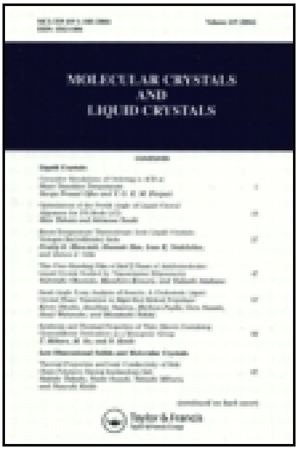

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Structural, Lattice-Dynamical and Magnetic Properties of Alkali-Metal Intercalated Vermiculite

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Vermiculite was intercalated with alkali metals by vapor transport. Synchrotron x-ray, Raman and neutron scattering experiments were conducted to study the structure and lattice dynamics of the new intercalation compounds. Also, magnetization measurements were carried out with use of a SQUID. A drastic increase in conductivity upon intercalation and its relationship to the structure and charge transfer are discussed.

Keywords: vermiculite; alkali-metal intercalation; x-ray diffraction; Raman scattering; neutron scattering; magnetic properties

INTRODUCTION

Recently, zeolite, similar to layered silicates in its chemical composition, has been shown to be intercalated with alkali-metal atoms by vapor transport[1-3]. The resulting zeolite intercalation compounds exhibit interesting properties such as ferromagnetism at low temperatures[3]. So, we envisioned that layered silicates, a highly anisotropic, insulating material, might become a quasi two-dimensional conductor if alkali metals were successfully introduced in the interlamellar space[4]. Below, we report our experimental results on alkali-metal intercalated vermiculite, one of the typical layered silicates, and discuss their physical properties.

EXPERIMENTAL

Original Llano vermiculite samples (its chemical composition is approximately $(Si_{5.72}Al_{2.28})(Mg_{5.58}Al_{0.10}Fe_{0.03}Ti_{0.02})O_{20}(OH)_4\ Mg_{0.93})$[5] were first cation-exchanged, then dehydrated in vacuum, and were finally heated in an evacuated glass tube with a desired intercalant metal in a two-temperature-zone furnace. After completing the intercalation process, the color of samples changed, i.e., alkali-metal-intercalated vermiculite acquired a metallic silvery appearance.

Synchrotron-radiation x-ray diffraction experiments were carried out at the Photon Factory of the High Energy Accelerator Research Organization, and neutron scattering was done at the NIST Center for Neutron Research using a filter-analyzer spectrometer. Raman scattering was conducted using an Ar-ion laser ($\lambda = 5145$ Å), double monochromator and CCD detector. A SQUID magnetometer (MPMS, Quantum Design) was used for magnetization measurements.

RESULTS AND DISCUSSIONS

Figure 1 shows how the resistance of a single-crystal vermiculite varied as a function of time. Measurements were done on a Rb cation-exchanged sample (~4x4x1 mm^3 in size) to which Cu electrodes were connected with silver paste. Once evacuated, the ampule temperature of sample part was set at 525 K, while the Rb-metal part was set at 425 K. When the measurement began, the resistivity of the sample was too high to measure. In a couple of hours, however, the resis-

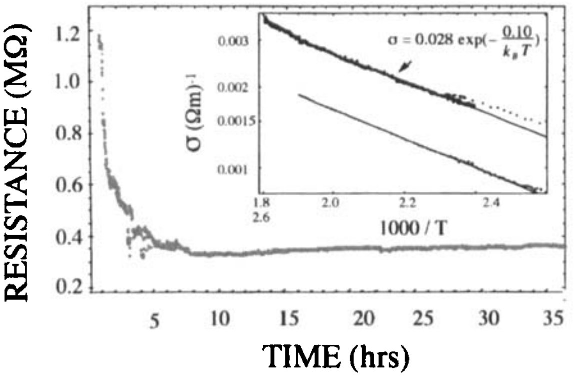

FIGURE 1 Resistance of Rb vermiculite as a function of time. The insert shows conductivity vs. 1000/T at constant Rb vapor pressure.

tance dropped drastically as seen in the figure. After ~8 hours, the resistance approached a relatively constant value. While keeping the Rb-atom vapor pressure constant, the DC conductivity was measured as a function of sample temperature in a short time (~30 mins). The results are shown in the insert of Fig. 1. The conductivity was found to be energy-activation type and could be fitted with

$$\sigma = \sigma_0 \exp\left(-\frac{E}{k_B T}\right),$$

where k_B is the Boltzmann constant. E was found to be ~0.1 eV and σ_0 depended on the vapor pressure (or the amount of intercalant in the interlamellar space).

