Synthesis and optical properties of $Zn_{1-x}Co_xO$ as nanoparticles, thin film and single crystal

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Abstract

Since the last 50 years a huge amount of research has been made about ZnO due to its optical and electronic properties as a wide band gap semiconductor. This research has increased even more the last decade with the development of the nanoscience, paying more attention to ZnO nanostructures (nanoparticles, thin films, nano wires) doped with transition metals ions such as Co^{2+} or Mn^{2+}. These materials show a wide variety of applications in the optoelectronic industry, bioscience, sensors or even in cosmetics.

In this work, thin films (TF) were grown following the pulsed laser deposition (PLD) method over a sapphire substrate. A SEM image (**Figure 1.A**) shows several round shape $Zn_{1-x}Co_xO$ of ca. 15 nm and thickness about 100 nm. Colloidal nanoparticles of wurtzite (W) $Zn_{1-x}Co_xO$ were prepared using hydrolysis and condensation of acetates solution in dimethyl sulfoxide [1]. Some TEM images (**Figure 1.B**) show spherical nanoparticles with an average diameter of ca. 4 nm. ZnOCo single crystals with different Co^{2+} concentrations have been obtained by physical vapour transport (PVT) for comparing their optical and magnetic properties with those observed in nanostructures.

We report an investigation of their optical properties under high pressure and low temperature by means of optical absorption and photoluminescence. In $Zn_{1-x}Co_xO$ thin films [2], absorption spectrum of W-$Zn_{1-x}Co_xO$ shows three main differences with respect to pure W-ZnO: i) the fundamental band-to-band absorption edge is shifted to higher photon energies, ii) a broad band related to charge-transfer transition appears at energies just below (and overlapping) the band-to-band edge, and iii) well defined absorption bands related to d-d transitions of tetrahedral Co^{2+} are observed. All these features are observed at pressures as high as 15 GPa for most concentrations. By contrast, in nanoparticles, the transition to the rock-salt (RS) phase is observed at progressively lower pressures as the Co^{2+} concentration increases [2], and in bulk is observed around 9 GPa and with an abrupt change in the visible absorption band intensity.

The transition to the RS phase is observed in the three absorption features: i) the fundamental edge shifts to much higher photon energies, ii) the charge-transfer band virtually disappears (or overlaps the direct transition of the RS phase), and iii) the d-d Co^{2+} absorption band around 2 eV decreases its intensity by a factor 10 and shifts to higher energies (2.5 eV) as a consequence of the modification from a tetrahedral to a octahedral coordination symmetry.

A comparison between low temperature Co^{2+} photoluminescence at around 1.8 eV, which is assigned to the $^4T_2 \rightarrow {}^4A_2$ transition, is shown in **Figure 2.**

The high-pressure behaviour of optical phonons in W-ZnCoO is studied by Raman spectroscopy at room temperature. The pressure dependence of the zone-centre phonons (E2, A1, and E1) was measured for the W structure up to the hexagonal-to-cubic phase transition near 14 GPa. Above this pressure no active mode was observed. In the pressure down-stroke and independently of the Co^{2+} concentration, all studied nanoparticles remain in the RS phase at ambient pressure. This behaviour is also in contrast to the one observed in ZnCoO thin films, in which only films with Co^{2+} concentrations larger than 25% remain in the RS phase at ambient pressure.

References

[1] D.A. Schwartz, N.S. Norberg, Q.P. Nguyen, J.M. Parker, D. R. Gamelin, J. Am. Chem. Soc. **125**, (2003) 13205.

[2] J. A. Sans, A. Segura, J. F. Sánchez-Royo, Ch. Ferrer-Roca, and E. Guillotel, Phys. Status Solidi (b) **244**, (2007) 407.

Figures

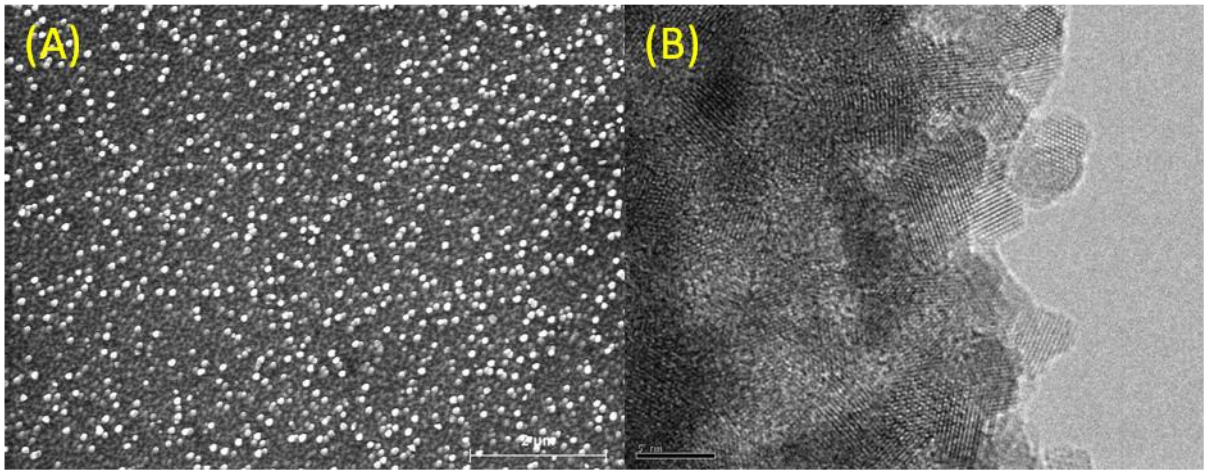

Figure 1 .- SEM image from ZnO:20%Co^{2+} thin film layer growth through PLD in the ICMUV, Valencia by G. Almonacid (A). TEM image of ZnO:5%Co^{2+} nanoparticles growth hydrolysis and condensation of acetates solution in DMSO method by R. Martín-Rodríguez in Washington University (Seattle) (B).

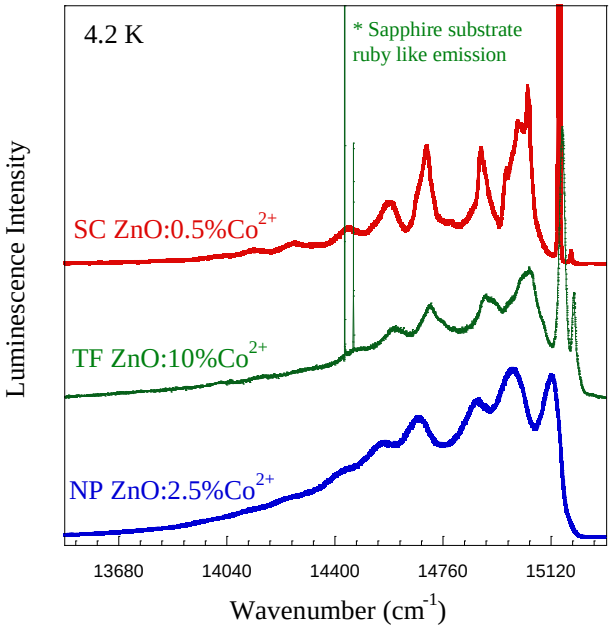

Figure 2 .- Luminescence spectra of Co^{2+} in ZnO lattices at low temperature and in different structures. We have observed that Co^{2+} in single crystal or bulk (SC), thin films (TF) and nanoparticles (NP) emits in the red visible spectral region.