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Science-Driven Candidate Search for New Scintillator Materials

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PNNL-22859

Annual Report

Science-Driven Candidate Search for New Scintillator Materials

PL13-SciDrivScintMat-PD05

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Date:	**Friday, September 20, 2013**

Science-Driven Candidate Search for New Scintillator Materials

PL13-SciDrivScintMat-PD05

1. AIM AND SIGNIFICANCE

The main objective of this project is to further develop, apply, and validate a suite of computational modeling tools to explore the relationship between material properties and scintillator performance by determining the key elementary processes that give rise to a material's light yield, decay times, nonproportionality, energy resolution, and potential particle discrimination capability. The objective of this project will be met, in part, by on-going collaborations with researchers at Lawrence Livermore National Laboratory, who are generating first-principles inputs for our kinetic model of scintillation, and researchers at Wake Forest University, who are conducting experiments to validate model predictions.

A large set of inorganic scintillators, including CsI, NaI, BaF_2, CaF_2, $LaBr_3$, SrI_2, YAP and YAG, has been explored to date to develop general rules that will guide the design of new scintillator materials. In particular, our recent work has focused on new, bright scintillator materials, $LaBr_3$ and SrI_2, and thereby demonstrated the applicability of our computational capabilities for studying new radiation detection materials. The modeling results have agreed with a wide range of experimental measurements and other theoretical studies, such z-scan experiments to correlate quenching mechanisms, relative light yield, the track radius near track end and thermalization distances.

2. COMPUTATIONAL STRATEGY

We employ a wide array of numerical methods to simulate the various stages of the scintillation process in gamma-ray detectors: the initial electron cascade to produce hot, free carriers, the thermalization of these carriers into low-energy excitations, and the relaxation of these excitations to produce scintillation light. We have combined simulations of these individual stages to produce a unified approach that can predict scintillator performance from knowledge of a few material parameters (Fig. 1).

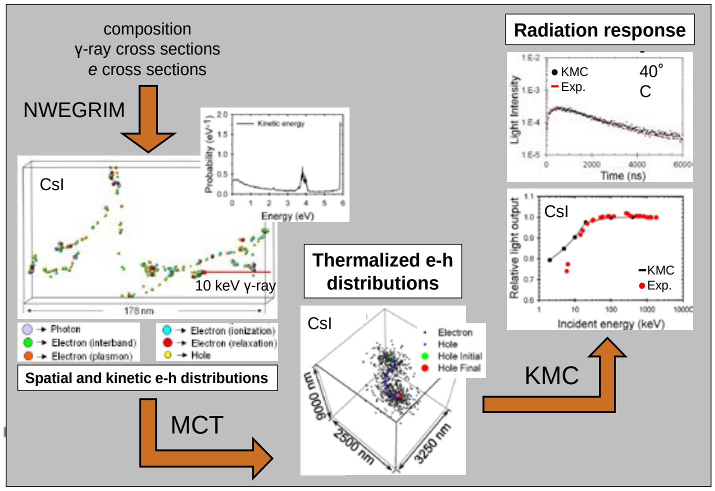

Fig. 1. Flow chart of our modeling process.

Quantities accessible by our methods include the dependence of the light yield on time, temperature, energy of the exciting radiation, and composition of the detector material.

The primary method employed is Monte Carlo (MC) simulation of a parameterized model of the scintillation process. Where feasible, we employ *ab initio* methods to determine the parameters of this model, including the cross-sections for the particles in the electron cascade to create secondary excitations, the energy distribution of the secondary excitations, and the electronic structure of the host material and dopants, including localized excitations like self-trapped holes and electrons. To accomplish these calculations we use both in-house codes developed by our group (MC and electronic-structure) as well as publically available quantum chemistry and electronic structure codes, where applicable. When accurate *ab initio* calculations are not feasible, we use experimental data to fix our model parameters.

3. SCIENTIFIC FINDINGS

We have completed simulations of a collection of popular scintillators including alkali and alkaline-earth halides and high-performance materials like SrI_2, YAG, and YAP. The theoretical light yield for these materials is shown in Fig. 2. We find a simple linear relationship between the band gap and the maximum theoretical light yield. Other interesting properties calculated by our simulations are listed in Table 1. Where we have found ways to validate our models by comparison with experiment, we have found the simulations to be accurate. Hence we have developed a tool that can quantitatively predict the performance of candidate scintillator materials. From these simulations, we have observed some properties that good scintillators must possess: bright scintillators have a small mean excitation energy *W*, while detectors with good energy resolution have a small number of active energy loss channels and relatively linear track structure in the electron cascade.

In an effort to understand the origins of the nonproportionality of the light yield to γ-ray energy, we worked collaboratively with experimentalists to describe the non-linear quenching of self-trapped excitons in alkali halide materials. The MC simulations of carrier dynamics were able to reproduce both the kinetics and efficiency of scintillation and revealed that nonlinear quenching occurs very rapidly, within a nanosecond (Fig. 3). This finding will enable experiments designed for studying nonproportionality to focus on the appropriate time scales. Additionally, these models will enable more realistic simulations of the nonproportional response of inorganic scintillators.

