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The Ionic Conductivity of Hydrogen Vermiculite

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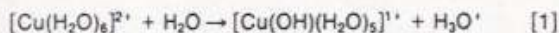
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ABSTRACT

Single crystals of hydrogen-vermiculite have been synthesized at room temperature by ion exchange from Na-vermiculite using 1M acetic acid for one week. The ionic conductivity was measured and shown to be much lower than that of many other monovalent cations in the same host lattice. Its enthalpy of motion is also much lower. These marked differences suggest that protonic species do not play a significant role in charge transport in these layered materials. The hydrogen-vermiculite was characterized using x-ray powder diffraction and acid-base titration.

Many structures with open crystal lattices exhibit fast ionic conductivity. One class of these materials, prevalent in nature, consists of the layered aluminosilicates such as montmorillonite, vermiculite, and mica. These are found in all sizes from the finely divided form, the common montmorillonite clay, to large single crystals such as those found in the case of mica. Their structures consist of negatively charged aluminosilicate sheets between which reside cations that are often hydrated. These compounds show rapid ion mobility when the ions between the aluminosilicate sheets are solvated; they are pure cationic conductors with a cation transference number of unity [see Ref. (1)]. However, there is much disagreement (2-7) in the literature about whether the intrinsic cations or protonic species (2, 7) are the primary charge carriers. Such a determination is important if they are to be used in electrochemical devices, or if the natural potentials in the earth used in oil well logging are to be understood. We have made a study of some single-crystal aluminosilicates, where one can measure the bulk properties of the material without contributions from the surface which might dominate, as in the case of fine powders. Vermiculite from Llano, Texas, was chosen because it is readily available in single-crystal form with few impurities. It has the idealized formula $M'(Mg_3)(Si_7AlO_{10})(OH)_2 \cdot yH_2O$, where y can vary from 0 to above 5, and M' is normally a monovalent or divalent cation. M can be ion-exchanged for other cations.

We have previously reported on the ionic transport properties of the sodium, magnesium, and calcium ion-exchanged materials (1, 8). We anticipated (8) that the incorporation of hydrolyzable cations into the structure would lead to an increased concentration of protonic species, as shown in Eq. [1] below



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This, in turn, should have led to an increased conductivity. However, the copper vermiculite had a very low conductivity (9). Subsequently we found that any protonic species formed were exchanged for more copper ions, leading to a higher copper concentration rather than to more protons. We therefore set out to prepare single crystals of hydrogen ion vermiculite so as to determine the mobility of the protonic species. This letter describes the synthesis, characterization, and ion transport properties of H vermiculites. Such compounds have not been previously been reported in the literature.

Experimental

The vermiculite single crystals used here are from Llano, Texas, and were obtained through the Clays Minerals Society. They were immersed in aqueous sodium chloride solution at 60°C for two months to ensure complete exchange to the sodium form and then had the formula (1, 10)



where y is a function of the water vapor pressure, and for this material varies from 0 to 4.6 (11). The basal spacing of the lattice is 14.89 Å, determined on a powder diffractometer using CuK_{α} radiation.

The sodium crystals were then immersed in a 1M solution of acetic acid for about seven days, which converted them totally to the hydrogen form; no sodium ions were detectable. Use of mineral acids caused destruction of the crystalline lattice. The reaction was monitored daily using x-ray diffraction. After seven days a single phase was obtained with a basal spacing of 13.90 Å, as shown in Fig. 1.

Chemical analysis of the H content of the vermiculite was determined by titration with 0.001M NaOH using Thymol Blue indicator. About 50 mg of crushed H vermiculite was reacted with an excess of 0.001M NaOH for two days; the excess base

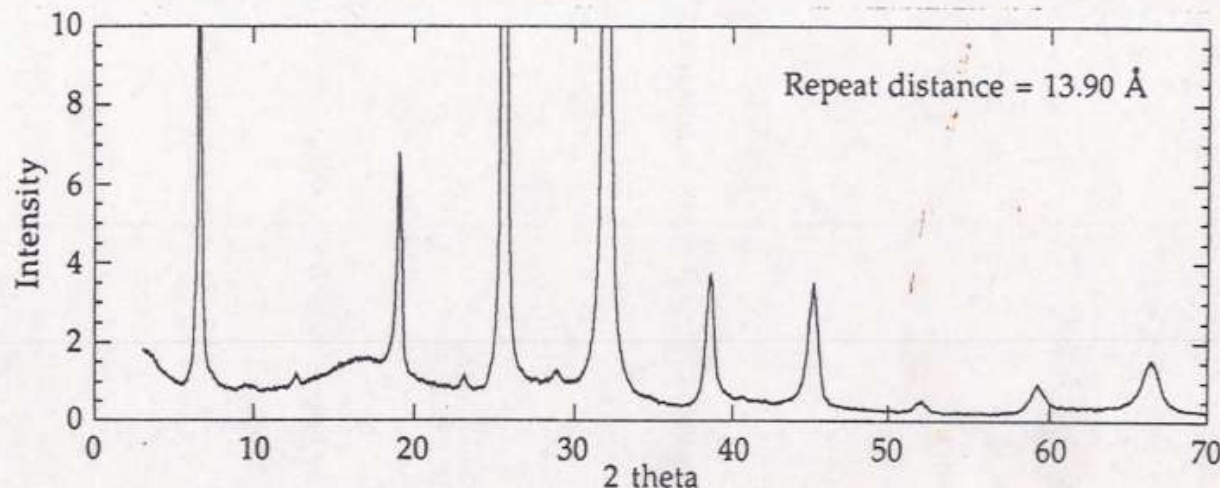


Fig. 1. X-ray powder diffractogram of hydrogen vermiculite showing its single-crystal nature; the diffraction lines are associated with the 001 reflections from the basal planes. CuK_{α} radiation.