The Effect of Thermal Treatment on the Electric Conductivity of Muscovite

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It is well known that large, well-crystallized sheets of muscovite are resistant to thermal decomposition at temperatures above 500°C. According to Grim and Bradley,[1] the differential thermal curves for coarse-grained muscovite showed only a single dehydration reaction, beginning at about 800°C with a peak at about 900°C. On the other hand, Roy[2] reported that the dehydration curve for muscovite showed a slow, relatively gradual loss of water up to about 800°C, without any restricted interval of large water loss, and that its differential thermal curve was characterized by the lack of a definite peak. Gaines and Vedder[3] demonstrated the loss of structual hydroxyl groups

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[1] R. E. Grim and W. F. Bradley, "X-ray Identification and Structure of the Clay Minerals," Mineralogical Society of Great Britain Monograph, (1951), p. 147.

[2] R. Roy, *J. Am. Ceram. Soc.*, **32**, 202 (1949).

[3] G. L. Gaines., Jr., and W. Vedder, *Nature*, **201**, 495 (1964).

by infrared spectroscopy when a thin sheet of muscovite was heated for a long enough time at 600°C. Arizumi and Maekawa[4] investigated the mechanism of gas evolution from muscovite in vacuo and suggested that there were two sources of gas evolution, one of which was a surface contamination and the other was the OH^- ion, a component of the crystal network. They reported that the temperature at which muscovite became opaque was between 720°C and 750°C, and that dehydration began to take place at the lower temperature. It is clear, therefore, that the dehydration process occurs in muscovite without a general destruction of the crystal lattice. The primary step in this process is the formation of water molecules from structural OH^- groups. Fripiat and Toussaint[5] investigated the dehydroxylation of kaolinite by conductivity measurements.

As is well known, muscovite is a good electric insulator. However, when muscovite sheets were heated at high temperatures in vacuo, it behaved characteristically in its conductivity. In this paper, the conductivity will be measured in order to explain some behavior associated with the dehydroxylation.

Experimental

A large well-crystallized sheet of muscovite was cut into pieces 20 mm. square. The thickness of the sheet was in the range from 0.05 to 0.1 mm. Aluminum metal was evaporated onto the freshly-cleaved surface as electrodes. For the surface electrical conductivity measurements, the distance between electrodes was 10 mm. in width and 0.5 mm. in length. For the volume conductivity measurements, electrodes were prepared on both planes of the muscovite sheet by the evaporation of metal. The diameter of the electrodes was 10 mm., and the distance from an electrode to the guard ring was 8 mm. The crystallographic principal axes of muscovite were determined in its basal plane by the use of a polarizing microscope. The muscovite sheets thus prepared were placed in a Pyrex glass tube of 30 mm. in diameter. The glass tube was wrapped with a grounded copper foil in order to keep it from the stray electric field and then inserted in an electric furnace. The conductivity was measured at a pressure of about 5×10^{-5} mmHg with a vibration-reed electrometer apparatus. Since the plate of methacrylic resin which was used as an insulator in the conductivity apparatus had a resistivity of about 10^{15} Ω, it was impossible to measure a higher resistivity than 10^{16} Ω·cm. for the specimen.

Results

The muscovite sheets were heated up to temperatures below 450°C, held at that temperature, and then cooled to room temperature in vacuo. The temperature dependencies of the surface and volume conductivities were measured by continuous heating and cooling. Figure 1 shows the change in the volume conductivity observed when the temperature of muscovite is increased and decreased.

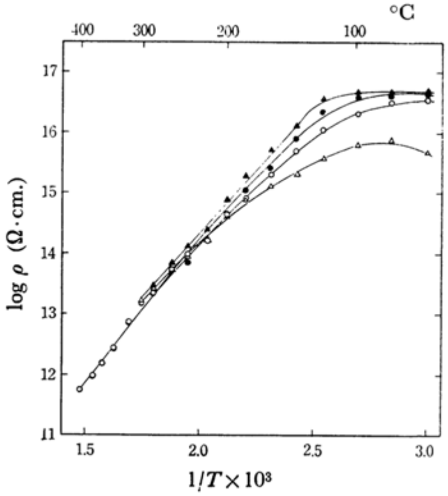

Fig. 1. Temperature dependency of volume conductivity.
Heat treatment up to 300°C:
△, heating process; ▲, cooling process
Heat treatment up to 400°C:
○, heating process; ●, cooling process

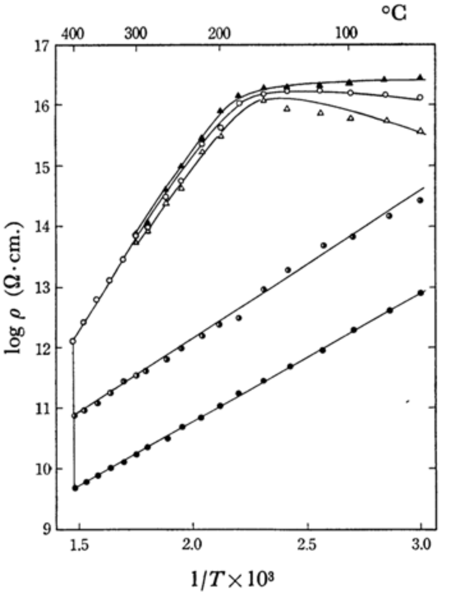

Fig. 2. Temperature dependency of surface conductivity.
Heat treatment up to 300°C:
△, heating process; ▲, cooling process
Heat treatment up to 400°C:
○, heating process; ◑, cooling process along the a-axis; ●, cooling process along the b-axis.

