Title

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Physics of Scintillator Nonproportionality

LB12-ScintProp-PD2Jf

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1. INTRODUCTION

The energy resolution of current scintillators is known to be limited by the adverse impact of light yield nonproportionality. This effort aims to advance the understanding of the physics underlying nonproportionality sufficiently to enable breakthrough performance, by achieving energy resolution beyond the present limit of 2.5% at 662 keV. While we have formulated several mechanistic frameworks that quantitatively describe the basic processes and are able to deduce the impact on resolution (Figure 1), we are in the midst of developing theoretical means of knowing *a priori* which material properties mediate these intrinsic mechanisms. Addressing the experimental and theoretical challenges of elucidating these mechanisms, we aim to develop and apply a predictive model guiding the improvement of scintillator performance.

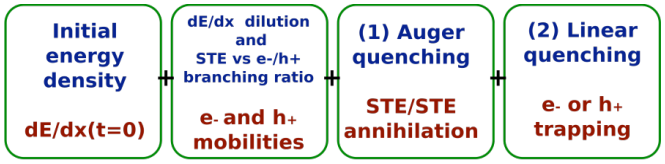

Figure 1: Summary of the four main mechanisms thought to be responsible for nonproportionality.

2. GOALS

Numerous experimental and theoretical pathways are being pursued simultaneously toward two primary research goals (Figure 2): (i) Nonproportionality mechanism or how to understand and predict nonproportionality behavior based on material properties; and (ii) Scintillator material engineering or how to control nonproportionality through engineered crystal growth procedures.

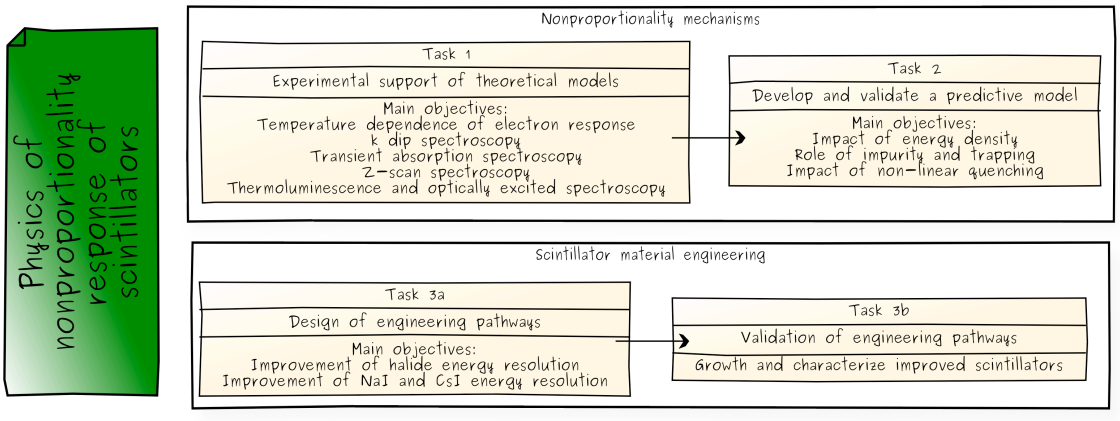

Figure 2 - Summary of the main tasks and objectives of the project

3. RESULTS, DISCUSSION AND CONCLUSIONS

There are two main research avenues that have been explored in term of experimental support of the theoretical model, namely improvement of the global characterization of the electron response and improvement of the independent probing of microscopic mechanisms impacting the nonproportionality response.

An important and successful effort has been done toward upgrading the SLYNCI apparatus to allow for a measurement of the electron response as a function of the temperature. In parallel, the development at the advance light source (ALS, LBNL) of a k-dip spectroscopy setup has giving us the possibility to rapidly probe the low energy electron responses at an unprecedented level of accuracy (Figure 3).

