EXAFS study of zinc ferrite thin film on glasssubstrate

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Extended X-ray absorption fine structure (EXAFS)measurements are not only helpful to understand the cation redistribution butalso provides the information of co-ordination numbers andmetal-oxygen/metal-metal bond lengths in tetrahedral (A-site) and octahedral(B-site) environment of spinel structure. These measurements are successfullyapplied to ferrite nanoparticles as well as thin films. Thus, EXAFS investigation are applied to zincferrite thin films for determination of cation site occupancies amongtetrahedral and octahedral sites.

Zinc ferrite thin film of thickness ~65 nm weregrown using radio-frequency sputtering method These films were grown on glasssubstrate in oxygen environment at base pressure of $2+10^{-6}$ Torr for sputtering duration of 40min. As-grown films were annealed at 200^{o}C for duration of 1, 3 and5 h. X-ray diffraction studies envisagesexistence of peaks corresponding to (311) and (400) plane of cubic spinelstructure. XRD peak positionscorresponding to these planes shift towards higher values exponentially. Thiseffect is associated with relaxation of stress strain and lattice strain withannealing time. Lattice parameters (a) and crystallite size (D) correspondingto plane (311) are collated in Table 1. Lattice parameters for these films are 8.38‡0.01, 8.40‡0.01, 8.42‡0.01and 8.44‡001Å for annealing times of 0, 1, 3 and 5 h, respectively. Fourier transform infraredspectroscopic investigation shows the presence of bands corresponding to metal-oxygenbands in these films which are associated with Fd3m space group.

To get quantitative information of siteoccupancies of metal ions, EXAFS spectraat Fe and Zn K-edge of these films were simulated using ARTEMIS. Fe-Obond distances at A-sites and B-sites are 1.89 and 2.04Å respectively foras-grown thin film. In this case, Fe-O distance at A-site is slight less thanthat reported for $ZnFe_2O_4$ nanoparticles, however, thevalue at B-site is equivalent to that reported in previous studies. This valueat A-site decreases slightly with increase of annealing time. Similar behaviorof this distance is observed at B- site. On the other hand, values of Zn-Odistance are 1.819 and 2.040Å at A-site and B-site respectively for as grownthin film. With increase of annealing time, A site Zn-O distance increaseslightly and attains a value of 1.821Å for GZF25 thin film. Zn-O distance atA-site is less than Fe-O distance at this site for corresponding thin films.This may be due to insertion of ions of larger ionic radii (Zn^{2+}) toA-site of radius 1.96Å. Zn-O distance at B-site has almost similar value thatare observed for Fe-O distance. This may be due to almost 3/2 large size ofB-site. Due to larger size of B-site, size of occupied ions is not significant.Occupancy of Fe^{3+} ions at A-site is 1.20, 1.18, 1.14 and 1.09 forannealing duration of 0, 1, 3 and 5 h respectively. Zn^{2+} occupanciesat this site are 0.23, 0.27, 0.34 and 0.36 for corresponding films.

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