Defect Engineering via Isovalent and Aliovalent Co-Doping for Enhanced Scintillation Performance in CsI:Tl Single Crystals

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CsI:Tl is the well-known scintillator material with high light yield ~ 64,000 photons/MeV relatively low hygroscopicity, excellent mechanical stability, and well-established single crystal growth process [1]. The scintillation decay scheme of CsI:Tl involves multiple radiative channels with distinct decay components, arising from different Tl-related luminescence centers [2]. The presence of these multiple decay components enables pulse shape discrimination (PSD) makes it attractive for mixed-field radiation detection. However, the same complex decay scheme also leads to significant afterglow, which limits high count-rate applications, and adversely affects energy resolution in certain detection scenarios [1]. To reduce the afterglow component while maintaining the PSD capability, a defect engineering approach was adopted. In this approach, both isovalent (Na^+) and aliovalent (Sr^{2+} and Eu^{2+}) co-dopants were selected based on band-structure calculations to rationally tailor the scintillation decay scheme of CsI:Tl. Band structure calculations reveal that Na^+, Sr^{2+}, and Eu^{2+} form cation-cation bonded defect centers, which introduce new deep electronic states within the band gap. These deep states are likely responsible for effective trapping of charge carriers, thereby contributing to the suppression of afterglow. Based on the theoretical predictions, single crystals of CsI:Tl and CsI:Tl co-doped with Na^+, Sr^{2+}, and Eu^{2+} were successfully grown. Experimental studies, including thermoluminescence and afterglow measurements (Figure 1 (a)), clearly demonstrate a significant reduction in afterglow upon co-doping, in excellent agreement with the theoretical results, thereby confirming the effectiveness of the proposed defect-engineering approach. Further, scintillation decay profiles under gamma and alpha irradiation were recorded to evaluate the PSD capability. The comparative PSD analysis reveals that Eu^{2+} and Sr^{2+} co-doping reduces the PSD contrast between gamma and alpha radiation, whereas Na^+ co-doping effectively preserves the PSD capability, comparable to that of pristine CsI:Tl as shown in Figure 1 (b). These results demonstrate that theory-guided defect engineering enables effective suppression of afterglow in CsI:Tl, while highlighting Na^+ co-doping as an optimal strategy to retain PSD performance, offering a balanced route for tailoring scintillation properties for mixed-field radiation detection applications.

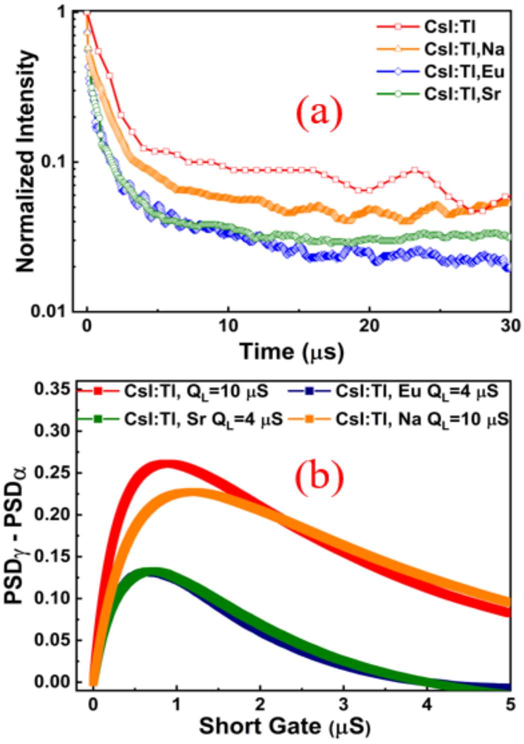

Figure 1. (a) Afterglow characteristics and (b) variation in the PSD parameter for CsI:Tl and CsI:Tl co-doped with Na^+, Sr^{2+}, and Eu^{2+}.

[1] D. S. Sisodiya *et al.*, "Optimizing the Scintillation Kinetics of CsI Scintillator Single Crystals by Divalent Cation Doping: Insights from Electronic Structure Analysis and Luminescence Studies," *The Journal of Physical Chemistry C*, vol. 128, no. 1, pp. 197–209, Jan. 2024, doi: 10.1021/acs.jpcc.3c06098.

[2] P. A. Rodnyi, *Physical Processes in Inorganic Scintillators*, 1st ed. CRC Press, 2020. doi: 10.1201/9780138743352.