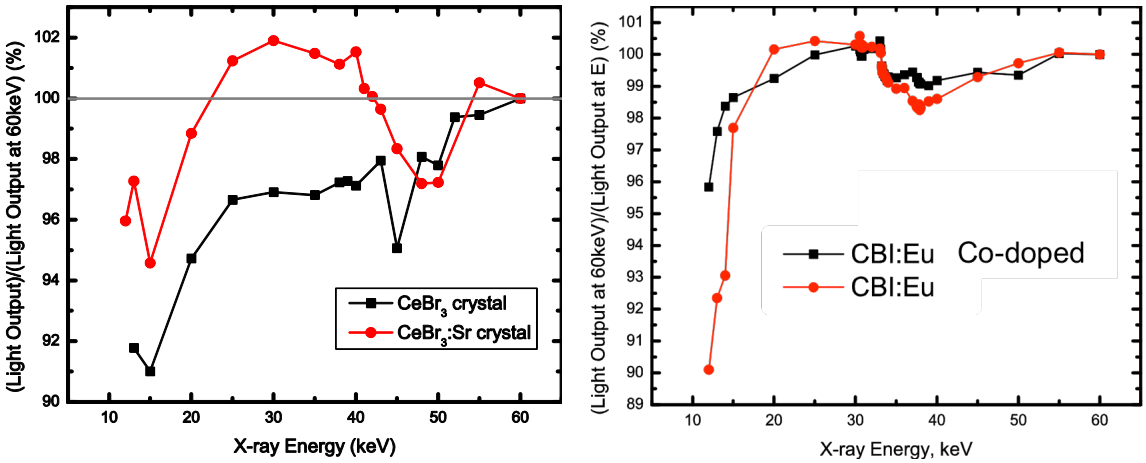

Figure 3 - Synchrotron/k-dip spectroscopy measurements of Ba_2CsI_5 showing improvement of the nonproportionality response resulting from addition of a co-dopant.

A second experimental effort has been done toward the individual probing of the mechanisms related to the nonproportional response of materials. These mechanisms, underlined in the previous SLYNCI lifecycle, are listed hereafter:

- Primary Electrons creation.
- dE/dx Dilution: Electron/hole mobility, lifetime and diffusion coefficients.
- Linear Quenching: Impact of trapping mechanisms on nonproportionality.
- Nonlinear Quenching: exciton-exciton annihilation and Auger quenching as a function of carrier excitation density.

These mechanisms are challenging to experimentally resolve due to their inherent interdependence. However, it was done successfully by developing appropriate diagnostic tools. For example, diffusion and nonlinear quenching that occur together in the particle track have been independently measured from Laser Photon Density Response and/or obtained from the literature for CsI, CsI:Tl, NaI:Tl, SrI_2:Eu, BGO, and $CdWO_4$ (Figure 4). Similarly, the linear quenching mechanisms have been successfully and independently studied using a set of experiments developed specifically for this project such as thermoluminescence, afterglow emission and time response, optically stimulated emission – all of them as a function of temperature (Figure 5).

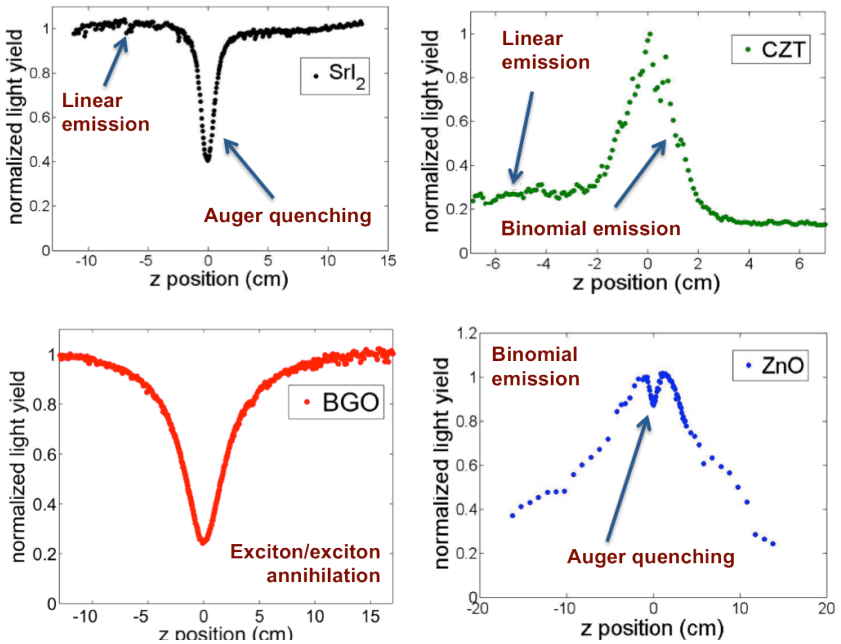

Figure 4 - Example of Laser Photon Density Response. The measurement allows for a snapshot of the nonlinear mechanisms in a scintillator.

