

Research Article

Latest updates in growth and performance of Ce-doped Tl_2LaCl_5 and Tl_2GdBr_5 and Eu-doped TlCa_2Br_5 and TlSr_2I_5

R. Hawrami^{a,*}, E. Ariesanti^b, A. Burger^b, H. Parkhe^b

^a Xtallized Intelligence, Inc., Nashville, TN, 37211, USA

^b Fisk University, Nashville, TN, 37208, USA



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ABSTRACT

Nuclear and high energy physics research has a need for new, high performance scintillators with high light yields, high densities, fast decay times, and radiation hardness. In this paper we present crystal growth and results from 16-mm diameter cerium (Ce)-doped Tl_2LaCl_5 (TLC) and europium (Eu)-doped TlCa_2Br_5 (TCB) as well as one-inch diameter cerium-doped Tl_2GdBr_5 (TGB) and europium-doped TlSr_2I_5 (TSI), each grown in a two-zone vertical furnace by the modified Bridgman method. Samples extracted and processed from the grown boules are characterized for their scintillation properties like energy resolution, light yield, decay time and non-proportionality. Energy resolution (FWHM) at 662 keV of 5.1%, 3.4%, 4.0%, and 3.3% are obtained for samples of TGB, TLC, TCB, and TSI, respectively. Ce-doped TGB and TLC have single decay time components of 26 ns and 48 ns, respectively, while Eu-doped TCB and TSI have long decay times with primary decay constants of 571 ns and 630 ns. These compounds exhibit good proportionality behavior when compared to NaI:Tl and BGO.

1. Introduction

The field of inorganic scintillators has expanded in the last three decades, with the (re)discovery and successful growth of novel and advanced scintillation compounds [1]. Demand for high light yield, high density, and fast scintillators necessitate a continuous search for new materials. Traditional scintillators such as Tl-doped sodium iodide (NaI) and cesium iodide (CsI) have been very reliable standards, supported by decades of research and proven performance. However, various new applications require bright materials that also have high densities and fast decay times. For nearly two decades emerging new scintillators such as rare-earth binary compounds of CeX_3 [2–7] and LaX_3 [8–11], as well as ternary metal halide compounds of Cs_2AX_5 [12], where A = La or Ce, and X = Cl, Br, or I (halides), have demonstrated the potentials of these metal halides as next-generation scintillation detectors. Rediscovered Eu-doped SrI_2 [13], with a light yield as high as 110,000 photons/MeV and moderate density of 4.55 g/cm³, has also shown the potential of alkaline metal halide scintillators [14,15]. Commonly used inorganic scintillators like CsI:Tl, $\text{LaBr}_3\text{:Ce}$, as well as oxide-based LSO and PbWO_4 , are currently being used in high energy physics experiments [9, 10,16–18]. These scintillators have some, if not all, of the desired properties such as high densities, high light yields, and fast decay times.

The combination of high-light yield and fast response can be found in Ce^{3+} , Pr^{3+} , or Nd^{3+} -doped lanthanide scintillators, with one of the maximum light yield conversion of 100,000 photons/MeV can be found in Eu^{2+} -doped SrI_2 . However, growth of these oxide-based and lanthanide-doped scintillators is inefficient and expensive because of high growth temperatures. Many binary and ternary halides have low detection efficiency because they do not contain any constituents with very high atomic number (Z) and their density is moderate. These factors not only impact their overall photon stopping power but also compromises the photofraction (or peak-to-total ratio) [19,20] for detection of low-energy gamma-rays. Higher photo-fraction is important, because it provides more counts in the desired photopeak region of the energy spectrum, making the task of isotope identification easier and faster.

Recently high detection efficiency Tl-based scintillation crystals have attracted good attention from worldwide scintillator researchers. These compounds have been investigated and very promising initial results have been published, for example Ce-doped Tl_2LaCl_5 (TLC) [21,22] as well as *intrinsic* (i.e., undoped) TlMgCl_3 (TMC) and TlCaI_3 (TCI) [23–25]. These new compounds are of high atomic numbers and high densities (>5 g/cm³), as well as bright (light yields between 31,000 and 76,000 photons/MeV for 662 keV photons), fast decay times (36 ns (89%) for TLC; 46 ns (9%) for TMC; 62 ns (13%) for TCI), and moderate melting

* Corresponding author.

