher activation energy, the reason for which is not clear.

Electronic Conductivity Mechanism and the Nature of the Charge Compensating Defects

The appreciable electronic conductivity in the alkali ferrites, which contrasts with the low electronic conductivities found in the aluminium and gallium analogs, suggests that Fe^{2+} is responsible for their different behavior, as first proposed by Hever (*1*). Furthermore, Roth and Romanczuk (*3*) established that the analytically determined Fe^{2+} content was greater in samples having a higher electronic conductivity. However, in their studies the conductivity could be altered by varying the partial pressure of oxygen over the sample at 973°K or the temperature of annealing in pure oxygen. The nature of the defects associated with the observed changes in the Fe^{2+} content was uncertain. We have been able to minimize such high-temperature equilibration reactions by working at much lower temperatures, up to 573°K, and by changing the number of charge carriers by altering the potassium content coulometrically.

Kennedy and Sammells were, however, unable to detect Fe^{2+} by Mössbauer spectroscopy in a cathode of approximate composition $Na_2O \cdot 11\,(Fe_{0.9}Al_{1.1}O_3)$ (with the β-alumina structure) when the sodium concentration was coulometrically increased to an activity corresponding to a cell voltage of 1 V with respect to sodium metal at 393°K. They concluded that the conduction was the result of incorporation of excess oxygen during the high-temperature preparation, resulting in a reaction of the type:

$$\tfrac{1}{2}O_2 + V_0^{\cdot\cdot} \rightarrow O_0^x + 2h^{\cdot}$$

and subsequent incorporation of sodium during discharge of their cell according to the reaction:

$$V'_{Na} + Na + h^{\cdot} \rightarrow Na_{Na}^x$$

However, this mechanism would result in a decrease in the hole concentration as the sodium ion concentration was increased coulometrically and hence one would expect a corresponding decrease in the electronic conductivity. This is just the converse of what is obtained in our system. Furthermore, the same behavior is observed for samples made by vacuum hot pressing in which excess oxygen cannot be present. Two other possible traps for the excess electrons which might charge compensate the excess potassium ions, viz. K^+ ions themselves or anion vacancies can be excluded also on energetic grounds and by the fact that the aluminium and gallium analogs, which could also have these traps, are electronic insulators. Nevertheless, Mössbauer spectra of our samples (*4*) also did not resolve a separate Fe^{2+} resonance, but we consider this reasonable in view of the relatively low concentrations involved and the probable superimposition of the spectrum with that of the predominant Fe^{3+} due to rapid electron exchange between Fe^{2+} and Fe^{3+} such as has been observed in magnetite (*10*).

Studies on several cubic and hexagonal ferrites show conductivity behavior very similar to that observed in this work. Samokhvalov and Rustamov (*11*) studied the spinels $Ni_{1-x}Fe_x^{2+}\,Fe_2O_4$ and $Zn_{1-x}Fe_x^{2+}Fe_2O_4$ and concluded that the n-type conductivity observed occurs by a small polaron mechanism involving electron hopping between Fe^{2+} and Fe^{3+} in octahedral sites. Nicolau et al (*12*) presented more data on the nickel spinel for $0 < x < 0.4$ and found that the energy of activation fell from 0.48 to 0.05 eV over this range. σ_0 values calculated from $\sigma = \sigma_0 \exp E_a/RT$ gave an approximately straight line passing through the origin when plotted against the number of Fe^{2+} ions per unit volume and with a slope 70% of that for potassium ferrite. Simsa et al. (*13*) reported a conductivity value for a single crystal based on the phase $BaCo_2Fe_{16}O_{27}$ which is closely related to magnetoplumbite and in turn to potassium ferrite. Of the iron, 2.5% was present as Fe^{2+} and assuming that this was distributed among the 13 octahedral sites in the formula unit it gave a σ_0 value for conduction perpendicular to the axis again of about 70% of the value for potassium ferrite with the same Fe^{2+} concentration. The activation energy in this case was 0.083 eV. The close similarity in conductivity and activation energy among these phases clearly points to the same mechanism of conduction.

The Defect Chemistry of Potassium Ferrite

On the above conduction model the composition corresponding to essentially zero electronic conductivity would be $KFe_{11}O_{17}$. However, by analogy with β-alumina it might be expected that there would be iron vacancies or oxygen interstitials "frozen in" from the relatively high temperature of preparation. The composition could then be represented by $K_{1+y}Fe_{11-y/3}O_{17}$ or $K_{1+y}Fe_{11}O_{17+y/2}$ respectively. (This is a better representation than the form $K_2O \cdot nFe_2O_3$ which does not allow subsequent inclusion of Fe^{2+}.) Potassium analyses of samples at the initial and final compositions of the coulometric titrations allowed y to be calculated as 0.09 ± 0.04, though this figure would be sensitive to any impurities below the X-ray detection limit that might be present. This value for y is rather less than those in the Na_2O–Al_2O_3 (*14*) and Na_2O–Ga_2O_3 (*15*) systems at their minimum alkali contents but in these systems there is not the opportunity for neutralizing the excess positive charge associated with the extra alkali ions by reduction of the oxidation state of Al^{3+} or Ga^{3+}. Which of the two types of compensating defect is involved has been uncertain for some years, but recently Roth (*16*) has proposed a model consistent with much experimental data, including recent neutron diffraction work in which the charge compensating defect is an oxygen ion interstitial in the sodium ion conduction plane associated with an Al^{3+} ion displaced from an octahedral site (*12*) into an interstitial position nearer the plane. When some cations with lower charge are present (e.g., Li^+, Mg^{+2}) the number of interstitial oxygen ions required to maintain charge balance is reduced. Since the latter would be expected to hinder sodium ion conduction, the observed increase in ionic conductivity on incorporation of say Mg^{2+} is explained. In K-ferrite, Fe^{2+} might fulfill a similar role as suggested by Brinkhoff (*17*).

The composition of the samples used in this work is thus most probably best represented by the general formula $K_{(1.09+x)}Fe^{III}_{(11-x)}Fe^{II}_xO_{17.05}$. This can be applied both to the two-block and three-block structures which differ only in the manner the $[Fe_{11}O_{16}]^+$ blocks are stacked together and in the β-alumina system have been shown to coexist coherently (*18*).

Acknowledgments

We thank Dr. Wynn-Jones of Chloride Silent Power Limited for supplying the sodium β-alumina. One of us (G.J.D.) is indebted to the Science Research Council for support.

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