

Determination of the Structure of ZnS:RE TFEL Phosphors using X-ray Absorption Spectroscopy

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Introduction

Recently, great progress has been made in the calculation and prediction of the energy levels of dopants in phosphor hosts. Many calculations have been performed using the ZINDO code developed at UF [1]. For systems such as Mn^{+2} in various sulfide hosts, the calculations compare very well with experiment. The energy levels and oscillator strengths of the dopant atoms can depend very strongly on the local structure of the crystal lattice in the vicinity of the dopant. Systems such as ZnS:Mn present no difficulties in determining the structure of the lattice in the vicinity of the Mn, due to the nearly equivalent size and charge of the Mn to the Zn.

However, many phosphor systems do not exhibit this excellent match between dopant and phosphor. We have developed a number of rare-earth (RE) doped ZnS thin film electroluminescent (TFEL) phosphors for use in applications requiring IR emission. In this case, most of the RE elements are incorporated into the host as a trivalent ion and their size is quite large compared to the Zn. Transmission electron microscopy (TEM) and x-ray diffraction (XRD) studies have suggested that the ZnS:RE TFEL phosphors have poor crystallinity, particularly in the as-deposited condition. In spite of this apparent poor crystallinity, these phosphors have been shown to provide very useful levels of IR emission, with the emission intensity being well above typical “black body” radiators. However, the intensity of the emission is found to be extremely sensitive to a post-deposition anneal. It has been found that for ZnS:ErF₃, the intensity of the IR emission exhibits an extremely sharp maximum at an annealing temperature of 425 °C [2]. This could be due to changes in crystallinity, structure (dopant location), or stoichiometry (e.g. fluorine concentration).

The local chemical and structural environment is very important to the performance of the phosphor, however, typical analytical techniques of XRD and TEM cannot provide detailed information on the local environment. Indeed, it is nearly impossible to even tell whether a ZnS thin film is a cubic or hexagonal structure, due to overlap of nearly all of the XRD peaks for the two ZnS phases. We have used x-ray absorption fine structure spectroscopy (XAFS) to fill in the missing structural information. In this study, sputter deposited ZnS and ZnS:ErF₃ [1mol%] TFEL phosphors were annealed at various temperatures. XAFS spectra were obtained at the Materials Research Collaborative Access Team (MR-CAT) at the Advance Photon Source at Argonne National Labs [3]. Data were collected in fluorescence mode using a 13-element Ge detector, XIA digital signal processing electronics and the MX control system. The samples were mounted on a high speed sample spinner. The data were processed using the Horae and IFEFFIT programs [4,5].

Results & Discussion

In preliminary results of the XAFS analysis, several interesting effects of the ErF₃ doping have been noted involving

both the structure of the ZnS host and the local environment of the Er. The first is a confirmation of the effect of annealing temperature on crystallinity. Samples that were annealed at higher temperatures, show more well defined peaks at higher radii in the Fourier transformed data (Fig. 1.). This is indicative of longer range crystallinity as a result of higher annealing temperatures.

In pure sputter deposited ZnS thin films, it has been previously found that the ZnS structure consists of a mixture of cubic and hexagonal phases [6]. This is not surprising, given that there is a very small energy difference between the two phases. XAFS data from pure ZnS thin films are consistent with this structure. However, the data for as-deposited ZnS:ErF₃ show a very different structure consisting of a first shell with 3 sulfur atoms equidistant and one S atom at a closer distance. This is modeled quite well by a hexagonal lattice with a compressed c-axis, suggesting that Er doping induces a “defective” hexagonal phase. The exact nature of this structure is still being determined by fitting of more shells.

XAFS spectra of the Er edge also show interesting results.

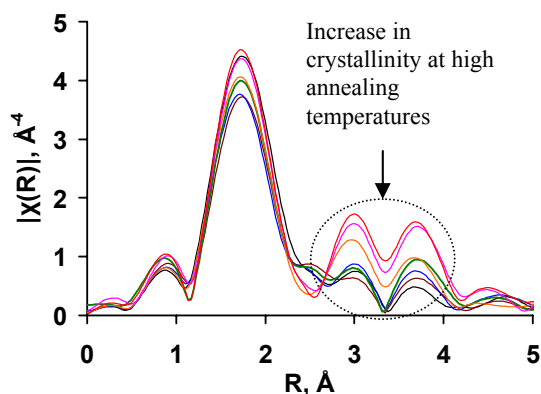


Figure 1. EXAFS Fourier transformed data for ZnS:ErF₃ films at various annealing temperatures: As deposited (black), 300 °C (brown), 375 °C (blue), 400 °C (green), 425 °C (orange), 450 °C (pink), 475 °C (red).

The data are inconsistent with a simple substitution of Er on a ZnS site. However, Er surrounded by 2 F atoms at one distance and one F atom at another reasonably fits the data from the as-deposited samples. It is also possible that an O atom could occupy one or more of those sites. Further refinements of the model are in progress.

In conclusion, we have used XAFS to help elucidate the effect of ErF₃ doping on the structure of ZnS thin films. We have found that the ErF₃ doping induces significant structural changes in the ZnS, and that the Er in the lattice is likely

surrounded by F. More detailed analysis of the data is still underway. It is likely that the structural and/or stoichiometric changes found using XAFS are responsible for observed changes in intensity of the various Er emission lines.

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