E-mail address: hawrami@xtalintel.com (R. Hawrami).

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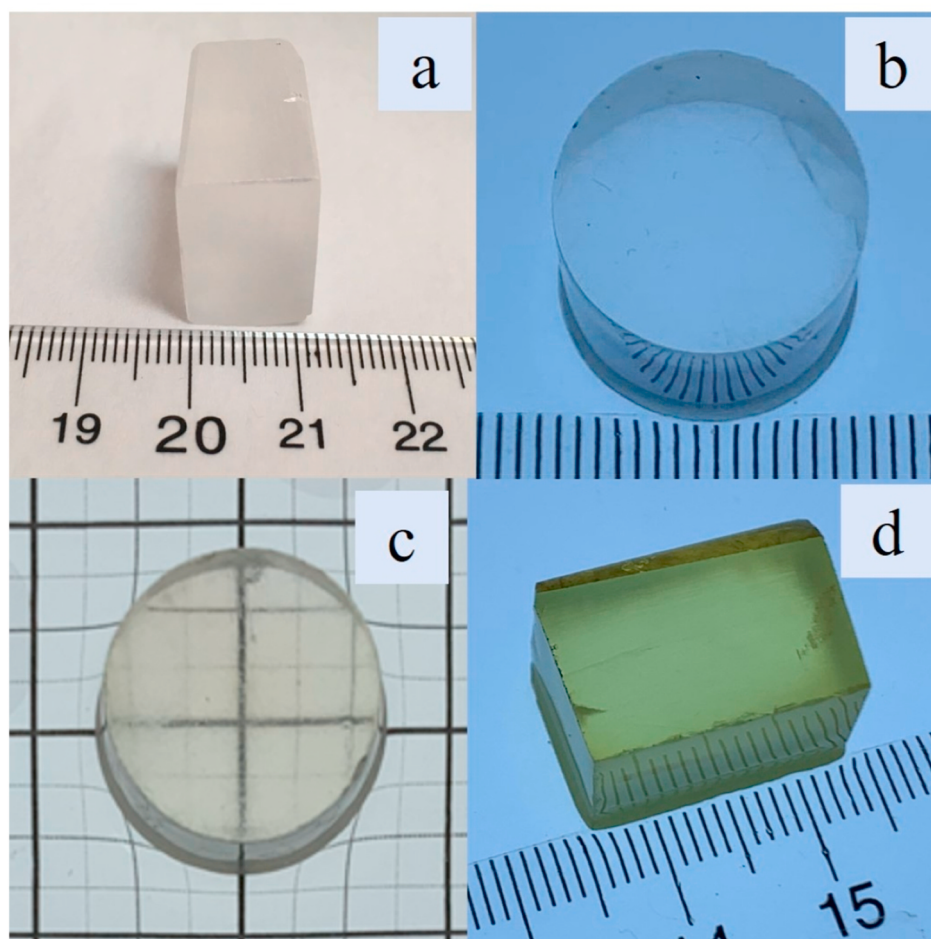


Fig. 1. Samples that were cut and processed from successfully grown crystal boules of (a) $\varnothing$ 1-inch TGB ($10 \times 25 \times 30 \text{ mm}^3$ sample size), (b) $\varnothing$ 16-mm TLC (16 mm sample thickness), (c) $\varnothing$ 16-mm TCB (8 mm sample thickness), and (d) $\varnothing$ 1-inch TSI ($12 \times 15 \times 20 \text{ mm}^3$ sample size).

points (between 500 and 700 °C). As seen further in the published results [1,21–30], many Tl-based scintillators such as the ones previously mentioned have promising properties desirable for high energy physics as well as homeland security applications. In this paper we are reporting on the growth and scintillation characterization (^{137}Cs spectra, decay times and non-proportionality behavior) of cerium-doped Tl_2LaCl_5 (TLC) and Tl_2GdBr_5 (TGB) as well as europium-doped TlCa_2Br_5 (TCB) and TlSr_2I_5 (TSI) scintillation crystals.