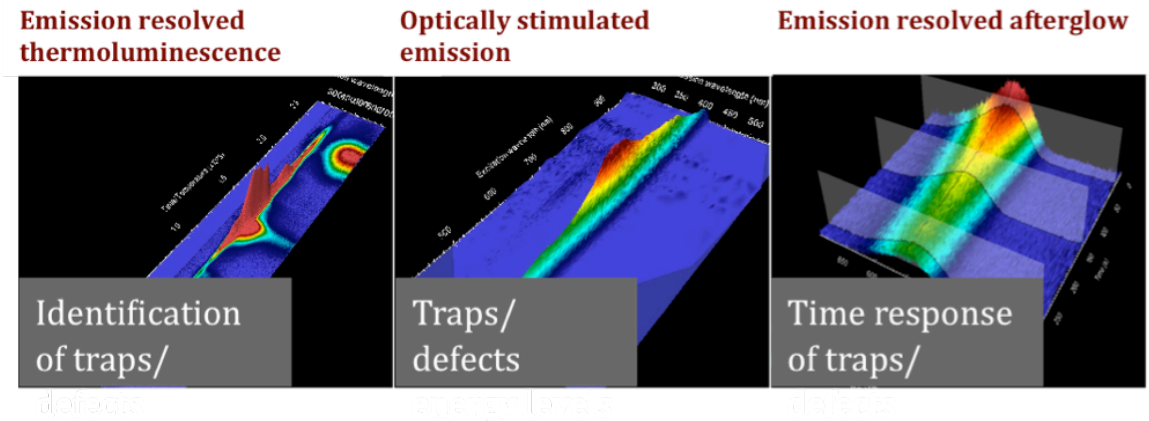

Figure 5 - Defect impact on scintillation mechanisms – Experimental study

These high quality and strongly constraining data have allowed testing, validating, and strengthening our mechanism-based predictive model of nonproportionality.

There has been an ongoing debate in the scientific literature regarding the importance of the multiple primary electrons created by gamma rays and the impact of delta rays on the amount of nonproportionality. To resolve the issue, we have used a Geant4 based code to calculate and map the straggling of dE/dx as a function of the energy of initial particle and an analytical approach to quantify the impact of delta-rays creation on the cascade mechanism (Figure 6). The results have shown that the density, while impacting the nonproportionality response as initial conditions of the following processes, is not a decisive one. Our calculation shown that there is little difference in term of initial excitation density between the various materials studied. Worth noting is the similarity between compound such as NaI, a poor performer in term of energy resolution, and SrI2, a scintillator among the best ones in term of energy resolution. These results

strengthened our hypothesis that the main impact connecting to excitation density to energy resolution degradation is related to the "dilution" of the initial excitation density due to mechanisms of energy carrier transport and trapping.

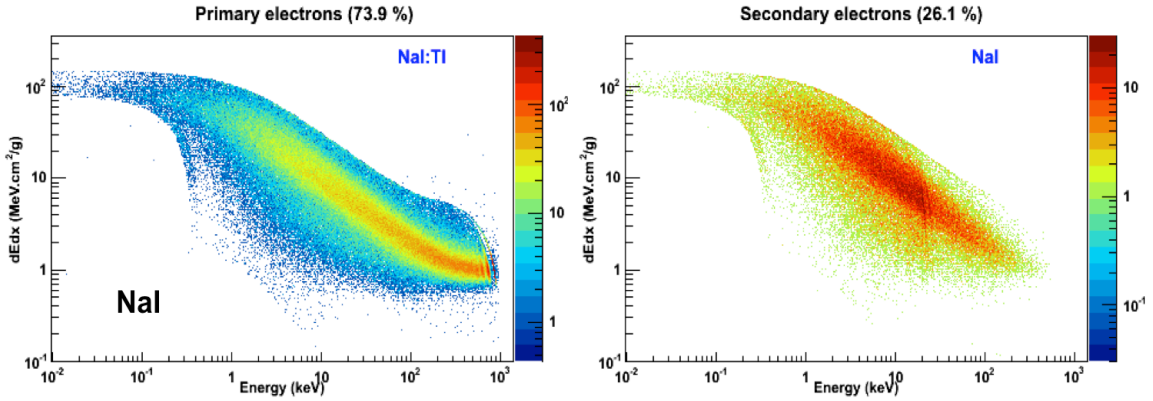

Figure 6 - Geant4 simulation showing the linear energy density deposited as a function of the electron energy in NaI. The simulation takes into account the Landau fluctuation and the creation of secondary particles. The dE/dx mapping allows us to quantify the contribution to energy resolution of each individual mechanisms encountered in the track.

