

TEM Studies of Electron Beam Sensitive Clay Mineral Nanotubes of Imogolite and Pseudo-Boehmite

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A few tubular structures of nano-meter-scale are found in natural products although carbon nanotubes are known as entirely artificial synthetic products [1]. Some of layer structures of almino-silicate $\text{Al}_2\text{O}_3\text{-SiO}_2\text{-H}_2\text{O}$ clay minerals are known to have a cylindrical form such as chrysotile asbestos. The reason for forming a cylindrical structure is well explained by a mismatch in dimension between the octahedral sheets and tetrahedral sheets. Imogolite is another example of a tubular form of almino-silicate clay minerals [2] but its diameter (2.1nm) is about one tenth of those of chrysotile, and therefore the origin of the curvature might be different. Being in a constant diameter should be explained in terms of crystallography. Another question with imogolite morphology is concerned with its highly anisotropic growth along its tube axis. Here we will propose a growth model for the tubular imogolite. Our model is based on a hypothesis of a chiral structure of imogolite in which the substances could be continuously deposited at the tip end of the tube. Our HRTEM images of imogolite supporting our hypothesis, where linear arrays of periodic dots with about 0.4nm interval are seen at only one side of the tube wall. If the imogolite has an orthorhombic symmetry, the dots image should appear equally on both sides of the tube walls. A similar observation has been utilized in determining the chiral structure of a single-walled carbon nanotube [3].

The second example of the tubular structure is concerned with our newly proposed structure model for the aluminum monohydroxide febrile pseudoboehmite $\text{AlO}(\text{OH})$ [4]. This mineral is considered as the case where there is no silica in an $\text{Al}_2\text{O}_3\text{-SiO}_2\text{-H}_2\text{O}$ almino-silicate system. Boehmite $\text{AlO}(\text{OH})$ is found in a stable crystalline form in nature but pseudoboehmite (PB) is synthesized as sol, a metastable form in a very slow reaction process. In XRD characterization the dried PB sol shows diffused ring patterns corresponding roughly to boehmite. The basic crystal structure of boehmite is a layer of two staggered edge-shared Al-O octahedra held together by hydrogen bonds. A low magnification image of the fibrous PB and an electron diffraction pattern taken from a bundle of the fibers, which accords with that of XRD. A HRTEM image of the portion of the isolated PB fibers suggested that the fiber has a tubular structure with a diameter of 2nm. A possible crystal structure of PB will be discussed.

The above-mentioned two clay minerals contain a lot of hydroxyl OH^- or proton H^+ in their structures, and therefore the mineral structures are unstable under the normal TEM observation condition. Because of it the TEM observation is extremely difficult and needs special caution to prevent EB damages.

References

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