1.1. Experimental procedure

Based on stoichiometric calculations, the appropriate amounts of starting halide compounds (all in powder form with 4 N purity) were loaded into a growth ampoule: for Tl_2GdBr_5 (TGB) is 2 TlBr + GdBr₃ with 3% CeCl₃ as dopant; for Tl_2LaCl_5 (TLC) is the mix of 2 TlCl + LaCl₃ with 3% CeCl₃, as dopant; for TlCa_2Br_5 (TCB) is TlBr + 2CaBr₂ with 5% EuBr₂ as dopant; for TlSr_2I_5 (TSI) is TlI + 2SrI₂ with 5% EuI₂ as dopant. TGB and TSI growth runs were conducted in $\varnothing$ 1-inch (inner diameter) quartz ampoules, while TLC and TCB growth runs in $\varnothing$ 16-mm (inner diameter) quartz ampoules. Material loading was conducted inside a glove box with inert atmosphere. After loading, each ampoule was subsequently sealed under high vacuum 2.4×10^{-5} Torr and placed in a two-zone vertical Bridgman furnace. Furnace zone temperatures were set such that the temperature profiles would facilitate melting at around 780 °C, 680 °C, 550 °C, and 630 °C for TGB, TLC, TCB and TSI, respectively. For each experiment, the crystal growth process commenced at a rate of 15–20 mm/day and the post-crystallization cooling at a rate of 100 °C–150 °C/day.

After the cooling down procedure was completed, the ampoules were retrieved from the furnaces and samples were harvested from the boule. Each sample was lapped and polished with Al₂O₃ and/or SiC sandpapers. Mineral oil was used for lubrication during processing as well as for sample protection from moisture because TLC, TGB, TCB and TSI were hygroscopic. The polished samples were tested for their radiometric and scintillation properties. To measure energy resolution and non-proportionality behavior, each sample was placed in mineral oil in a quartz cup wrapped with Teflon tape as a reflector. A piece of Gore® flexible Teflon sheet was used as the back reflector. Using BC-630 optical grease, the oil cup was coupled to a R6231-100 Hamamatsu $\varnothing$ 2-inch super bi-alkali photomultiplier tube (PMT). The signals from the anode were fed to a Canberra 2005 preamplifier, a Canberra 2020 amplifier, and a MCA8000D multi-channel analyzer. ^{137}Cs spectra were collected for each sample and analysis of the full energy peak of 662 keV was conducted to obtain energy resolution and light yield information. Spectra from other gamma-ray check sources, including ^{22}Na , ^{57}Co , ^{60}Co , ^{133}Ba , ^{152}Eu , and ^{241}Am , were also collected to determine the non-proportionality data for each compound. Scintillation decay time profiles due to γ -ray radiation were measured with a ^{137}Cs check source and the signal waveforms collected at the PMT anode were recorded with CAEN DT5720C digitizer and then were analyzed offline.

2. Results and analysis

2.1. Crystal growth and sample processing

Samples from successfully grown crystal boules of $\varnothing$ 1-inch TGB,

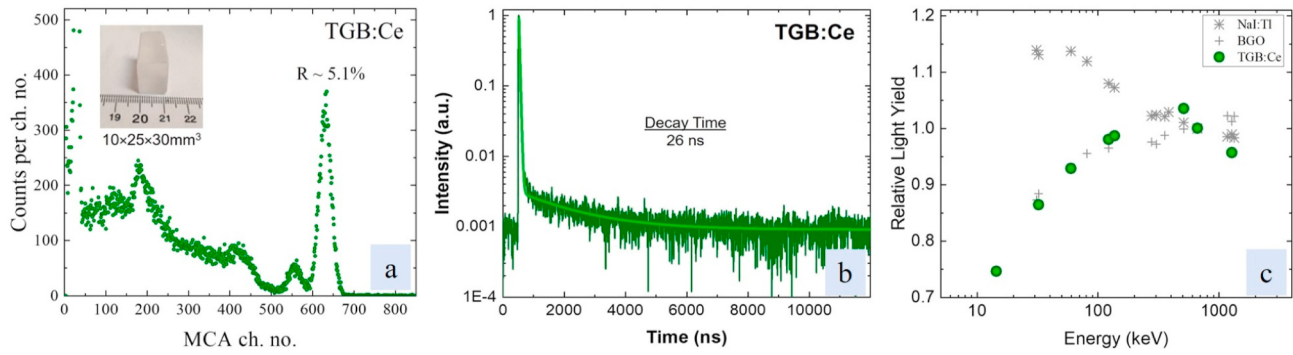


Fig. 2. (a) ^{137}Cs spectrum collected with the TGB sample. (b) Decay time profile of TGB. (c) Non-proportionality data for TGB.

