Supplementary Materials

Optical and Structural Characteristics of Rare-Earth-Doped ZnO Nanocrystals Prepared in Colloidal Solution

Maria Toma[1], Oleksandr Selyshchev[2,3,*], Yevhenii Havryliuk[2,3,4], Aurel Pop[1], and Dietrich R. T. Zahn[2,3]

[1]Babes-Bolyai University, Physics Faculty, M. Kogalniceanu No.1, 400084, Cluj-Napoca, Romania;
[2]Semiconductor Physics, Chemnitz University of Technology, 09126 Chemnitz, Germany;
[3]Center for Materials, Architectures, and Integration of Nanomembranes (MAIN), Chemnitz University of Technology, 09126 Chemnitz, Germany;
[4]V. E. Lashkaryov Institute of Semiconductor Physics NAS of Ukraine, 03028, Kyiv, Ukraine;
* e-mail: oleksandr.selyshchev@physik.tu-chemnitz.de

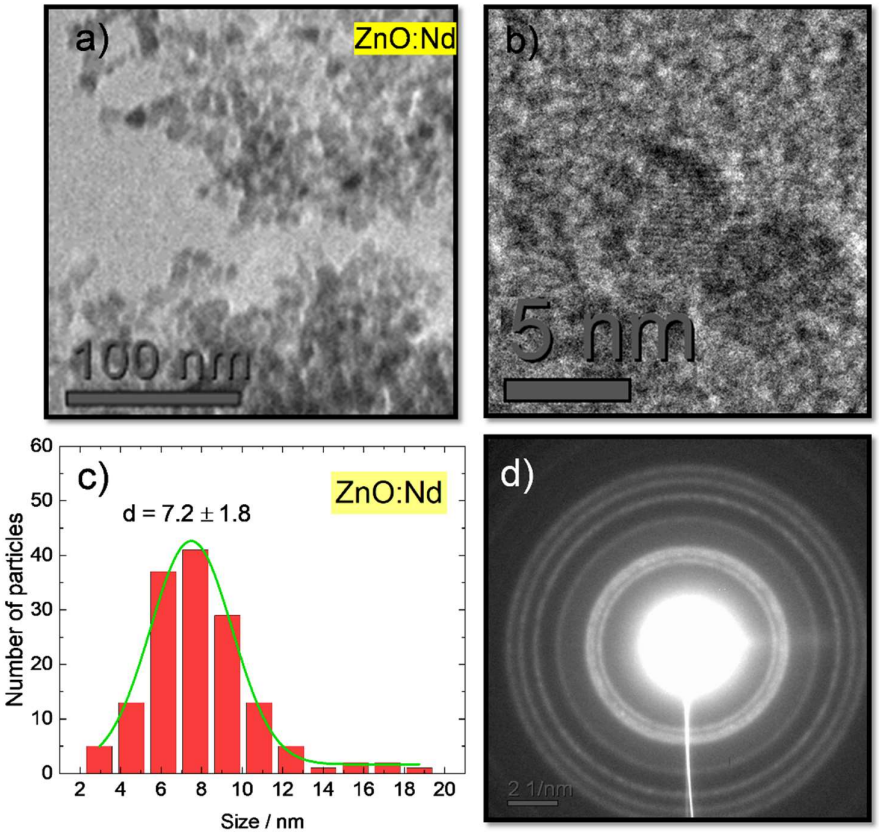

Figure S1. (**a,b**) TEM overview and HRTEM image of Nd doped ZnO NCs; (**c**) statistical distribution of ZnO:Nd NCs; (**d**) SAED pattern (wurtzite phase) of ZnO:Nd NCs.