The energy density dilution mechanism has been studied by means of Geant4 simulation, analytical modeling and first principle calculation. This framework has allowed to successfully model the role of free-carrier fraction η_{eh} and their mobilities on proportionality, which is in turn controlled by the highest optical phonon frequency (Figure 7). The latter is also impacted by the presence of trapping mechanisms that compete with the intrinsic mobility of energy carriers and in turn influence the excitation density dilution process. To understand the complex energy flow resulting from the presence of defects and impurities, we develop a model of energy transfer that account for the role of "temporary storage defects". The model was successfully developed by combining experimental results and theoretical calculations. The study has mainly focused on the Ba mixed halide known to have properties ranging from storage phosphor (BaBrF) to efficient scintillator (BaBrI). This study allows for a clear understanding of the complex interplay between energy transfer, defect complex and energy resolution. It has shown that intrinsic defects dependence on nonproportionality is more complex than this simple detrimental mechanism. If energetically and spatially tuned, defects can be beneficial (e.g. temporary energy storage), and eventually improve proportionality (Figure 8). This mechanism is thought to be more global than a particular case of Ba halide compounds and has now been extended to explain the mechanism involving extrinsic impurity such as co-doping. The root causes are similar in both cases. The intrinsic defect and the extrinsic co-dopant impurity are creating a beneficial defect (step stone) maximizing the energy transfer toward the emitting centers.

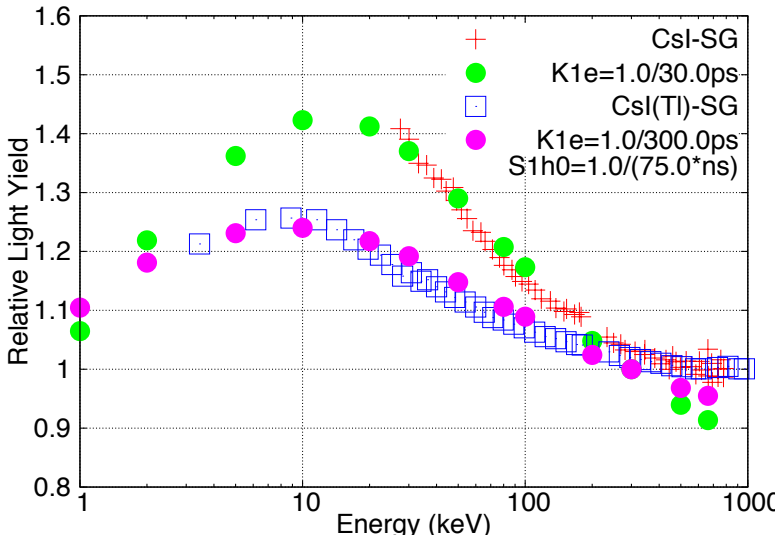

Figure 7 - Comparison of experimental and calculation of the electron response of CsI. Magenta circular points plot the calculated proportionality curve (electron response) using the combined parameters from literature and experiments. The model curve is overlaid on the Compton-coincidence experimental proportionality curve of CsI:Tl (0.082 mole%) at 295 K shown by the open green squares.