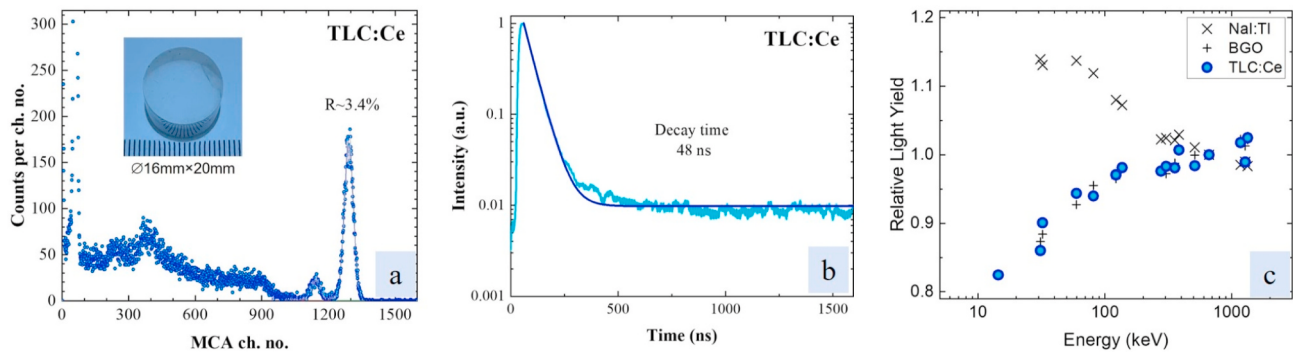


Fig. 3. (a) ^{137}Cs spectrum collected with the TLC sample. (b) Decay time profile of TLC. (c) Non-proportionality data for TLC.

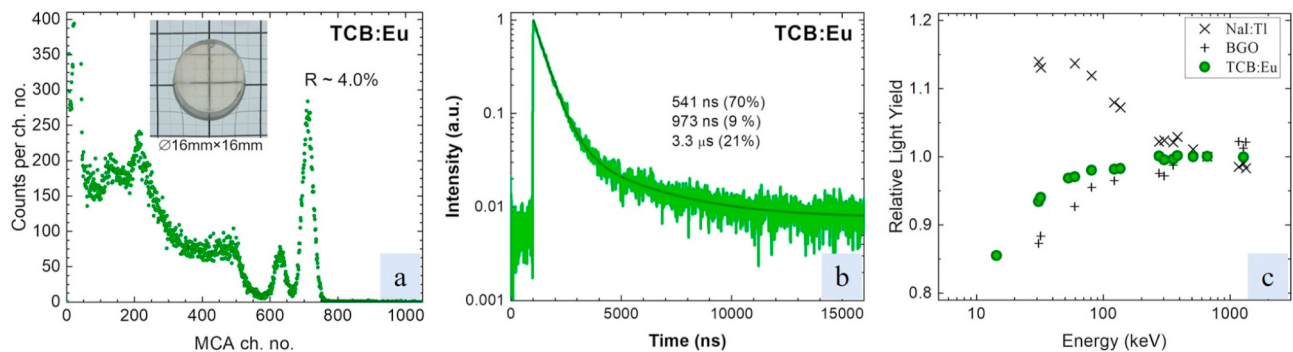


Fig. 4. (a) ^{137}Cs spectrum collected with the TCB sample. (b) Decay time profile of TCB. (c) Non-proportionality data for TCB.

