ChE210D final project: Local structure of the Ce dopant in the excited state from MD simulations of the YAG:Ce phosphor

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A molecular dynamics (MD) simulation of cerium-doped yttrium aluminum garnet(YAG:Ce) shows that the excitation characteristics can be modeled using a Buckingham and truncated Coulomb interaction potential, but that the emission properties have too high an energy with the potential functions used here. The MD simulation enables investigation of the pair distribution function around Ce the optically active dopant in YAG in the excited state. Such analysis is not currently achievable experimentally due to the short-lived $4f^1$ excited state of Ce^{3+} in YAG:Ce, which is in the 10's of nanoseconds.

Inorganic phosphors enable the blue-to-yellow down-conversion that underlies the operation of most white LED devices. These devices are highly efficient, durable, and long-lived, enabling a new generation of improved lighting sources. The most commonly used phosphor in white LED devices, cerium-doped yttrium aluminum garnet, is highly efficient, yet clear reasons for its high quantum efficiency remain clandestine. Since Ce is usually doped at small concentrations, investigation of the local structure and dynamics near Ce is near impossible to achieve experimentally. Furthermore, the excited state of Ce after it has absorbed a 2.7 eV (blue, 460 nm) photon only exists for tens of nanoseconds, making experimental investigation of the local structure around Ce in this excited state unfeasible. Molecular dynamics (MD) simulation techniques enable the investigation of the local structure around the Ce dopant ion in both the excited and ground states, shedding new light on reasons for the high quantum efficiency of YAG:Ce.

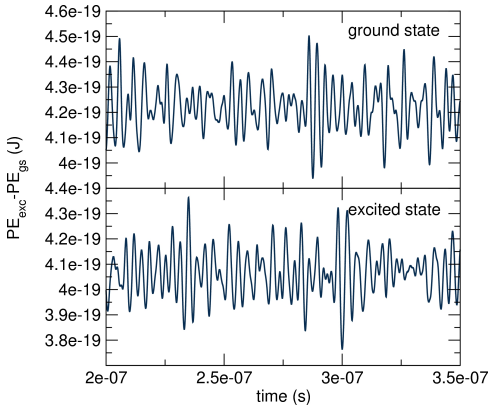

Figure 1: Difference in potential energy from the excited to ground state for YAG:Ce run in both the ground and excited states in a MD simulation at 300 K.

A MD simulation is only as good as the potential functions used. Buckingham potentials according to

$$U_{ij} = A_{ij}e^{-r_{ij}/\rho} - C_{ij}/r_{ij}^6 \tag{1}$$

were used with the potential parameters given in Table 1.[1] The Coulombic potential was approximated by a method developed elsewhere that approximates the full Ewald summation with a smoothly decaying function, with the α parameter taken as 0.2.[2] A cut-off distance of 12 Å was used for both potential functions. The initial structure was created from a Rietveld-refined structure from synchrotron X-ray and neutron data. The velocity Verlet algorithm was used, with periodic velocity rescaling performed according to

$$\lambda = \sqrt{\frac{n_{DOF}k_BT/2}{0.5mv^2}} \tag{2}$$
$$v_{new}^N = \lambda v,$$

atom pair	A_{ij} (eV	ρ (Å^{-1})	C_{ij} (eV Å^6)s
Al–O	1725.2	0.28971	0
Y–O	1766.4	0.33849	19.43
Ce–O (ground state)	2010.18	0.348	23.11
Ce–O (excited state)	2010.18	0.3558	23.11
O–O	9547.96	0.2192	32

Table 1: Buckingham pair potential parameters used in the MD simulation.[1]

and forces calculated as the derivative of the potentials. Velocities and acceleration of atoms were initialized randomly according to a uniform distribution. A time step of 10^{-12} s was used in accordance with the Frank-Condon principle. The excitation and emission energies were calculated by taking the difference between the potential energy of the system in the ground and excited states, as done previously.[3] Three simulations in the excited state and three in the ground state were run at 300 K. Data for g(r) were extracted from the last 20000 MD moves.

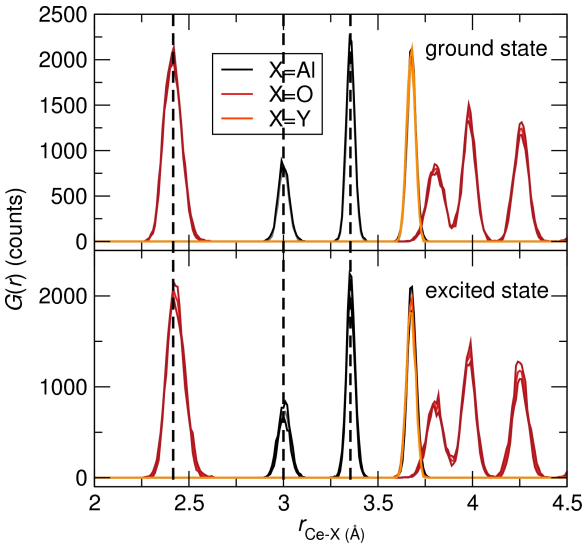

Figure 2: The pair distribution functions around the Ce dopant ion in YAG from MD simulations run at 300 K. Lines drawn above and below the center data lines represent the data $\pm$ one standard deviation. The data was averaged from 3 runs.

The Ce–O ρ parameter was adjusted until the instantaneous difference between the ground and excited states was near 2.7 eV (460 nm or 4.33×10^{-19} J), the absorption energy of Ce^{3+} in YAG. As shown in Figure reffig:pes, the difference in potential energy between the ground and excited states when YAG:Ce is run in the ground state matches the desired energy of around 4.3×10^{-19} joules, shouwing that the excitation energy can be successfully modeled with these parameters. The difference in potential energy when run in the excited state is slightly higher than the 3.7×10^{-19} energy desired. This may possibly be due to the system not being fully equilibrated, too big of a time step, or may be an intrinsic limitation of the model.

The pair distribution function around the Ce ion can also be investigated, which is extremely interesting in the excited state since this cannot be measured experimentally. The PDFs in Figure 2 show the local structure only expands around Ce slightly, which is expected based on the small increase in the ρ parameter in the model. The small expansion and small change in ρ needed to match the excitation energy reflects the very compact nature of the YAG lattice, which is likely related to the high quantum efficiency.

The simulation could be improved by initializing the velocities and acceleration of atoms according to a Boltzmann distribution, and using a more advanced thermostat such as the Anderson thermostat or the Bussi-Donadio-Parrinello thermostat. The equlibration time should also probably be extended, and a shorter time step should be used that is closer to 10^{-15} s. Future work on such a simulation should include studying the energetics and $G(r)$ as a function of temperature and Ce concentration, the effect of Ce clustering in the YAG lattice, and the effect of substitution of other

dopants in the YAG lattice. The potential parameters of Ce should also be further tuned to match the excitation and emission energies of 2.7 eV and 2.4 eV, respectively. A full Ewald summation instead of cutting off Coulombic interactions should also be employed, or at least checked to see if the type of Coulombic potential function effects the system properties. Calculation of the Debye-Waller factors from the position distribution and comparison to experimental results is also in order. The phonon dispersion curves could be found from this simulation using velocity correlation functions or by a 2-D Fourier transform of the positions with time. A more thorough tuning of potential parameters and error analysis would also be needed for further study.

References

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[3] T. F. Soules, R. L. Bateman, A simulation of radiationless relaxation in phosphors by molecular dynamics, *J. Lumin.*. **24** (1981) 701–704. [doi]