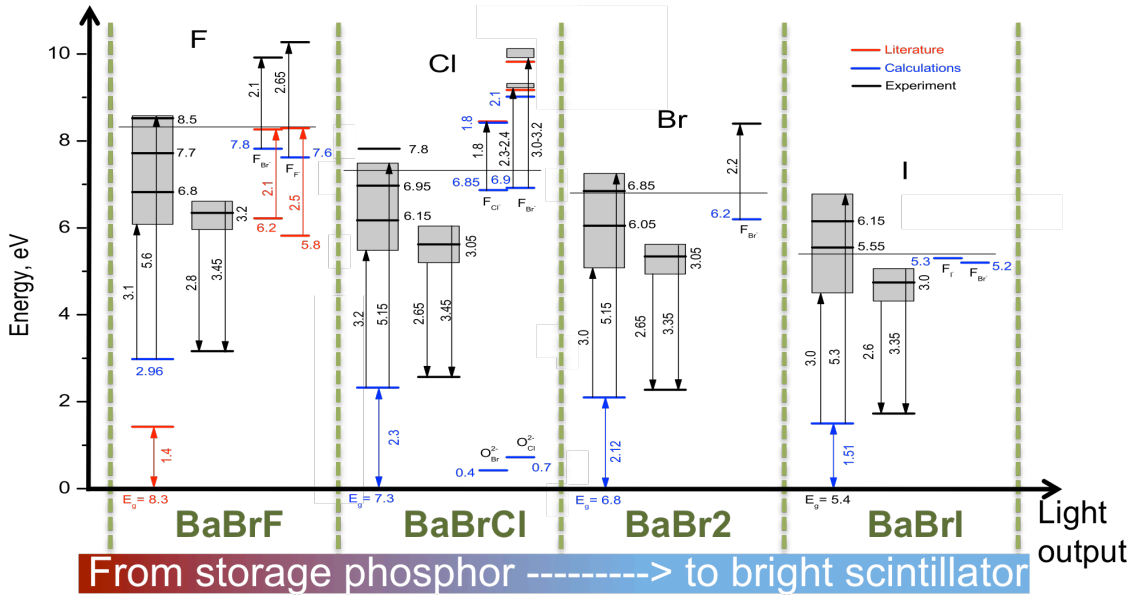

Figure 8 - Energy band diagram summarizing the impact of F centers energy level position on the global behavior of the compound, from storage phosphor (BaBrF) to brigh scintillator (BaBrI)

Based on our theoretical work, we have developed crystal growth pathways to improve the energy resolution of scintillators. Two different avenues have been explored, (i) the improvement of the performance via the mitigation of intrinsic defects toward the minimization of detrimental trapping mechanisms and (ii) the improvement of performance via the addition of beneficial extrinsic impurities toward the maximization of the energy transfer of the material. The work has targeted two classes of materials. The first class focused on the recently discovered Eu-doped Ba based halide compounds such as BaBrI, BaBrCl. The second class is the "historical" halide compounds such as NaI and CsI.

For the Ba-based scintillators, we have succeeded to improve the performance by mitigation the impact of detrimental intrinsic defect (Figures 9 - 10) but also by developing different co-doping strategy (Figure 11) that greatly improve the energy resolution even at very low europium concentration (from 9 to 5% at 662 keV for 0.5% europium doped BaBrCl samples). This is an important finding for any europium-doped scintillator. To date, high performance europium-doped scintillators require high dopant concentration usually of about 5%. Maintaining high scintillation performance at low europium concentration (less than 1%) has been shown to mitigate the difficulties inherent to europium-doped materials (e.g., contamination, non-uniformity, cracking, self-absorption) at the expense of degraded scintillation performance. Based on these results, it appears co-doping will facilitate their growth, improve the production yield and therefore ease their transition toward industry.

Figure 9 – Picture of a single crystal of BaBrCl grown in a standard Bridgman furnace (left) and one grown after a scavenger procedure (right). The yellow color is due to the presence of color centers/defects created during the growth process. The scavenger process allows for a mitigation of the defects and so an improvement of the material performance.

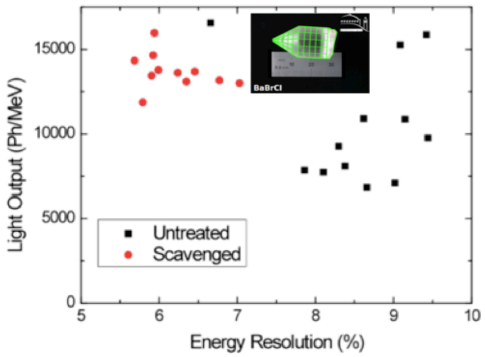

Figure 10 - Example of scintillation property measured on raw and engineered samples of BaBrCl. The results indicate an improvement of the energy resolution when an in situ control of defect is implemented during the growth of the compound.

