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 °C or 1000 °C 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 $P4_2/mnm$) 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$_2$O with Cu$^{1+}$ and CuO with Cu$^{2+}$ correspond to the electronic configuration of 3$d^{10}$ (diamagnetic) and 3$d^9$ (paramagnetic) respectively. Figure 1 represents XANES spectra of (Sn$_{0.95}$Cu$_{0.05}$)O$_2$ as compared with Cu$_2$O 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$_{0.95}$Cu$_{0.05}$)O$_2$ for the Cu K edge at 300 K.

Fig. 2: Magnetization against magnetic field of (Sn$_{0.95}$Cu$_{0.05}$)O$_2$ and SnO$_2$ at 300 K.

References


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