Diffraction experiments were done on the samples using both synchrotron x-ray and neutron beams. Fig. 2 shows diffraction patterns taken from Rb vermiculite at room temperature. Upon intercalation, the c-axis lattice constant was found to be shorter than that of the original (~3 % shrinkage). The c-axis contraction was also found in Rb and K vermiculite by our neutron diffraction experiments. In Na vermiculite, however, the basal spacing was observed to expand upon intercalation. One can also notice in the figure that the features at $Q \approx 1.8$ Å^{-1} that were mainly from the Rb intercalant appear to be more pronounced in the doped

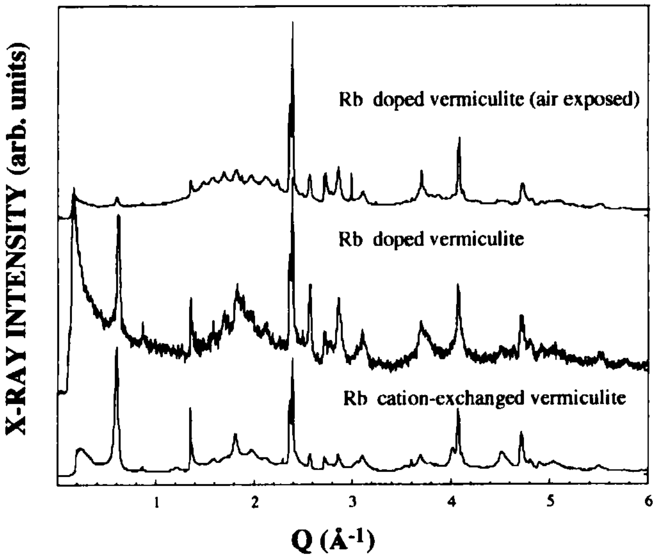

FIGURE 2 Synchrotron x-ray diffraction patterns taken from powdered Rb vermiculite. Diffraction intensities from glass ampule was subtracted from the raw data.

sample. Once the intercalated sample was exposed to the air, a drastic change in the diffraction pattern was found, indicating that the samples are quite air-sensitive.

To see how the lattice dynamics of vermiculite are influenced by the extra interlamellar intercalants, we conducted both Raman and inelastic neutron scattering experiments. Fig. 3 depicts Raman spectra taken from K vermiculite at room temperature. The as-is sample contained some interlamellar water molecules. Once dehydrated, the Raman spectrum changed slightly and the luminescence appeared to increase substantially. The Raman spectrum of intercalated vermiculite differed drastically from the two other spectra shown in the figure; (1) the peak at 680 cm^{-1} seemed to have disappeared, (2) the peak at 350 cm^{-1} seemed to downshift by 25 cm^{-1}, (3) the Raman peak widths became wider upon intercalation. In case of Rb-vermiculite, the original Raman peak at 189 cm^{-1} upshifted to 193 cm^{-1}, while the peak at 352 cm^{-1} seemed to downshift to 328 cm^{-1} upon intercalation. In addition, the peak at 679 cm^{-1} also appeared to have disappeared. These changes found in the Raman features indicate that the intercalants added to the host material altered the lattice dynamics substantially. Especially, regarding the large increase in conductivity by intercalation, we suspect that these changes may be strongly related to charge transfer from the intercalants to the host layers.