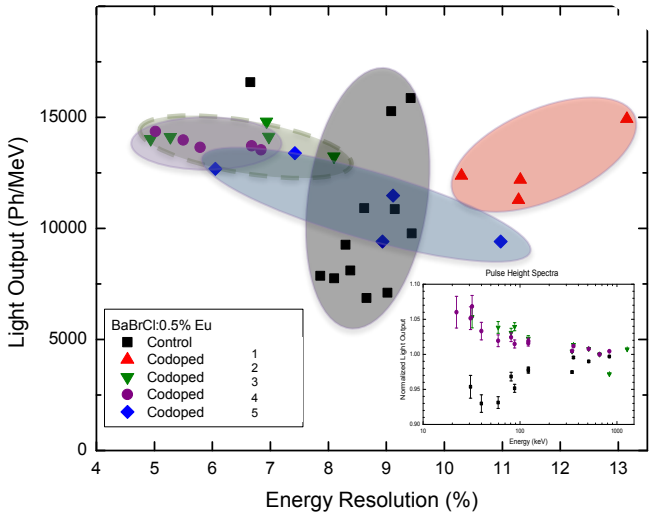

Figure 11 - Example of co-doping scheme developed through the program to control nonproportionality and energy resolution of BaBrCl. The inset presents the nonproportionality response for a reference, the two best co-doped samples

The strategy toward the improvement of alkali halide scintillators is different compared the Ba-based halide family. This subset of scintillators is known for its "ease"

of growth (large size and excellent production yield) but also to have moderate performance. Improving the performance without impacting the growth process and its cost will be a game changing in the scintillation market.

To engineer alkali halide scintillation performance, we have leveraged the development and use of modern data mining techniques (statistical multi-regression methods) and our capability to synthesize (LBNL's DHS/DNDO-funded High-Throughput Scintillator Discovery project) and rapidly grow/evaluate single crystals (LBNL's DOE/NA22-funded Crystal Growth project) to probe in a timely manner a large parameter space of possible beneficial impurities. The approach has been demonstrated successful in improving NaI(Tl) performance. Figure 12 compares the photopeak measured on a reference NaI(Tl) sample to one obtained with our current best co-doping scheme. The energy resolution of our co-doped NaI is improved by more than 1.5% to reach 4.9% at 662 keV while the light output has been increase of more than 10,000 ph/MeV. Further improvements are expected as we are now moving toward optimization of the process. This subset of scintillators is known for its "ease" of growth (large size and excellent production yield) but also to have moderate performance. Improving the performance without impacting the growth process and its cost will be a game changing in the scintillation market.

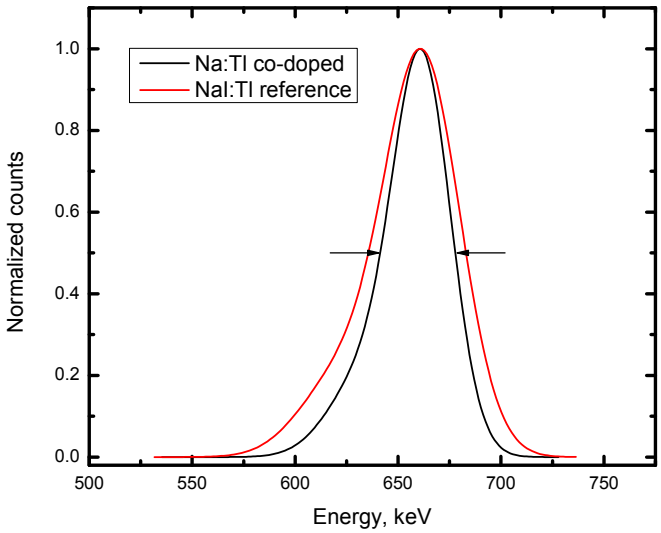

Figure 12 - Photopeak measured on two NaI samples, reference and co-doped, respectively. The co-doped sample has seen its energy resolution going from 6.5 to 4.9%.

The project has demonstrated unprecedented successes in terms of improving energy resolution of scintillators guided by a deeper understanding of microscopic scintillation mechanisms. These successes have been possible and driven by the joint efforts of three institutions (LBNL, LLNL, and Wake Forest University) to develop a fundamental understanding of nonproportionality. These breakthroughs in understanding have opened several pathways to implement the findings toward the control of nonproportionality through engineered growth for the next generation of scintillators.

