Formation and Luminescence of Oxygen Impurites on Silicon Carbide Quantum Flakes

Joseph Granlie[1], **Dmitri Kilin**[2], **and Erik Hobbie**[1]

[1]*Department of Physics, North Dakota State University, Fargo, ND 58108, United States*

[2]*Department of Chemistry and Biochemistry, North Dakota State University, Fargo, ND 58108, United States*

A common problem in the synthesis of quantum dots is the presence of impurities which generally hinder their luminescence. Control of the formation reaction would provide a way to avoid impurities or use them for benefit. Recent results suggest that Si-C vibrational strong coupling could be particularly useful[1]. In this work, oxygen impurities in silicon carbide quantum flakes (SiCQFs) are explored from two directions - photochemistry and photophysics. From the perspective of photochemistry, we simulate the formation of oxygen impurities in SiCQFs from gas phase precursors. From the point of view of photophysics, we investigate the luminescence of specific surface oxygen impurities. Time-dependent excited state molecular dynamics[2] (TDESMD) is used to determine how oxygen impurities appear in gas phase synthesis of SiC. This method treats the situation where electron density is driven by a strong laser field, which induces Rabi Cycles between the excited and ground states. While in the excited state, nuclear kinetic energy is accumulated to overcome the precursor dissociation barrier and promote formation of a SiCQF. The formation of oxygen impurities is studied through mass spectra and geometry optimization of the intermediate structures in the simulated photoreaction. These results show that small chains of silicon, carbon, and oxygen are likely intermediates in the photoreaction. It is expected that this chain will act as a nucleation site for the formation of a full SiCQF, resulting in a surface oxygen impurity. The intermediate structures that are found in TDESMD are used as a basis for studying luminescence of expected oxygen impurities in full SiCQFs. Luminescence of oxygen impurities are studied using first principles modeling and density matrix dissipative dynamics. Using density functional theory the density of states, absorption spectra, and charge distributions of the ground states are analyzed. The models are then heated and molecular dynamics is run which is then used as a basis for on-the-fly nonadiabitic couplings and Redfield Tensor calculations. By modeling the dissipation of energy from electronic to nuclear degrees of freedom, treated by the Redfield equation of motion for the reduced density matrix[3], multiple impurities are found to have significant photoluminescence quantum yield (PLQY). Pure SiCQF is found to have a PLQY of 55.37%, while methoxy, hydroxy, and silicon oxycarbide ligands are found to have a PLQY of 41.49%, 19.43%, and 7.69%, respectively. The combination of TDESMD and PLQY results suggest that oxygen impurities found in gas phase synthesis of SiCQFs are not as inhibitory to PL as expected.

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