# Nonradiative relaxation for $Ce^{3+}$ ion in different crystalline environments

Ge Yao[1,3], Qingguo Meng[2], Mary T. Berry[1], P. Stanley May[1], Jianwei Wang[3], Dmitri S. Kilin[1]*

1. Department of Chemistry, University of South Dakota, Vermillion, South Dakota
2. Department of Natural Science and Kinesiology, Laredo Community College, Laredo, TX
3. Department of Geology and Geophysics, State University of Louisiana, Baton Rouge, LA

The $Ce^{3+}$ ion as a dopant acts as a blue emitter in β-$NaYF_4$ nanocrystals and is important for both fundamental studies and technological applications. Typically, trivalent lanthanide ions, $Ln^{3+}$, exhibit luminescence in the (ultraviolet) UV, visible or near-infrared spectral regions under photoexcitation and emission corresponding to 4f→4f transitions. Shielded by the occupied 5s and 5p subshells, the 4f valence electrons of lanthanide ions have weak interactions with their lattice matrix. However, the optical properties of $Ce^{3+}$, which has a $[Xe]4f^1$ ground state configuration, are dramatically affected by a low-lying $4f^05d^1$ state. The 5d orbitals experience strong ion–lattice interactions. Thus, comparisons of electronic relaxation process of $Ce^{3+}$ ion in different crystalline environments will be benefit for finding efficient optical materials. Based on previous publication of nonadiabatic coupling for β-$NaYF_4$: $Ce^{3+}$ nanocrystals,[1] on-the-fly nonadiabatic couplings of $Ce^{3+}$ in different host materials including α-$NaYF_4$, α-$CaF_2$, α-$Al_2O_3$, $LaPO_4$, $Y_6AL_{10}O_{24}$ have been computed along their nuclear trajectories by combining time-dependent density matrix methodology and *ab initio* electronic structure methods at different temperatures (77K, 200K, and 300K respectively). Electronic properties as well as transition rates between individual orbitals and integrated rates of nonradiative processes of $Ce^{3+}$ in different host were calculated for better understanding the relaxation process of $Ce^{3+}$ ion. The trend of quantum efficiency for $Ce^{3+}$: $4f^05d^1$ luminescence in different host materials were compared by calculating the radiative and nonradiative lifetimes. The trend agrees with the experimental results.

1. Yao, G.; Meng, Q.; Berry, M. T.; May, P. S.; S. Kilin, D., Molecular dynamics in finding nonadiabatic coupling for β-NaYF4: Ce3+ nanocrystals. *Molecular Physics* **2014,** (DOI 10.1080/00268976.2014.972475).