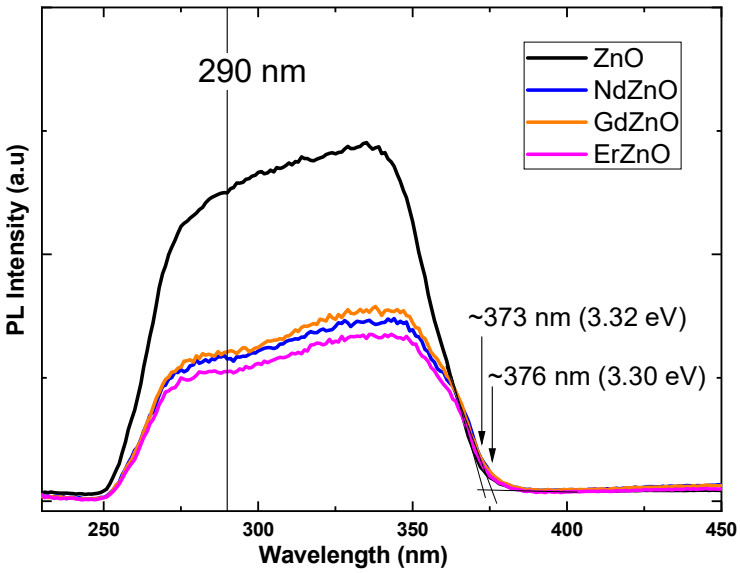

Figure S2. PL excitation (PLE) spectra for pristine and RE doped ZnO NCs registered at λ = 550 nm. Based on these results, $\lambda_{ex.}$ = 290 nm was chosen for excitation of the PL spectra reported in the manuscript. The second order contribution was cut using a 295 nm cutoff filter for the luminescence and a 430 nm cutoff filter for the excitation spectra. As can be seen, the PL excitation in ZnO NCs starts at ~373 nm (3.30 eV) for undoped and ~376 nm (3.32 eV) for RE doped samples, which is close to the bandgap determined from the UV-vis absorption spectra.

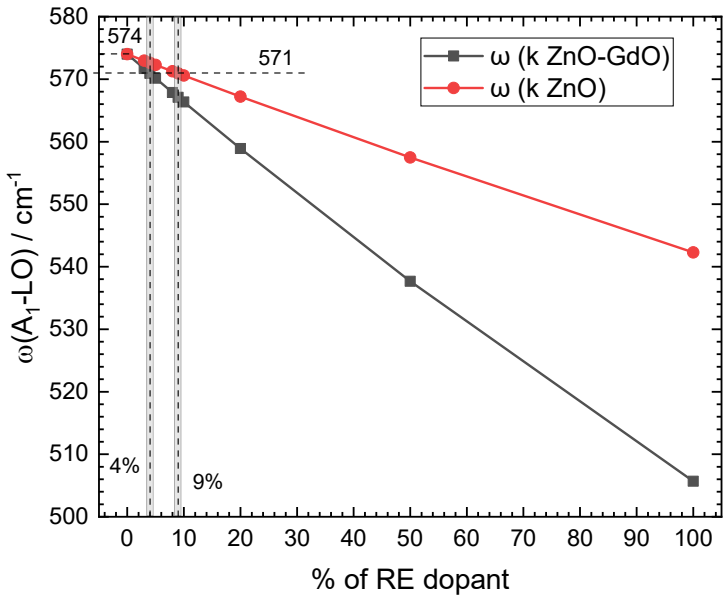

Figure S3. A simplified model of the frequency shift when doping with RE atoms. $\omega\ (k\ ZnO)$ takes into account only the effect of the reduced mass different to that of ZnO according to the equations (1,2). $\omega\ (k\ ZnO - GdO)$ considers both the mass effect and the force constant according to equation (3).

$$\mu = \frac{m_{Zn} \cdot m_O}{m_{Zn} + m_O} \quad (1)$$

$$\mu(d) = d \cdot \frac{m_{dopant} \cdot m_O}{m_{dopant} + m_O} + (1-d) \cdot \frac{m_{Zn} \cdot m_O}{m_{Zn} + m_O} \quad (2)$$

where m_{Zn}, m_O, m_{dopant} – the atomic masses of Zn, O, and RE dopants, μ - the reduced atomic mass, d – the dopant concentration.

$$k(d) = k(ZnO) \frac{L(Zn-O)}{\cdot L(dopant-O) + (1-d) \cdot L(Zn-O)} \quad (3)$$

Where k(ZnO) and k(d) – force constants for pristine ZnO and RE-doped ZnO with the dopind level d. L(Zn-O) and L(dopant-O) atomic distances between ZnO and RE-O both in tetraedral coordination.

$$\omega = \frac{1}{2\pi} \cdot \sqrt{\frac{k(d)}{\mu(d)}} \quad (4)$$

ω – Raman frequency of the mode in cm^{-1}.

Table S1. Number of atoms per spherical ZnO NC of wurtzite phase.

D, nm	V (NC) = $4/3\pi R^3$, nm^3	N unit cells in the particle	O + Zn atoms	Zn atoms
1	0.5230	11	44	22
2	4.186	89	355	178
3	14.13	300	1198	599
4	33.49	710	2840	1420
5	65.42	1387	5546	2773
6	113.0	2396	9583	4792
7	179.5	3805	15218	7609
8	267.9	5679	22716	11358
9	381.5	8086	32344	16172
10	523.3	11092	44367	22184
a = 0.324 nm c = 0.519 nm V (unit cell) = $0.866 \cdot a^2c$ = 0.0472 nm^3, where 0.866 is a packing factor				