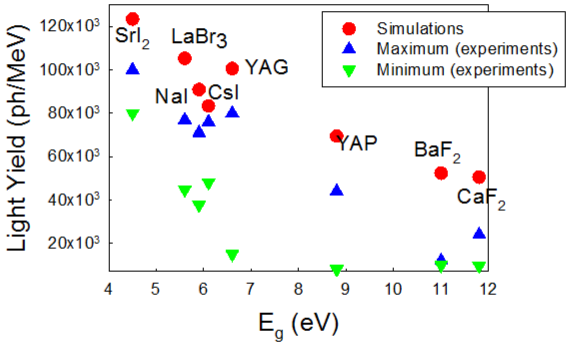

Fig. 2. Maximum theoretical light yield as a function of band gap energy in scintillator materials.

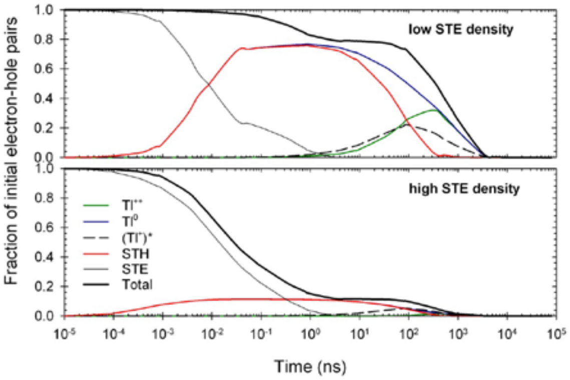

Fig. 3. Simulated time dependence of the relative populations of excitations in UV-excited CsI(Tl).

Table 1. Intrinsic properties, track structure and spatial distribution of scintillator materials.

Material	CaF_2	BaF_2	CsI	NaI	$LaBr_3$	SrI_2
Max. light yield (ph/MeV)	50,505	52,356	82,333	91,743	105,263	123,457
W (eV)	21.4	19.1	12.0	10.9	9.5	8.1
Fano factor	0.23	0.19	0.30	0.28	0.21	0.23
e-h pair channels (%)						
Interband	63.1	63.7	65.2	60.2	72.1	72.2
Plasmon	31.6	29.3	18.2	29.1	21.9	19.2
Ionization	4.4	4.4	11.1	6.4	3.2	4.3
Track structure	Clustered	Clustered	Slightly clustered	Slightly clustered	Linear	Linear
Constant rel. light yield for E_p> (keV)	0.8	0.9	10.0	2.0	2.0	0.2

4. PATH FORWARD

We plan to incorporate improved treatments of the electron-phonon interaction and low-energy carrier transport (including Auger recombination and other quenching mechanisms) in our simulations in an attempt to quantitatively explain finer details of scintillator performance, especially nonproportionality.

The development of the modeling tools has led to state-of-the-art computational capabilities and will yield a predictive simulation framework for evaluating candidate scintillator materials by focusing searches on the most promising potential new radiation detection materials. Also, it will be possible to quickly simulate complete series of scintillator materials, such as the elpasolites (CLLB, CLLC, and CLYC) and the new halide scintillators (e.g. Ba_2CsI_5 and BaBrI) and to provide a pathway for the science-driven candidate search for new scintillator materials.

5. FY 2013 PUBLICATIONS AND INVITED PRESENTATIONS

"Excited state electronic properties of sodium iodide and cesium iodide" L.W. Campbell and F. Gao *Journal of Luminescence* 137, 121-131 (2013).

"Formation, stability, and mobility of self-trapped excitations in NaI and $NaI_{1-x}Tl_x$ from first principles" M. P. Prange, R. M. Van Ginhoven, N. Govind, and F. Gao *Physical Review B* 87, 115101 (2013).

"Kinetic Monte Carlo simulations of excitation density dependent scintillation in CsI and CsI(Tl)" Z. Wang, R.T. Williams, J.Q. Grim, F. Gao, S. Kerisit *Physica Status Solidi B* 250, 1532-1540 (2013).

"Kinetic Monte Carlo simulations of scintillation processes in NaI(Tl)" S. Kerisit, Z. Wang, R.T. Williams, J.Q. Grim, and F. Gao *IEEE Trans. Nucl. Sci.* **in review**.

"Off-center Tl and Na dopants in CsI" R.M.Van Ginhoven *Phys. Condens. Matter* **in review**.

"Experimental and computational results on exciton/free-carrier ratio, hot/thermalized carrier diffusion, and linear/nonlinear rate constants affecting scintillator proportionality" R. T. Williams, Joel Q. Grim, Q. Li, K. B. Ucer, G. A. Bizarri, S. Kerisit, F. Gao, P. Bhattacharya, E. Tupitsyn, E. Rowe, V. M. Buliga, and A. Burger *SPIE Conference Proceeding* **in review**.

"Understanding fundamental mechanisms of nonproportionality in inorganic scintillators" F. Gao at *SPIE Conference* August 26-29 2013, San Diego, CA.

"Microscopic mechanisms of electron-hole generation and their spatial distribution in inorganic scintillators" F. Gao and "Mechanisms of scintillator radiation response: Insights from Monte Carlo simulations" S. Kerisit at *International Conference on Advanced Scintillation Materials* September 23-27 2013, Kharkov, Ukraine.