

XAFS Studies of Nanocrystals of a Dilute Magnetic Semiconductor $Zn_{1-x}Mn_xO$

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Introduction

Dilute magnetic semiconductors (DMSs) are semiconductor solid solutions, where a small percentage of the cations are replaced by magnetic ions such as Mn, Co, Fe, etc and they exhibit properties dissimilar to those of the host compounds [1]. Magnetically doped DMS nanocrystals in dilute limits are a unique system where by varying the composition of the magnetic ion, a fine tuning of the band gap energy and drastic modifications in luminescence properties are possible. Quantum size effects arising from reduction of the particle size, enhance these properties further. The unusual properties of this class of systems are dependent on the local atomic coordination including bond length, bond angle, valency and the site symmetry of the magnetic ion as well as atomic structure of the host lattice. In this paper, we report recent progress in the study of the local environment of Zn and Mn in the DMS system $Zn_{1-x}Mn_xO$ ($x = 0.005 - 0.025$) using EXAFS (extended xray absorption fine structure) and XANES (xray absorption near edge spectroscopy).

Methods and Materials

Mn doped ZnO nanocrystals have been prepared by a novel wet chemical technique [2]. To obtain smaller sized particles of the order of 5 nm or less with uniform size distribution, the nanocrystals have been capped with polyvinylpyrrolidone. The size of the nanocrystals in this study is ≈ 4.7 nm and the amount of Mn dopant is varied from 0.5% to 2.5%.

Mn K-edge and Zn K-edge x-ray absorption measurements were performed at the MRCAT 10-ID and CMC-CAT 9-BM beamlines at the Advanced Photon Source, Argonne National Laboratory. At MRCAT, the Si(111) double crystal monochromator was scanned continuously so that the data was collected in quick scanning mode. The size of the incident x-ray beam on the sample was ~ 0.5 mm². For Mn edge measurements, 9 regions were selected on the sample and 2-10 scans were taken at each location depending on how rapidly the sample was damaged by the radiation as indicated by changes in the absorption spectrum.

XANES spectra were collected from -50 eV below the Mn k-edge to 150 eV above with 0.2 eV step size. XANES spectra are sensitive to the oxidation state and geometry of the absorbing atom and are related to the unoccupied electronic states of the absorbing atom. The reference compounds MnO, MnCO₃, Mn₃O₄, Mn₂O₃, MnO₂ and KMnO₄ were measured in transmission and compared to the XANES spectra of the Mn doped ZnO samples. The relative energy of the sample and reference compound spectra were calibrated with a Mn foil measured with the samples and reference standard compounds.

Results and Discussion

Figure 1 shows the XANES of the bulk and nanoparticulate $Zn_{1-x}Mn_xO$ along with two of the Mn standards. The rise in the Mn absorption edge of all the DMS samples lies between that of

Mn²⁺ and Mn³⁺ standards. Differences in the shape of the XANES of the bulk Mn spectra as compared to the nanocrystal spectra indicate that the local structures are unique. The XANES spectrum from the bulk sample is not consistent with any of over 30 Mn standard spectra taken from our own library or those previously published [3]. However, the bulk sample spectrum is similar to the Zn-edge spectrum from the same sample, indicating a similar atomic structure of Mn and Zn in the bulk samples. The inset of Figure 1 shows the pre-edge region used to fingerprint the coordination symmetry of the Mn absorber. Increased intensity of the pre-edge peak for the bulk sample as compared to the nano-particulate sample suggests tetrahedral Mn sites within the bulk sample which is consistent with Mn substitution for Zn within the bulk sample. The Mn edge position of the nanocrystals is coincident with Mn₂O₃ edge position. Hence, majority of the Mn atoms in the nanocrystals are not replacing Zn as in the bulk. Detailed analysis of this system by using the EXAFS spectra to determine the specifics of the coordination geometry of Mn within these samples is in progress.

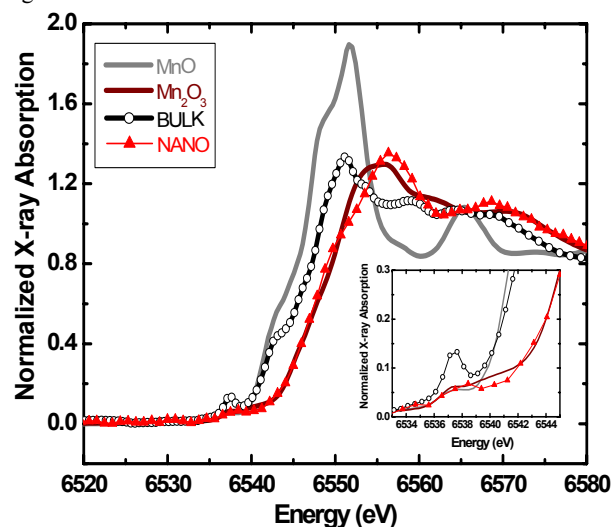


Figure 1: Comparison of XANES spectra for 4nm nanoparticulate and bulk $Zn_{1-x}Mn_xO$, $x = 0.01$, samples and selected Mn standards.

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Reference

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