

Temperature dependence of XRD for hybrid chiral metal complexes and its applications as energy materials (in 2012)

Takashi Akitsu^{1,*}

¹ Department of Chemistry, Faculty of Science, Tokyo University of Science, 1-3 Kagurazaka, Shinjuku-ku, Toyo 162-8601, Japan

1 Introduction

We have investigated controlling static structures or dynamic distortion of crystals composed of metal complexes as well as coordination polymers. For example, thermally-accessible lattice strain and local pseudo Jahn-Teller distortion of $[\text{CuL}_2]_3[\text{M}(\text{CN})_6]_2 \cdot 4\text{H}_2\text{O}$ ($\text{L} = 1,2$ -diaminocyclohexane) have been reported previously. In its crystal packing of one-dimensional cyanide-bridged bimetallic assemblies and mononuclear Cu(II) complexes, (pseudo) Jahn-Teller effect play an important role in flexible distortion of crystal structures especially Cu(II) coordination environment.

In this year (2012), we designed obviously anisotropic one-dimensional zigzag chiral coordination polymers, $[\text{CuL}_2][\text{Cr}_2\text{O}_7]$ and composite materials of the coordination polymers and a complex bimetallic oxide obtained from $[\text{CuL}_2][\text{Cr}_2\text{O}_7]$ after firing and some battery materials. Interestingly they have successfully observed that the complex bimetallic oxide as the composite exhibited anisotropic thermally-accessible lattice distortion by surface adsorption of the chiral one-dimensional coordination polymer.

2 Experiment

Brown prismatic single crystals of $[\text{CuL}_2][\text{Cr}_2\text{O}_7]$ were obtained by slow diffusion of an aqueous solution (45 mL) of a precursor $[\text{CuL}_2(\text{H}_2\text{O})_2](\text{NO}_3)_2$ (0.0150 g, 0.0332 mmol) [17] onto the surface of an aqueous solution (5 mL) of Na_2CrO_4 (0.0107 g, 0.0661 mmol) at 298 K for several days. Yield 0.0040 g (17%).

IR spectra of a coordination polymer $[\text{CuL}_2][\text{Cr}_2\text{O}_7]$, a Cu(II)-Cr(VI) complex bimetallic oxide obtained from $[\text{CuL}_2][\text{Cr}_2\text{O}_7]$, and their composite materials with the (w/w) ratios of coordination polymer : bimetallic oxides = 0:10 (pure coordination polymer), 1:9, 2:8, 3:7, 4:6, 5:5, 6:4, 7:3, 8:2, 9:1, 10:0 (pure bimetallic oxides). Formation of bimetallic assemblies could be confirmed by disappearing XRD peaks of $[\text{CuL}_2][\text{Cr}_2\text{O}_7]$ (which are not similar to neither CuO nor Cr_2O_7), emerging IR bands of Cr-O at 934 cm^{-1} .

Powder XRD patterns of the precursor complexes and resulting composite materials were measured at BL-8B (8 keV, $\lambda = 1.54\text{ \AA}$) at 100 and 300 K

3 Results and Discussion

Figure 1 depicts XRD patterns of the composite materials. Predominant peaks of the $[\text{CuL}_2][\text{Cr}_2\text{O}_7]$ coordination polymer appeared at about 21, 28, 30°, while and those of the bimetallic oxide appeared at about 23 and 29°. All the peaks showed obvious shifts by changing temperature in the range of 100-300 K. Especially the behavior of pure $[\text{CuL}_2][\text{Cr}_2\text{O}_7]$

coordination polymer (10:0) are in agreement with that of the single crystals, and pure bimetallic assemblies (0:10) can be suggested isotropic positive thermal distortion of the crystal lattice. Thermal-accessible distortion was also discussed elsewhere [1,2].

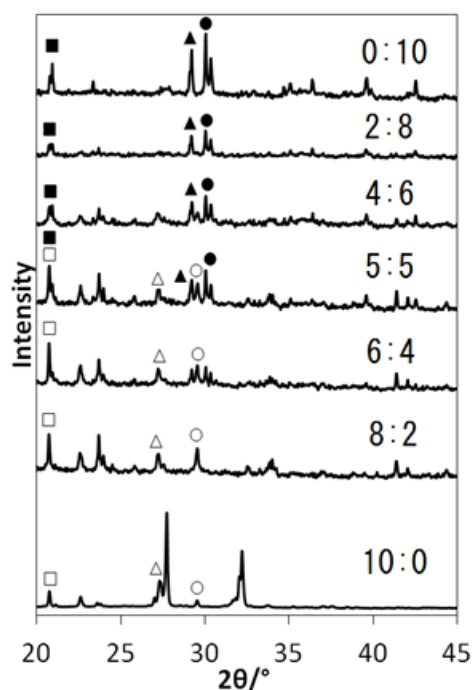


Fig.

1: XRD patterns at 300 K for the composite materials of various ratios; coordination polymer: bimetallic oxides = 0:10 (pure coordination polymer), 2:8, 4:6, 5:5, 6:4, 8:2, 10:0 (pure bimetallic oxides). Filled squares, triangles, and circles denote predominant XRD peaks of the coordination polymers and the bimetallic oxides, respectively.

References

- [1] N. Hayashi, T. Akitsu, *J. Chem. Chem. Eng.* **7**, 306 (2013).
- [2] D. Tazaki, Y. Orii, T. Akitsu, *Cobalt: Characteristics, Compounds and Applications*, Nova Science Publishers, Inc.(NY, USA), in press.

* akitsu@rs.kagu.tus.ac.jp