Ferromagnetism and photoluminescence of wurtzite ZnS:Ni nanospheres

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1. 서론

ZnS has been identified as an excellent host semiconductor for supporting room temperature ferromagnetism when doped with a variety of 3d transition metal ions. The ferromagnetism observed at or above room temperature makes ZnS-based diluted magnetic semiconductors (DMS) promising candidates for spintronic device applications. As compared to cubic ZnS, wurtzite ZnS and related materials could have enhanced optical properties. However, due to the difficulty in stabilizing the wurtzite phase at room temperature, there has been only few reports on wurtzite ZnS DMS nanomaterials. In this work, we report the synthesis of wurtzite Ni doped ZnS nanospheres via a versatile hydrothermal method. The structural, morphological, and magnetic properties will be discussed.

2. 실험방법

In this study $Zn_{1-x}Ni_xS$ (x=0.00-0.05) nanospheres were synthesized using $Zn(NO_3)_2 \cdot 6H_2O$, $(NH_2)_2CS$, and $Ni(NO_3)_2 \cdot 6H_2O$ as the precursors. All precursor materials were dissolved in a mixed solution of ethylenediamine and DI water and stirred for 2 h. Then the solution was transferred into a Teflon lined autoclave, which was sealed and maintained at 180 ^oC for 12 h before being cooled to room temperature naturally. The resulting precipitate was washed several times with DI water before dried in air at 100 ^oC for 4 h, and the final product was ZnS powder with a white-yellow color.

3. 실험결과

The XRD patterns of the as-prepared $Zn_{1-x}Ni_xS$(x=0.00 ~ 0.05) revealed that the diffraction peaks of all the samples can be perfectly indexed to wurtzite ZnS (ICDD 36-1450). No characteristic diffraction peaks arising from the possible impurity phases such as Zn[EN]S, ZnO and dopant related secondary phases like NiS and NiO etc., were observed, indicating that pure phased wurtzite ZnS:Ni powders were prepared hydrothermally at low temperature (180 ^oC). The stability of the wurtzite phase ZnS can be attributed to the surface and bonding modulation effect of ethylenediamine.

The surface morphology and elemental analysis of the obtained products were assessed by SEM and EDS. The SEM image in Fig. 1 clearly shows that the samples are comprise of relatively uniform nanospheres and their coarse surfaces are actually formed by many smaller particles around 5 nm. The EDS analysis showed the Zn, S and Ni signal peaks and the approximate atomic ratio was found to be consistent with the designed stoichiometry. Figure 2 presents the room temperature magnetization (M) *vs*. magnetic field (H) curves of the $Zn_{1-x}Ni_xS$ nanospheres. Although the undoped ZnS was diamagnetic, all Ni doped ZnS showed well-defined ferromagnetic features at room temperature, which could result from the unpaired spins provided by Ni ions. In additional to room temperature ferromagnetism, doping with Ni ions also affected the optical properties of the host ZnS. With 2 at.% Ni doping, the intensity of photoluminescence (PL) was increased near 50%. On the other hand, doping concentration over 3 at.% quenched the PL intensity.

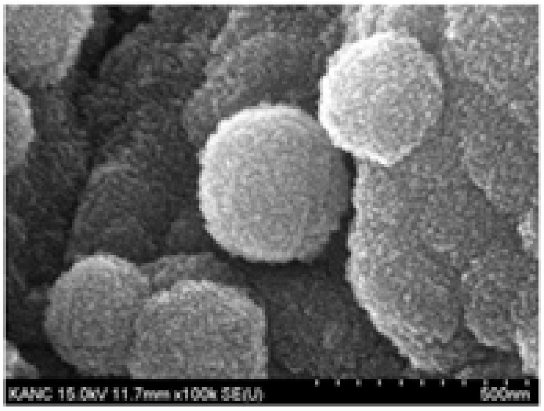

그림 1 FESEM of ZnS:Ni nanospheres showing that nanospheres are consisted of much smaller nanoparticles.

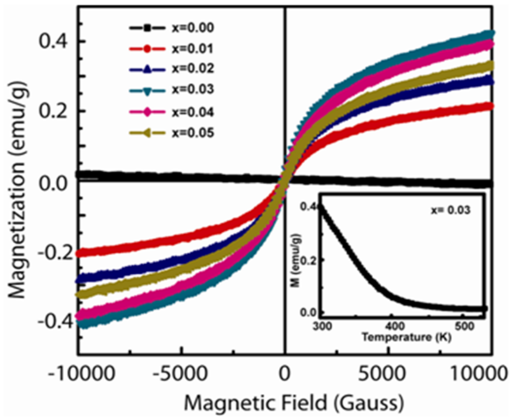

그림 2 M-H curves of ZnS: Ni nanospheres. The inset shows the dependence of magnetization with temperature.

4. 결론

In summary, wurtzite ZnS:Ni nanospheres were successfully prepared through a facile low temperature hydrothermal approach with the assistance of ethylenediamine. The FE-SEM results revealed that the prepared nanospheres are homogeneous, and each nanosphere was composed of nanoparticles around 5 nm. The XRD spectra demonstrated successfully substitution of Ni cations to the Zn site in the ZnS wurtzite structure. Enhanced blue-green emission and room temperature ferromagnetism were observed in the Ni doped samples.