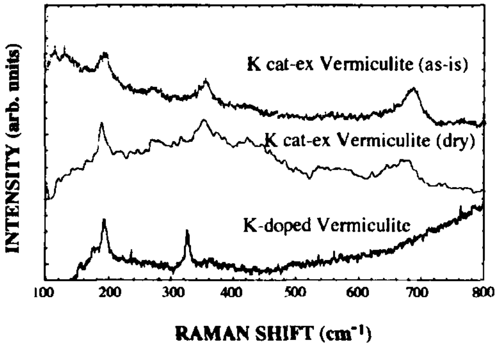

FIGURE 3 Raman spectra taken from K vermiculite. Scattering from the glass ampule is subtracted.

As shown in Fig. 4, incoherent inelastic neutron spectra taken by a filter-analyzer spectrometer suggest that substantial reduction in the (hydrogen-related) phonon density of states had occurred upon intercalation. The inelastic neutron features at 75 meV originate from hydroxyl vibrations[6]. The hydroxyls are located just below the center of pseudo-hexagonal holes where intercalants are supposed to reside. Thus, we expect that the intercalants and charge transfer should directly affect the hydroxyl vibrations.

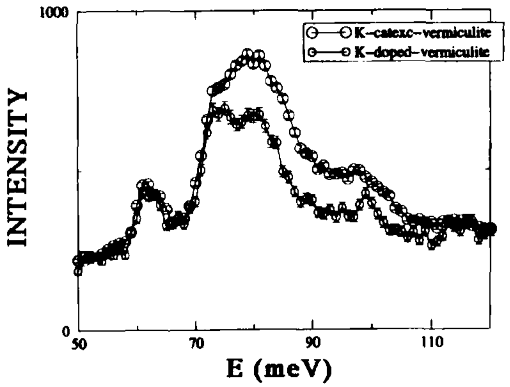

FIGURE 4 Inelastic neutron scattering spectra taken from K vermiculite with a filter-analyzer spectrometer. The two spectra were normalized using the phonon sideband peak at 62 meV.

In addition, magnetic properties of Rb- and K-intercalated vermiculite were examined by a SQUID magnetometer. The magnetization of unintercalated and intercalated samples was measured as functions of temperature (5 K~300 K) and magnetic field (0~5.5 T). Fig. 5 shows the temperature-dependent magnetization of Rb cation-exchanged and intercalated vermiculite. To avoid any confusions due to naturally occurring samples, we used the same powder. Because of iron substitutions in the host layers, both magnetiza-

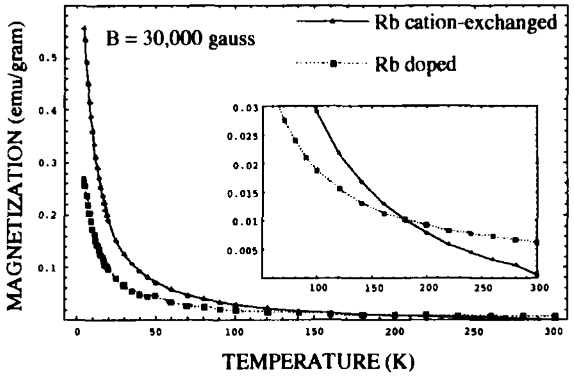

FIGURE 5 Magnetization of Rb cation-exchanged and doped vermiculite as a function of temperature. The applied field was 30,000 gauss. The insert displays an expansion of the higher-temperature data.

tion curves showed a strong Curie paramagnetic (1/T) behavior. However, the amount of free spins in the intercalated vermiculite appears to be much less than that of the cation-intercalated one. It is also noticed that a net paramagnetic component in intercalated vermiculite persisted at higher temperatures. This paramagnetic component could be attributed to Pauli paramagnetism; some domains of the alkali-metal intercalated vermiculite could be metallic.

CONCLUDING REMARKS

We have succeeded in preparing alkali-metal intercalated vermiculite by vapor transport. The dramatic increase in the conductivity upon intercalation suggests that some charge transfer from the intercalants to the host layer. Our experimental diffraction and phonon dynamical analyses support our conclusion that vermiculite can really accommodate alkali-metal interlamellar intercalants. Our magnetization measurements suggest that there may be some metallic domains in the intercalated vermiculite. More experiments and characterization of the samples are now on progress to further clarify the physical properties of the new intercalation compounds.

Acknowledgments

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