Structural Studies of Layered Oxychalcogenide $(LaO)CuS_{1-x}Se_x$

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1. Introduction

The layered oxysulfide (LaO)CuS is one of the few wide gap *p*-type semiconductors with transparency against visible light. The substitution of another chalcogen element, Se for S is important for application as optical materials. The successive changes of optical band gap and electrical resistivity of $(LaO)CuS_{1-x}Se_x$ against Se concentration were reported. However, precise structural properties have not been reported yet. In order to understand these property changes from the structural stand point, we have measured X-ray powder diffraction profiles precisely by using synchrotron radiation X-ray with high brightness.

2. Experimental

All samples were polycrystals synthesized by solid state reaction. The starting sources were powdered materials of La_2O_3, La, Cu, S, and Se. Any non-stoichiometric compounds were not used to avoid an introduction of unexpected defects. The powder sample with almost uniform grain size was sealed into quartz capillary with 0.2 mm bore diameter. X-ray powder diffraction profiles were measured using a Debye-Scherrer camera with an imaging plate as a high intensity X-ray detector at SPring-8 BL02B2 line. The wavelength of the incident X-rays was 0.4968 Å and exposure time was 20 min.

3. Results

Debye-Scherrer rings of these samples had a homogeneous intensity distribution. This reveals that these are valid for a reliable Rietveld analysis. Figure 1 shows a profile fitting pattern of (LaO)CuSe by Rietveld analysis assuming the same crystal structure as (LaO)CuS. The data up to 30 degrees in 2θ were used in the analysis. The obtained *R* factors are 4.4 % in R_{wp} and 1.9 % in R_I. The refined lattice constants are *a* (Se) = 4.0652 Å and *c* (Se) = 8.7865 Å. These are longer than those of (LaO)CuS [*a* (S) = 3.9952 Å, *c* (S) = 8.5102 Å]. The lattice constant ratios between S and Se [*a* (Se) / *a* (S) and *c* (Se) / *c* (S)] are 1.018 and 1.032 for *a* and *c* axis, respectively. The lattice constant change for *c* axes is lager than *a* axis. These anisotropic structural changes reflect the layered structures of these oxychalgogenides. Figure 2 shows the schematic illustrations of CuS_4 and $CuSe_4$ tetrahedran which are key for their physical properties. The bond lengths and angles are calculated based on the atomic coordinates obtained by Rietveld analysis. It should be noted that the $CuSe_4$ tetrahedron is distorted toward *c* axis. The analysis for the data of other samples is in progress now.

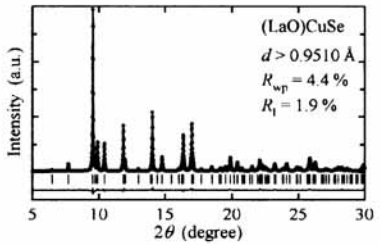

Fig. 1 Profile fitting by Rietveld analysis for data of (LaO)CuSe.

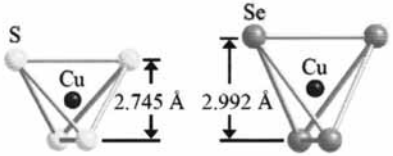

Fig. 2 Schematic illustrations of CuS_4 and $CuSe_4$ tetrahedran.

An investigation of gas molecules in nano-porous coordination polymer by X-ray powder diffraction

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Design and engineering of the micoro-porous structure for gas storage material has long been one of the most fascinating targets in chemistry. In the previous experiment at BL02B2, we revealed the structure of physi-sorped O_2 molecules in nano-channels, which shows forming 1D ladder structure aligned to the host channel of a microporous copper coordination polymer (CPL-1).[1] It has been demonstrated that crystalline microporous coordination polymer possessing uniform low-dimensional channels is relevant for a host framework where gas molecules are confined in their channels. On the basis, in order to get understanding of the interaction between the guest gas molecules and host nano-channels, we made the XRPD measurements of another nano-porous coordination polymer, abbreviated by CPL-2 which possesses a lager pore window size (6Å x 9Å) than that of CPL-1 (6Å x 4Å). We chose Kr as a guest gas molecule instead of O_2, because the noble gas is one of the best probe molecules for investigation of the host-guest interactions owing to its exact sphere shape. We carried out *in-situ* XRPD measurement of CPL-2 with Kr at 80kPa with cooling from 300 K to 120 K (Figure). Few changes were observed in the XRPD patterns at 300 K. On the other hand, cooling from 200 K to 120 K, the intensity of the peak characterized by (020) of the lowest 2_ decreased gradually, which indicates the gradual adsorption of Kr. Further investigations such as structure determination by MEM/Rietveld method are now in progress.

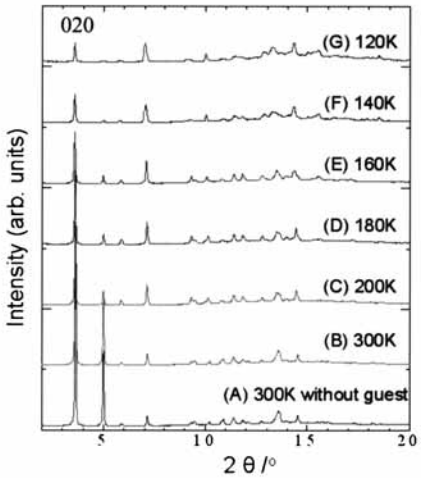

Figure. Synchrotoron XRD patterns of (A) CPL-2 *in vacuo* and (B to G) with Kr of 80 kPa with cooling from 300 K to 120 K

1) *Science*, **298**, 2358-2361 (2002)