

XAFS Study on Co²⁺ - Doped ZnO Nanocrystals

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Introduction

Diluted magnetic semiconductors (DMSs) are now attracting great interest in the field of spintronics. The development of high-T_c ferromagnetic DMSs remains a central challenge confronting this field. Room-temperature ferromagnetism has been reported for some Co²⁺-doped ZnO(Co²⁺:ZnO) synthesized by pulsed laser deposition technique^[1] or other methods, but there are contradicting reports on Co²⁺:ZnO^[2]. It is still open to discussion whether the observed ferromagnetism comes from DMSs or from other magnetic precipitates.

We adopted a direct chemical synthesis of colloidal Co²⁺:ZnO. A major concern in the preparation of DMS nanocrystals from solution is dopant extrusion during synthesis, which may compromise the desired physical properties. We investigated the local structure of the dopant of ZnO based DMSs with XAFS to understand the distribution of Co²⁺ in nanocrystals.

Experimental

Colloidal nanocrystalline Co²⁺:ZnO is prepared by the method described below. 10mL of 0.55M KOH in ethanol was added dropwise to a 20mL solution of Zn(OAc)₂ in DMSO. Transition-metal doping was achieved by addition of CoCl₂ to the precursor solution. The precipitate was washed with ethanol and dispersed in 0.05M oleilamine in 10mL of ethanol. After stirring for 3h, the precipitate was washed with ethanol and dispersed in ethanol and dried the precipitate to get a sample in the powder form. XAFS experiments were carried out at 12C station of Photon Factory in the transmission mode. All XANES spectra were taken at room temperature and EXAFS spectra at 20K.

Results and Discussion

Figure 1 shows Co K-edge XANES spectra of 1%, 3% and 5% Co²⁺:ZnO and Co(OH)₂. Three spectra have almost the similar form. In this synthesis, cobalt hydroxide is the most likely species contained as impurities. However, these spectra shows that Co²⁺ in synthesized Co²⁺:ZnO do not have the similar structure to Co(OH)₂.

Figure 2 shows the Fourier transform (FT) of Co K-edge EXAFS spectra of 1%, 3%, 5% Co²⁺:ZnO, cobalt hydroxide and the calculated Fourier transform intensity for Co²⁺:ZnO. It was calculated with the FEFF8.0 program for a cluster of wurzite ZnO in which a Co²⁺ ion substitutes the central Zn site. This figure shows that

Fourier transform intensities become very weak far from Co²⁺ ions. This suggests that Co²⁺ is mostly distributed near the surface of the nanocrystals. We cannot decide the local structure of Co²⁺ ions only by EXAFS. However, ligand-field electronic absorption spectra(not shown) indicate many of Co²⁺ ions has tetrahedral coordination. Thus we can conclude that many Co²⁺ ions are substitutionally doped at the Zn²⁺ sites of ZnO and distributed near the surface of the nanocrystals.

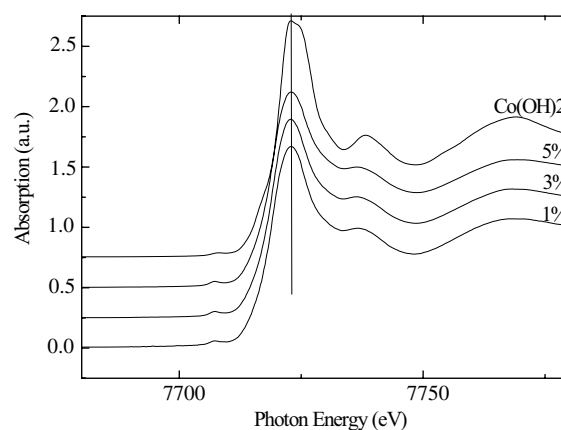


Figure 1. Co K-edge XANES spectra for Co-doped ZnO and Co(OH)₂.

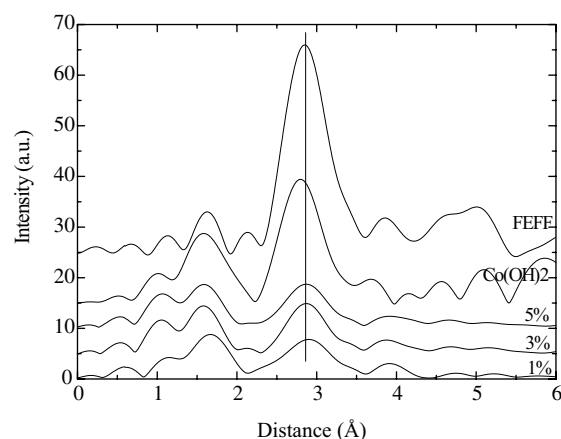


Figure 2. Fourier transform intensities for Co-doped ZnO, Co(OH)₂ and calculated Fourier transform.

References

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