Tuning Quantum Dot Host Lattice to Achieve Targeted Doping of Paramagnetic Species Using High Frequency EPR

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Introduction

Low dimensional materials like semiconductor quantum dots (QDs) allow systematic coupling of plasmonic and polaronic properties through the doping of magnetic ions. The electronic and magnetic exchange between atoms is directly influenced by the topography of dopant clusters in the lattice and the presence of vacancies, carriers. Our previous studies indicate phase segregation of Fe^{3+} in II-VI lattices leading to the formation of local inclusions. These local inclusions are formed due to the charge imbalance in the host lattice. This can be avoided by tuning the lattice itself by co-doping paramagnetic ions like Fe^{3+} or Gd^{3+} with Al^{3+} or Ga^{3+}. $ZnAl_2O_4$ is a known spinel **(Fig.1)** where Al^{3+} occupies O_h sites**.** When such a lattice is doped with aliovalent ions like Fe^{3+} or Gd^{3+}, the dopant ions will prefer neighboring O_h aluminum sites and thus the original geometry of the cluster would be maintained. Also, the ions produce lattice vacancies that localize at the QD surface leading to single dopant ion occupying a distorted O_h interstitial site on the surface. In present study the dilute addition of aluminium or gallium atoms into the host also stabilizes ferromagnetism.

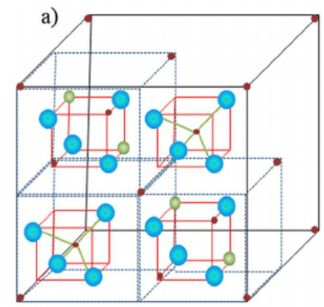

Fig.1 Schematic of spinel inclusion in a AB_2X_4 type lattice.

Experimental

HFEPR spectroscopy was carried out using the 12.5 T SC magnet and the associated heterodyne instrument to identify the dopant sites and the presence of Fermi level carriers induced by aliovalent ion incorporation. The studies were conducted to characterize the Gd^{3+} site symmetry in co-doped ZnO QDs and its analogues. The EPR field positions splitting of the spin-allowed transitions in the microwave frequency domain provides direct insight into contributions of defects, vacancies, transition metal dopant ions. Variable temperature measurements at 240 GHz were made for different concentrations of Gd doped ZnO, $Zn_xAl_{1-x}O_4$ and $Zn_x Ga_{1-x}O_4$ type lattices.

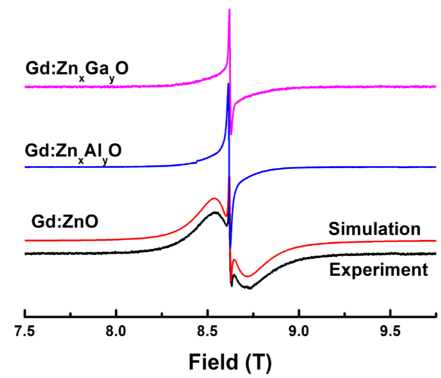

Fig.2 HFEPR of 5% Gd doped ZnO and its analogues at 240 GHz and RT.

Results and Discussion

Results of 240 GHz, room temperature experiments are shown in **Fig.2**. Experimental (black) and simulated (red) spectra of 5% Gd^{3+} doped in ZnO reveal two features that are assigned as (1) the dipolar broadened signal (g = 1.9898, ΔH = 304.90 mT) assigned to a tetrahedral site for the Gd^{3+} dopant, and (2) a sharp signal (g = 1.9888, ΔH = 15.68 mT). Incorporation of Al^{3+} and Ga^{3+} in the host lattice changes the EPR spectra (blue and magenta). Further, changes in g-values for the two signals were further investigated as a function of temperature, dopant concentrations and host lattices.

Conclusions

EPR spectra change upon tuning the lattice by incorporating Al^{3+} and Ga^{3+} in the host lattice. This indicates the change in local arrangement of dopant ions in these host lattices. A model of spinel type inclusion in these materials is being developed using these measurements. To further understand formation, structure and size of spinodal inclusions in QDs, DFT VASP calculations are being performed for a series of Gd doped ZnO QDs and its analogues with completion of this manuscript by the fall, 2019.

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References

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