

### Suppression of the charge ordering in $\text{AlV}_2\text{O}_4$ with doping

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Spinel  $\text{AlV}_2\text{O}_4$  becomes a charge-ordered state below 700 K,[1] where  $\text{V}^{2.5+}$  ions are separated into  $3\text{V}^{2+}$  ions forming the kagome lattice, and  $\text{V}^{4+}$  ions forming the triangular lattice. This charge-ordered phase (a trigonal phase) can be suppressed and a charge-disordered phase (a cubic phase) appears by doping, for example, the substitution of Cr for the V site.[2] Here, we tried the suppression of the charge-ordered phase in  $\text{AlV}_2\text{O}_4$  by (1) Mg substitution for the Al site and (2) the introduction of excess oxygen, and studied how the charge-disordered state evolves with these types of doping by measuring the x-ray powder diffraction using BL02B2.

Figure 1 shows the temperature dependence of the x-ray diffraction patterns around (440) (in the cubic setting) for  $\text{Al}_{1.95}\text{Mg}_{0.05}\text{V}_2\text{O}_4$ . As can be seen, the charge-disordered state (the cubic phase) appears above 600K, which is lower than the transition temperature of the parent compound  $\text{AlV}_2\text{O}_4$ , 700K. It was also found that the charge-ordered phase is totally suppressed (at least above 100 K) for  $\text{Al}_{1-x}\text{Mg}_x\text{V}_2\text{O}_4$ , with  $x \geq 0.1$ . This means that the Mg

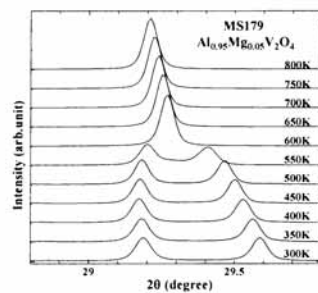


Fig. 1

substitution for Al, i.e. the hole doping into the V site, can suppress the charge ordering of  $\text{AlV}_2\text{O}_4$ .

The charge-ordered phase of  $\text{AlV}_2\text{O}_4$  can be suppressed also by introducing excess oxygen, i.e.,  $\text{AlV}_2\text{O}_{4+\delta}$ . Figure 2 shows the diffraction patterns of  $\text{AlV}_2\text{O}_{4+\delta}$  with  $\delta \sim 0.2$  at 300 K and 800 K. Both diffraction patterns are that of the cubic phase, but relative peak intensities are considerably different between these two temperatures. This change of peak intensities with temperature cannot be explained only by a displacement of the oxygen ions, which is the only variable parameter for the cubic spinel structure. It is speculated that, even though the global symmetry is cubic, there is a local lattice distortion in  $\text{AlV}_2\text{O}_{4+\delta}$ , which yields the deviation of the peak intensities from those of the ideal cubic spinel.

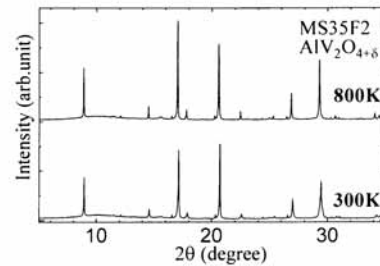


Fig. 2

[1] K. Matsuno et al., J. Phys. Soc. Jpn. 70, 1456 (2001).

[2] K. Matsuno et al., Phys. Rev. Lett. 90, 096404 (2003).

### Analyses of Aggregation Structure of Nanofillers and Their Polymer Nanohybrids

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Imogolite is a natural hollow nanotube with an external diameter of ca.2.5 nm, an internal diameter of 1 nm and lengths from several hundred nanometers to a micrometer, which has the general formula of  $\text{Al}_2\text{O}_3 \cdot \text{SiO}_2 \cdot 2\text{H}_2\text{O}$ . Due to the limitation of the pace for the report, this report is focused on the structural characterization of a (nanofiber/polymer) hybrid utilizing *in situ* synthesized imogolite.

The polymer nanohybrid was prepared by *in situ* synthesis of imogolite in the presence of poly(vinyl alcohol)[PVA] as aqueous solution. This method can be expected to improve the dispersibility of imogolite in the polymer matrix, compared with the hybrid prepared by the conventional blend method. PVA with a degree of polymerization of 630 was used. The solution being composed of aluminum chloride [ $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ ] and tetraethoxysilane [ $\text{Si}(\text{OEt})_4$ ] adjusted pH by NaOH and HCl solution was mixed with PVA aqueous solution, and refluxed at 369 K for 96 h. The mixed solution of imogolite and PVA was precipitated with ethanol, and the precipitate was filtered using a 450 nm Millipore filter and then rinsed with water and ethanol. The white product of (imogolite/PVA) hybrid was then obtained.

X-ray diffraction (XRD) measurement was carried out at the BL02B2 beam line of Spring-8 using white powder products packed in a quartz glass capillary. Diffraction from a sample was detected with imaging plate of a Debye-Scherrer camera in the BL02B2 beamline. XRD used incident X-rays with a wavelength,  $\lambda$ , of 0.10 nm. XRD measurement was carried out at room temperature.

Figure 1 shows wide-angle X-ray diffraction (WAXD) profiles of natural and synthetic imogolite and the (*in situ* imogolite/PVA) hybrid samples. Imogolite:PVA weight ratio was 1:1 for the hybrid. Scattering vector  $q$  [ $\text{nm}^{-1}$ ] is defined as  $q = (4\pi/\lambda)\sin\theta$  where  $\lambda$  and  $\theta$  are the wavelengths of the X-ray and scattering angle respectively. The XRD

patterns of imogolite consist of a number of broad reflections. The reflections at 1.77-1.27 and 0.79 nm for natural imogolite, and at 2.30-1.50 and 0.98 nm for synthetic imogolite, are associated with the hexagonally packed nanotube. The peak for the synthetic imogolite was observed at a lower  $q$  value than that for natural imogolite. This indicated that the external diameter of the synthetic imogolite is slightly larger than that of the natural imogolite. The sharp peak at 2.0 nm for the (imogolite/PVA) hybrid was ascribed to the rearrangement of parallel imogolite nanotube bundles. The absence of peaks except for imogolite and PVA in the XRD pattern, suggested that there were no by-products in the *in situ* synthesized hybrid. Even though the synthesis of imogolite was carried out in a polymer solution, imogolite fiber with high quality was obtained. Furthermore, the thermal stability of imogolite nanotube in hybrid is higher than synthetic imogolite from temperature dependence of WAXD measurement. Because the surface of imogolite and intermolecular imogolite bundle were adsorbed with PVA molecule.

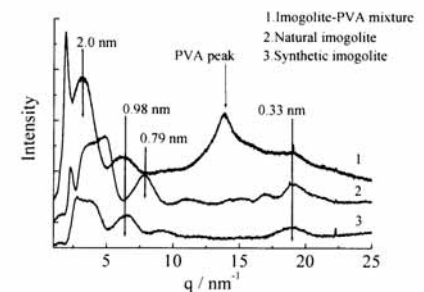


Figure 1 Wide-angle X-ray diffraction profiles of natural and synthetic imogolite and the (*in situ* imogolite/PVA) hybrid samples