BL-9C, 12C, NW10A/ 2012G032

XAFS study of Cu-doped SnO_2

Ikuo Nakai[1,*] Yuhji Yamao,[1] Toshimasa Inoue,[1] Takahiro Ishii,[1] Masaaki Chikaraishi,[1]
Ryouhei Hisamatsu,[1] Makio Kurisu,[2]
[1]Tottori Univ., Tottori 680-8552, Japan
[2]Ehime Univ., Matsuyama 790-8557, Japan

We report the electronic states, the local structure and magnetic properties of Cu-doped SnO_2 from the x-ray absorption fine structure, x-ray diffraction and magnetization measurements. It does not show ferromagnetism at room temperature but diamagnetism like a SnO_2 matrix.

1 Introduction

Diluted magnetic semiconductor oxides have been studied extensively as a candidate for applications to spintronics devices [1]. XAFS study shows that a room temperature ferromagnetic Co-doped TiO_2 has oxygen vacancies around Co atoms [2]. Here we report XAFS study of Cu-doped SnO_2.

2 Experiment

Synthesis of Cu-doped SnO_2 was performed by solid state reaction. Starting materials were high purity oxides of rutile type SnO_2 (99.99%) and monoclinic CuO (99.9%). The materials were mixed in the proper ratio of 5 at% Cu and ground in an agate mortar. The mixture was subsequently heated at 800 ºC or 1000 ºC for 40 hours in air. Hereafter we refer to it as $(Sn_{0.95}Cu_{0.05})O_2$.

X-ray diffraction with rotating Cu anticathode, magnetization up to 1 T using SQUID magnetometer and XAFS measurements were made at 300 K.

3 Results and Discussion

The x-ray diffraction shows that $(Sn_{0.95}Cu_{0.05})O_2$ has rutile type structure (space group *P42/mnm*) with a small amount of CuO and no other impurity phases such as $SnCuO_3$. We determine the lattice constants *a* and *c* of $(Sn_{0.95}Cu_{0.05})O_2$ from the Rietveld analysis, which are somewhat smaller than those of the SnO_2 matrix. It is reasonable to understand as follows. The Cu atom has two kinds of valence, that is, 1+ and 2+, of which ionic radii in the octahedral structure are smaller than that of Sn^{4+}. Therefore Cu ions are substituted with Sn atoms.

Cu_2O with Cu^{1+} and CuO with Cu^{2+} correspond to the electronic configuration of $3d^{10}$ (diamagnetic) and $3d^9$ (paramagnetic) respectively. Figure 1 represents XANES spectra of $(Sn_{0.95}Cu_{0.05})O_2$ as compared with Cu_2O and CuO, which shows the valence of the substituted Cu in the rutile type SnO_2 to be nearly 2+. Therefore Cu ions should have magnetic moments; $(Sn_{0.95}Cu_{0.05})O_2$ has a potential to be magnetic. As in Fig. 2, however, the magnetization measurement reveals that $(Sn_{0.95}Cu_{0.05})O_2$ is not ferromagnetic and not paramagnetic but diamagnetic at 300 K as well as the SnO_2 matrix. This is strange and hardly understandable. So we determine to investigate the local structure of $(Sn_{0.95}Cu_{0.05})O_2$ carefully.

The interatomic distance between Cu and O for $(Sn_{0.95}Cu_{0.05})O_2$ is by about 0.02 Å larger than that of the SnO_2 matrix, while the Sn-O distance of $(Sn_{0.95}Cu_{0.05})O_2$ is as same as that of SnO_2. That is, O neighbors keep away from the Cu atom. This may relate both of the Cu valence of 2+ and the charge neutrality.

Careful investigation about difference between the lattice constants as the average structure from the x-ray diffraction and the atomic distances as the local structure from EXAFS is now in progress.

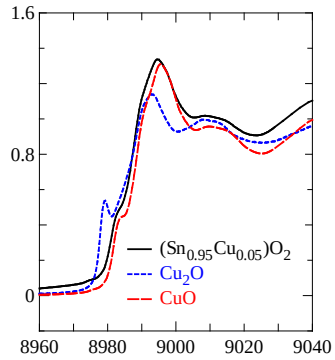

Fig. 1: XANES spectra of $(Sn_{95}Cu_{05})O_2$ for the Cu K edge at 300 K.

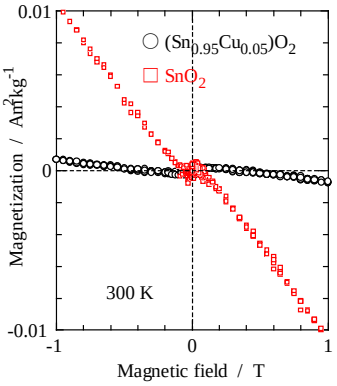

Fig. 2: Magnetization against magnetic field of $(Sn_{95}Cu_{05})O_2$ and SnO_2 at 300 K.

References

[1] J. M. D. Coey *et al*., *Nature Mater*. **5**, 173 (2005).
[2] I. Nakai *et al*., *J. Kor. Phys. Soc*. **63**, 532 (2013).

* nakai@ele.tottori-u.ac.jp