4. PUBLICATIONS

Book chapter

[1] R. T. Williams et al., "*Scintillation Detectors of Radiation: Excitations at High Densities and Strong Gradients*", Excitonic and Photonic Processes in Materials, Springer-Verlag, Berlin, 2014.

Publications

[1] Q. Li, J.Q. Grim, K.B. Ucer, R.T. Williams, G.A. Bizarri, and W.W. Moses "Predictive transport and quenching model for nonproportionality", IEEE Transaction on Nuclear Science.

[2] Qi Li, Joel Q. Grim, K. B. Ucer, A. Burger, G. A. Bizarri, W. W. Moses, R. T. Williams, "Host structure dependence of light yield and proportionality in scintillators on ωLO, μe, μh, and hot-electron vg", Physica Status Solidi (RRL) - Rapid Research Letters, Vol 6, Issue 8, pages 346–348, 2012.

[3] R. T. Williams, Joel Q. Grim, Qi Li, K. B. Ucer, G. A. Bizarri, S. Kerisit, Fei Gao, P. Bhattacharya, E. Tupitsyn, E. Rowe, V. M. Buliga, and A. Burger,*"Experimental and computational results on exciton/free-carrier ratio, hot/thermalized carrier diffusion, and linear/nonlinear rate constants affecting scintillator proportionality***",** SPIE Proceedings of the Symposium on Hard X-ray and Gamma Ray Detectors, San Diego, 2013.

[4] J. Grim et al., "*Nonlinear quenching of densely excited states in wide-gap solids* ", Phys. Rev. B, **7**, 125117, 2013.

[5] J. Grim et al., "*Electron energy response of NaI:Tl and SrI2:Eu calculated from carrier mobilities and measured 1st and 3rd order quenching*", MRS Com., **2**, 139-43, 2012.

[6] J. Grim et al., "*The roles of thermalized and hot carrier diffusion in determining light yield and proportionality of scintillators*", Phys. Stat. Sol. A, 209, 2421-2426, 2012. W.W. Moses, G. Bizarri, R.T. Williams and S.A. Payne, "*The origins of nonproportionality*", IEEE TNS, **59**, 2038-44, 2012.

[7] K. B. Ucer, G. Bizarri, A. Burger, A. Gektin, L. Trefilova, and R. T. Williams, "Electron thermalization and trapping rates in pure and doped alkali and alkaline-earth iodide crystals studied by picosecond optical absorption", Phys. Rev. B, 89, 165112, 2014.

Invited Presentations

[1] "Phenomenological and Computational Models of Scintillation Mechanisms: A Material Science Point of View" IEEE TNS/MIC, 2012.

[2] "Study of Nonproportionality in halide scintillators Phenomenological models and experiments" LUMDETR, 2012.

[3] "Physics of bright halide scintillators", ASM 2013.

[4] "*Picosecond time-resolved studies of scintillation materials and processes*" ASM 2013.

[5] "*Interband photon density response: LO and nonlinearity without electron tracks*", ASM 2013.

[6] "*Theory of the scintillation process*", invited tutorial on scintillation mechanism SCINT2013.

[7] "*Experimental and computational results on exciton/free-carrier ratio"* SPIE 2013.

[8] "*Nonlinear quenching of densely excited states in scintillators and semiconductors*", SCINT2013.

[9] "Scintillation Mechanism: From application to fundamental understanding" Phosphor Global Summit 2013.

[10] ""*Understanding scintillation physics for discovery of new scintillators*", 2013 NSSC summer.

[11] ""*New ideas for better inorganic scintillators*", SORMA'14, 2014.

[12] "*Activator Physics: First Principles Studies Ce and Eu doped Inorganic Scintillators*", NA22 Scintillator Workshop, 2014.

[13] "*K-dip spectroscopy*" NA22 Scintillator Workshop, 2014.

[14] "*Surrogate laser experiments & modelling*" NA22 Scintillator Workshop, 2014.

[15] High Performance Ba-Halide Scintillators. Energy Transfer and Scintillation Mechanisms" SORMA2012, 2012.