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[4] T. Arizumi and S. Maekawa, *Oyo Butsuri*, **23**, 150 (1954).

[5] J. J. Fripiat and F. Toussaint, *J. Phys. Chem.*, **67**, 30 (1963).

A linear increase of the log ρ versus the reciprocal absolute temperature curve was observed in the range from 150°C to 450°C. While the sheet was kept at a temperature lower than 300°C for one hour, the conductivity remained constant. The conductivity in the cooling process decreased in accordance with the same curve as that in the heating process. When the specimen was held at 400°C for one hour, the conductivity increased a little, while on cooling the curve decreased along the curve with a slope similar to that of the heating curve. In this case, the conductivites in the heating and cooling processes were of the same order, and the discrepancy between them was very slight. In contrast to the volume conductivity, the surface conductivity exhibited a characteristic behavior in the same range of temperatures. Figure 2 shows the changes in the surface conductivity along the a- and b-axes of muscovite caused by the thermal treatment. When a specimen was heated to 300°C, held at that temperature for one hour, and then cooled to room temperature, no apparent change was observed between the heating and cooling curves on the surface conductivity. On the contrary, it should be noted that the surface conductivity gradually increased and then became constant after about one hour while the specimen was kept at 400°C, and that the relatively high conductivity still remained after the cooling process. Although no discrepancy between the values obtained along the a-axis and those along the b-axis was observed in the heating curve, the conductivity along the b-axis increased considerably more than that along the a-axis while the specimen was kept at 400°C. The linear relations of the log ρ versus the reciprocal T curve in both cooling curves have similar inclinations, which are different from that in the heating curve. The activation energy was determined from the inclination to be 0.43—0.47 eV. for the former and about 1.08 eV. for the latter. This suggests that the surface conduction mechanism of muscovite was changed by the thermal treatment at 400°C.

Discussion

The crystal lattice of muscovite is characterized by the repetition of so-called subcells about 10 Å thick, with two sheets of oxygentetrahedron with a silicon or aluminum atom at the center, as is shown in Fig. 3. The triangular basal planes of tetrahedral sit on a plane of the cleavage face and are linked to one another to form a hexagonal network as a whole. Above each center of the hexagonal space formed by the six tetrahedra, a K^+ ion is located. On the other side of the layer, the centers of the hexagon defined by the tetrahedron apexes are filled with OH^- ions, forming a dioctahedral layer between two opposite-facing tetrahedron sheets. Although each layer has its own hexagonal symmetry, a monoclinic configuration is found in the subcell and a plane of symmetry passes through the OH^- ions perpendicularly to the layer. Tsuboi⁶⁾ and Vedder et al.⁷,⁸⁾ investigated the behavior of OH^- ions by infrared spectroscopy. Vedder and McDonald⁷⁾ concluded from the pleochroism of the OH^- stretching band that the vibrational transition moments are tilted out of the cleavage plane by about 16°. Their projection onto the cleavage plane makes an angle of about 32° with the b-axis. At 400°C, the surface conductivity along the a-axis was different from that along the b-axis. This finding suggested that the compositions included not only in the top layer but also in the subcells contribute to the surface conductivity. It is reasonable to postulate that the variation in muscovite structure occurred only in layers near the surface, since no apparent change was observed in the volume conductivity at this temperature.

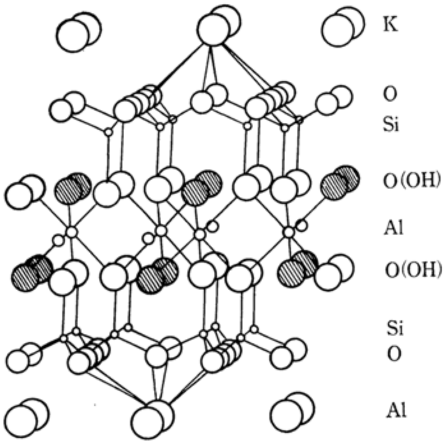

Fig. 3. Muscovite structure.

Fripiat and Toussaint⁵⁾ observed that when kaolinite was heated, the process corresponding to a slow increase in conductivity appeared between 100°C and 360°C. They suggested that this process was due to the delocalization of protons which involve the free hydrid orbitals of octahedral oxygens. Finely-divided muscovite begins to lose its structural water at an appreciable rate at temperatures as low as 450°C (Ref. 2).

By taking these facts into account, the dehydroxylation of muscovite may be explained as follows. The protons in the dioctahedral layer increase the delocalization with a rise in the temperature up to 300°C, thus giving rise to a slow increase in the conductivity. When the temperature of muscovite

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6) M. Tsuboi, This Bulletin, **23**, 83 (1950).

7) W. Vedder and R. S. McDonald, *J. Chem. Phys.*, **38**, 1583 (1963).

8) W. Vedder, *Am. Mineralogist*, **49**, 736 (1964).

reaches about 400°C, a water molecule is formed from the structural hydroxyl group and the dehydroxylation of muscovite begins, without a general destruction of the crystal lattice by the diffusion of the water molecules. In this process, lattice defects which are caused in layers near the surface by dehydroxylation contribute to an increase in the surface conductivity. The anisotropy of the conductivity is assumed to be due to the anisotropic arrangement of hydroxyl ions in the crystal lattice.

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