Defect assisted localization of Mn^{2+} activating ions in the core of the ZnS quantum dots

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Outline of the presentation

1. **Small nanocrystals (quantum dots – QDs) of luminescent cubic ZnS doped with transition ions.**
   - **Developing new materials from known semiconductors.**
2. **Localization and incorporation of Mn^{2+} ions in cZnS:Mn and other II-VI QDs.**
   - **Present situation and difficulties.**
3. **Self-assembled cZnS:Mn QDs, a nanomaterial with enhanced properties.**
   - **Synthesis, structure and morphology.**
4. **Localization and incorporation of substitutional Mn^{2+} ions in cZnS:Mn QDs.**
   - **Correlated multifrequency EPR and HRTEM investigations.**
   - **The defect assisted localization of the Mn^{2+} ions in the core of cZnS QDs.**
   - **The ELDA mechanism of impurity incorporation in cZnS QDs.**
5. **Conclusions : A new avenue of research opens !**

Small nanocrystals (quantum dots – QDs) of cubic ZnS doped with transition ions

Nanomaterials: developing known semiconductors in new materials:

- **Luminescent ZnS doped with transition ions ($3d^n$, $4f^n$) $\Rightarrow$ Phosphor and electroluminescent II-VI semiconductor. Non-toxic !!**

- **Nanosized cubic ZnS small nanocrystals (quantum dots – QDs). Under investigation since 90-ties (*Bhargava et al, Phys. Rev. Lett. 72, 416, 1995*)**

  The quantum confinement (QC) effect ($d \leq 6$ nm = $2R_{excit}$) $\Rightarrow$

  - ***Changes in the electronic structure of levels $\Rightarrow$ Shift of spectra: absorption (towards blue) and emission (towards red).***

  - ***Concentration of the oscillator strength in a few transitions*** $\Rightarrow$ ***Higher luminescence efficiency.***

New size related effects: ***Large surface + stabilizing coating + disorder***

Localization and incorporation of Mn^{2+} ions in cZnS and other II-VI QDs. Present situation

- **Localization of activating impurity $\Rightarrow$ controlling doping + resulting properties**
- **Electron Paramagnetic Resonance (EPR) = the experimental technique of choice to determine the localization of paramagnetic activating ions.**

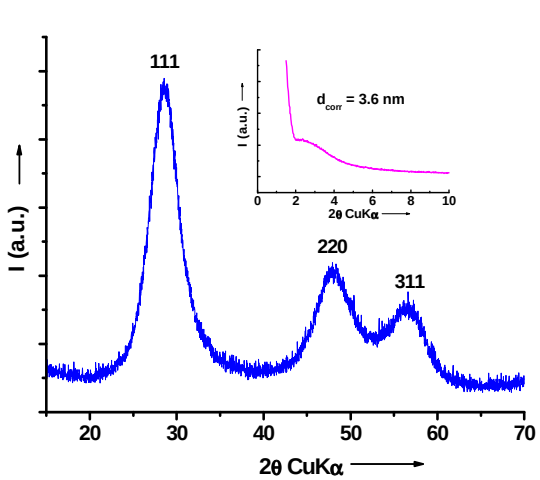
Present situation (after > 15 years of investigations):

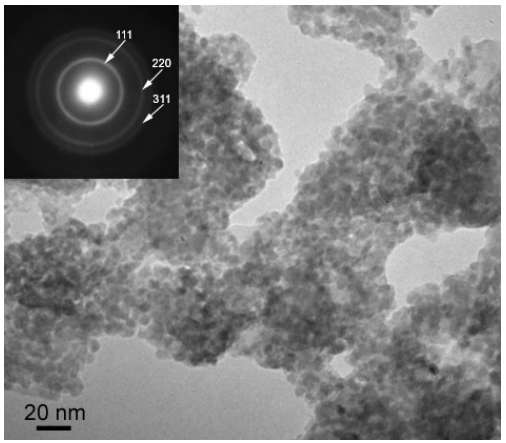
- ***EPR of cubic ZnS:Mn nanocrystals failed to determine accurately the spectra parameters and localization of the Mn^{2+} activating ions !***
- ***Too many (+ 20) reported Mn^{2+} centers with different EPR spectral parameters + unexplained local distortion at substitutional (T_d) cubic sites !***

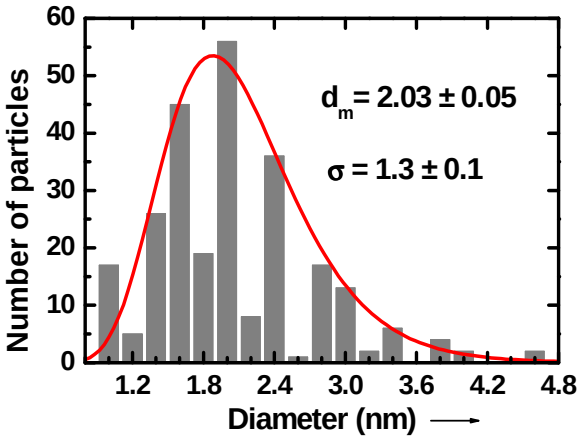
  ***P. A. Gonzales Beermann et al, J. Nanoparticle Res.* 8, 235 (2006) and ref. cited therein**