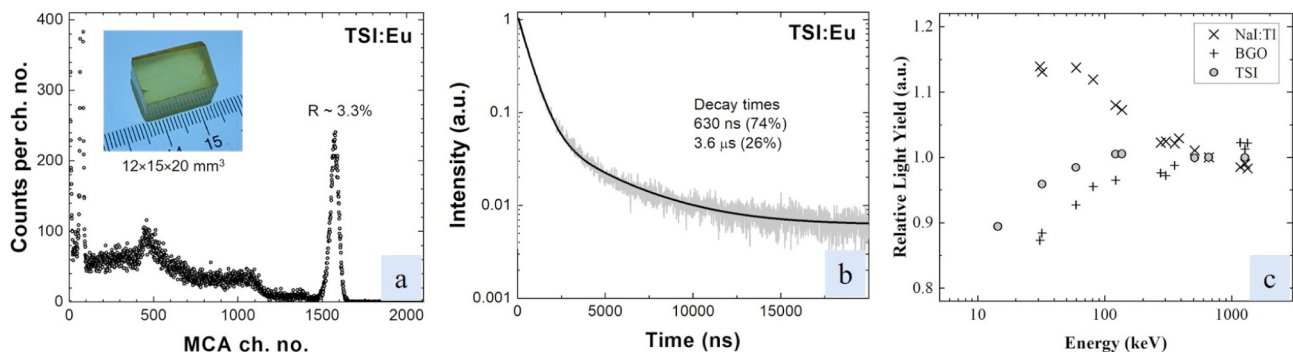


Fig. 5. (a) ^{137}Cs spectrum collected with the TSI sample. (b) Decay time profile of TSI. (c) Non-proportionality data for TSI.

Ø16-mm TLC, Ø16-mm TCB, and Ø1-inch TSI are shown in Fig. 1: $10 \times 25 \times 30 \text{ mm}^3$ TGB, Ø16-mm $\times$ 16 mm TLC, Ø16-mm $\times$ 8 mm TCB, and $12 \times 15 \times 20 \text{ mm}^3$ TSI. Each sample was processed immediately prior to characterization with previously described processing procedures.

2.2. Scintillation detector performance

Results for Ce-doped TGB and TLC are shown in Figs. 2 and 3, respectively. Energy resolution of 5.1% (FWHM) at 662 keV was calculated for TGB (Fig. 2(a)) while energy resolution of 3.4% (FWHM) was calculated for TLC (Fig. 3(a)). Ce-doped scintillators are known to produce fast decay times [1,21,22,26,27], as seen in Figs. 2(b) and 3(b), where single decay time constant of 26 ns was measured for TGB and 48 ns was measured for TLC. The proportionality behavior or the relative light yield data as a function of photon energy for each scintillator is shown in Figs. 2(c) and 3(c), respectively. For either sample less than linear response (outside of $\pm 5\%$ from unity) was observed for γ -ray energy less than 200 keV. The reasons are yet to be determined. Although the samples were characterized in oil to avoid moisture interaction, nevertheless, slight sample degradation might have occurred and could have decreased the apparent relative light yield as clearly shown in non-proportionality curve.

Results for Eu-doped TCB and TSI are shown in Figs. 4 and 5, respectively. Energy resolution of 4.0% (FWHM) at 662 keV was calculated for TCB (Fig. 4(a)) while energy resolution of 3.3% (FWHM) was calculated for TSI (Fig. 5(a)). Eu-doped scintillators are known to have long decay times [1,14,15,28–30], as seen in Figs. 4(b) and 5(b). The decay time profile for TCB (Fig. 4(b)) was fitted with three exponential functions, resulting in decay constants of 541 ns (70%), 973 ns (9%), and 3.3 μ s (21%). The decay time profile for TSI (Fig. 5(a)) was fitted with two exponential functions, resulting in decay constants of 630 ns (74%) and 3.6 μ s (26%). The proportionality behavior or the relative light yield data as a function of photon energy for each scintillator is shown in Figs. 4(c) and 5(c), respectively. For either sample less than linear response (outside of $\pm 5\%$ from unity) was observed for γ -ray energy less than 50 keV. The reasons are yet to be determined. Similar with the sample treatment for TGB and TLC, although the TGB and TSI samples were characterized in oil to avoid moisture interaction, nevertheless, slight degradation might have occurred, thus decreasing the apparent relative light yield.

3. Conclusions

This paper reports on successful growth runs and initial scintillating performance characterization of 16-mm diameter cerium-doped Ti_2LaCl_5 (TLC) and europium-doped TiCa_2Br_5 (TCB) as well as one-inch diameter cerium-doped Ti_2GdBr_5 (TGB) and TiSr_2I_5 (TSI), all grown by the vertical Bridgman method. Samples were extracted from the boules and processed for characterization. Energy resolution of 5.1%, 3.4%, 4.0%, and 3.3% are obtained for samples of TGB, TLC, TCB, and TSI, respectively. Ce-doped TGB and TLC have single decay time components of 26 ns and 48 ns, respectively, while Eu-doped TCB and TSI have long decay times with primary decay constants of 571 ns and 630 ns, respectively. These compounds exhibit good proportionality behavior when compared to NaI:Tl and BGO.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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