Structural Phase Transition in Absorbed and Non-absorbed Copper(II) *Trans*-1,4-Cyclohexanedicarboxylate

Nano-porous materials attract much attention because of their potential technological applications in gas storage, molecular sieves and catalysts among others. A series of copper dicarboxylate compounds such as copper(II) *trans*-1,4-cyclohexanedicarboxylate have recently been synthesized, and it has been found that they show a peculiar absorption/desorption of large amount of molecules. Here, we report our recent studies on the structural phase transition of copper(II) *trans*-1,4-cyclohexanedicarboxylate (Cuchd), which is strongly influenced by absorption of molecules.

Figure 1 shows the molar heat capacity of toluene-free and toluene-absorbed samples of Cuchd measured using a homemade adiabatic calorimeter between 13 and 300 K [1]. An anomaly with a maximum at about 160 K was found for the empty host compound of Cuchd. The shape of the anomaly is very broad, but it is clearly assigned to first-order phase transition, which is confirmed by the observation of super-cooling of the high temperature phase. The enthalpy and entropy of transition are determined to be 413.4 J mol^{-1} and 2.66 J K-$1mol^{-1}$, respectively. The partially absorbed sample (11 % toluene) exhibits a smaller anomaly at higher temperatures than the toluene-free sample. No anomaly is observed for the 65 % toluene-absorbed sample, which means that no phase transition takes place. Lattice distortion caused by the absorption of guest molecules may hinder phase transition and increase phase transition temperature. Thus, the fully absorbed sample should have the structure of the low temperature phase of the host compound even at room temperature.

Phase transition has also been studied by powder X-ray diffractometry with high-energy synchrotron radiation (λ = 0.8007 Å) at beamline **BL02B2** [2]. The sample Cuchd was put in a Pyrex glass capillary (0.3 mm inside diameter), connected to a vacuum line, evacuated, and sealed using a hand-torch after adding a small amount of helium gas. To prepare a fully toluene-absorbed sample, the evacuated host compound was exposed to saturated toluene vapor at room temperature. Powder X-rays diffraction patterns of the empty Cuchd were obtained in the heating direction from 100 to 300 K. A significant change is observed at around 200 K, and the lattice parameter

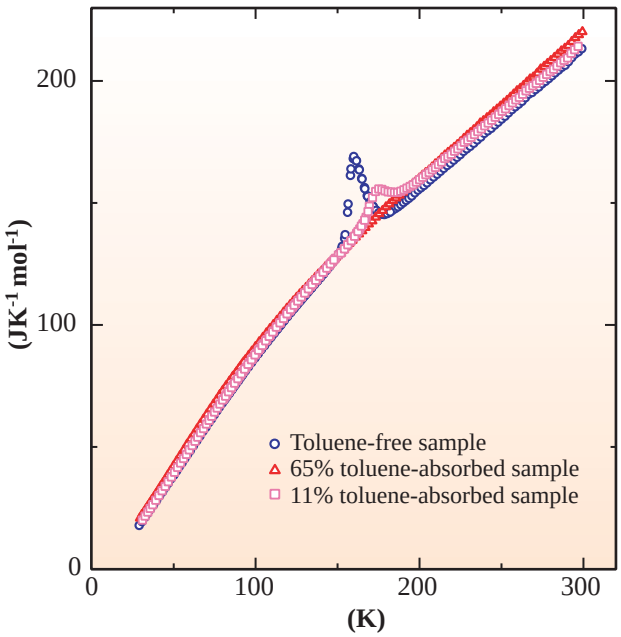

Fig. 1. Measured molar heat capacities of toluene-free and toluene-absorbed copper(II) *trans*-1,4-cyclohexane dicarboxylate.

change is large in the *c*-axis compared with those in the *a*- and *b*-axes. Such anisotropic nature should be caused by the difference between two binding forces: van deer Waals force in the *c*-direction and a strong covalent bond in the *a*- and *b*-directions. Using the obtained lattice parameters at 100 K, the stable structure of the empty Cuchd was estimated using molecular dynamics simulation with Cerius2. Rietveld refinement was carried out using the stable structure estimated by simulation as the initial structure. The program RIETAN-2000 was used for the analysis. In the process of the refinement, ten hydrogen atoms were excluded. The refinement yielded a final R_{wp} of 8.51 % (R_p = 6.37 %), and the refined structure is shown in Fig. 2, where nanopores are clearly seen. The structure of high temperature phase could not be refined completely because of some disorders in the structure and thermal motion: The position and isotropic displacement parameters of copper atoms were refined, but the positions of the oxygen atoms and the carbon atoms could not be determined. On the other hand, no structural change was observed between 100 and 300 K in the fully toluene-absorbed sample. Furthermore, the structure was similar to that of the low temperature phase of the toluene-free sample. The shrinkage of the crystal lattice due to the toluene absorbed was also observed. These results are in good agreement with the results of calorimetry. Thus, the host compound of copper(II) *trans*-1,4-cyclohexane dicarboxylate has a structural phase transition at about 160 K, and the fully toluene-absorbed sample has no phase transition and its crystal structure is fixed to the low temperature phase of the host compound by a strong host-guest interaction. Similar phenomena in structural phase transition were observed in the samples absorbing other guest molecules [3].

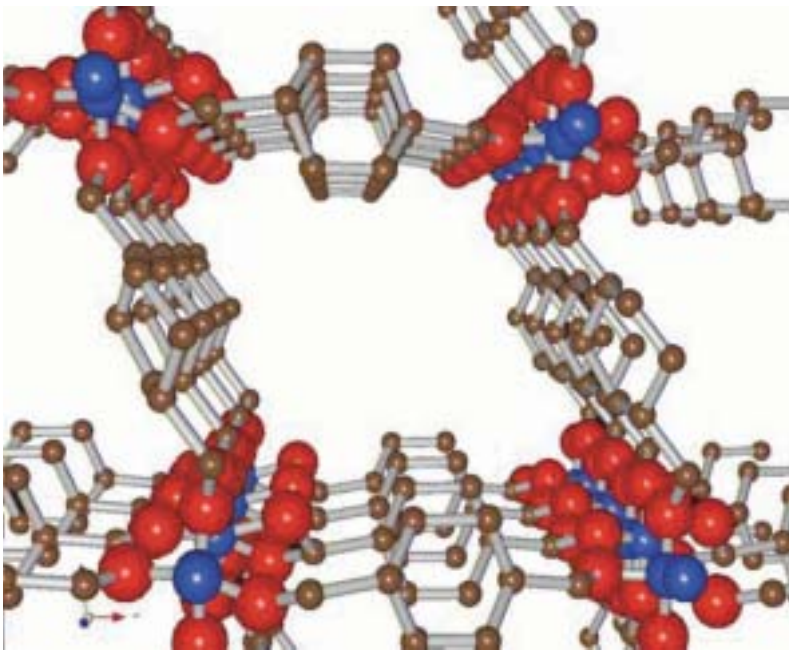

Fig. 2. Structure of low temperature phase (at 100 K) of copper(II) *trans*-1,4-cyclohexane dicarboxylate obtained by Rietveld analysis.

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References

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