- ***The observed high concentrations of Mn^{2+} impurity ions in cubic II-VI QD prepared by low temperature (< 350 ^oC) synthesis cannot be explained by present adsorption based mechanisms.* *S.C. Erwin et al., Nature 436, 91 (2005); D. J. Norris et al., Science 319, 1776 (2008)***

Self-assembled cZnS:Mn QDs, a nanomaterial with enhanced properties





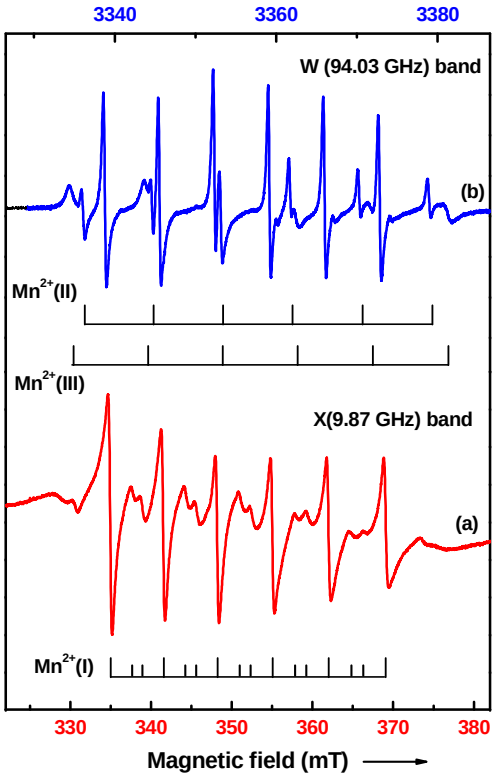


- **Luminescent cZnS QDs activated with Mn^{2+} ions, self-assembled into a mesoporous structure, have been prepared by colloidal chemistry in the presence of a nontoxic surfactant [1] .**
- **The restrictive effect of self-assembling yields a narrower distribution of sizes at d_m= 2 nm, and a higher degree of crystalline order [2] ⇒ Improved EPR spectra resolution = accurate spectral parameters.**

[1] *L. C. Nistor, C. D. Mateescu, R. Birjega, S. V. Nistor, Appl. Phys. A 92, 295 (2008)*

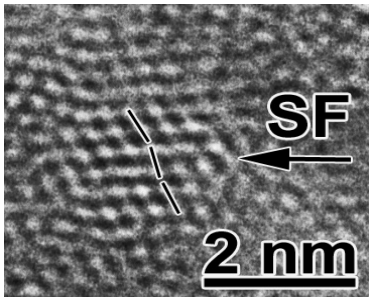
[2] *S. V. Nistor, L. C. Nistor, M. Stefan et al., Superlattices & Microstructures 46, 306 (2009)*

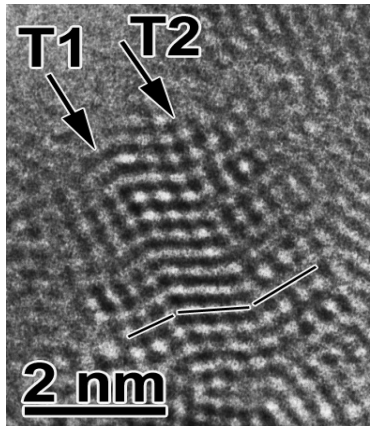
Localization and incorporation of Mn^{2+} activating ions in cZnS QDs



Analysis of multifrequency EPR spectra ⇒ Mn^{2+} ions localized at 3 positions:
- Substitutional Mn(I) and surface centers Mn(II), Mn (III).
- The substit. Mn^{2+} ions are localized at Zn^{2+} sites next to an extended lattice defect: twin (T) / stacking fault (SF).

- The HRTEM images ⇒ analysis shows such defects in ~ 30% of the cZnS QDs.





[3] *S. V. Nistor, M. Stefan, L. C. Nistor et al., Phys. Rev. B81, 035336 (2010)*

Conclusions. A new avenue of research is open !

- **Mn^{2+} activating ions are preferentially localized in the core of cZnS and of other cubic II-VI QDs at substitutional cation (Zn^{2+}) sites next to an extended lattice defect (twin / stacking fault).**
- **The neighboring defect induces a local distortion of the crystal field at the Mn^{2+} activating ion $\Rightarrow$ changed quantum properties.**
- **The extended planar lattice defects are essential in the incorporation and localization of Mn^{2+} activating ions in the core of cZnS and other cubic II-VI semiconductor QDs, prepared at low temperatures (T < 350 ^{o}C).**
- **The proposed extended lattice defects assisted (ELDA) incorporation of impurities mechanism offers the scientific basis for developing procedures for preparing cZnS QDs with controlled doping, for various applications: electro-luminescent devices, photocatalysts, functionalized biological markers, biomolecules separation, etc.**
- **Our results open a new avenue of research concerning the role of intrinsic lattice defects in the incorporation and localization of activating impurities and resulting properties of QDs.**

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2. **Q (34 GHz)-band ESR CW spectrometer ELEXSYS E500Q – Bruker.**
3. **Automatic liquid He plant LHeP18 from Cryomech.**
4. **X-band FT ESR spectrometer ELEXSYS E580 – Bruker (from May 2010).**