Electrical Conduction Phenomena in the Dion-Jacobson Phase $KCa_2Nb_3O_{10}$

G. Holstermann, V. Thangadurai, and W. Weppner

Faculty of Engineering
Chair for Sensors and Solid State Ionics
University of Kiel
Kaiserstr.2
D-24143 Kiel, Germany

Abstract

$KCa_2Nb_3O_{10}$ has a lamellar crystal structure, and is one of the so-called Dion-Jacobson phases, which have the general formula $A[A'_{n-1}B_nO_{3n-1}]$ where A is a monovalent, A' is a divalent and B is a tetra- or pentavalent cation [1]. The structure consists of dense blocks that are relatively close-packed, separated by isolated layers containing mobile cations [2]. The Dion-Jacobson phases are analogous to the beta-Aluminas, where dense blocks with the spinel structure are separated by layers containing both mobile cations, such as Na^+, and bridging oxide ions. In the case of the Dion-Jacobson materials, the dense blocks have the perovskite structure.

They were first synthesized in 1981 [1], and have a number of interesting properties. Because of the presence of the mobile cation layer, ion exchange reactions are possible [1,3], and intercalation and deintercalation can take place if there is a mechanism by which the required charge balance can be maintained [4].

The work reported here was performed because a recent publication indicated rather high electrical conductivity (10^{-3} to 10^{-4} S/cm at 400 °C) of the Dion-Jacobson phase $HCa_2Nb_3O_{10}$ in a hydrogen-containing atmosphere [5]. Structurally similar materials in which the A ion is Li^+, Na^+, K^+ or Cs^+ have also been shown to have appreciable values of electrical conductivity [6,7].

The present study includes measurements of the total conductivity of samples containing H^+ and alkaline cations in the bridging layer by employing impedance spectroscopy over the frequency range 5 mHz to 12 MHz as a function of temperature and gaseous atmosphere. One of the significant observations is the large change in the conduction behavior when these materials are heated to temperatures of around 300 °C. Upon cooling the conductivity remains high, with a small activation energy. However, there is a gradual reduction in the conductivity at lower temperatures and the conductivity returns to its initial behavior.

X-Ray diffraction and differential thermal analysis methods did not indicate a significant structural change, so the change in the conduction might be related to a temperature-dependent partial reduction of the niobium ions with increasing electronic conductivity. However the sample shows an emf of the order of several hundred mV at room temperatures when sandwiched between an oxygen and hydrogen electrode.

Measurements were performed to see the influence of the partial pressure of oxygen on the apparent conductivity between 400 and 800°C with and without the presence of hydrogen. It was found that the conductivity is much lower at high partial pressures of oxygen, in the range of pO_2 from 10^{-5} to 1.

References

1. M. Dion, M.Ganne, M.Tournoux, Mater. Res. Bull. **16**, 1429 (1981)
2. H. Fukuoka, I. Toshiyuki, S. Yamanaka, J. Solid State Chem. **151,** 40 (2000)
3. M. Fang, C. H. Kim, T. E. Mallouk, Chem. Mater. **11**, 1519 (1999)
4. T. Takano, et al. Solid State Comm. **103**, 215 (1997)
5. V. Thangadurai, A. K. Shukla, J. Gopalakrishnam, Solid State Ionics **73**, 9 (1994)
6. V. Thangadurai, W. Weppner, J. Mater. Chem. **11,** 636 (2001)
7. V. Thangadurai, W. Weppner, Ionics **7,** 22 (2001)