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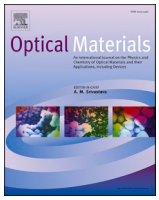

Latest growth of large diameter Tl-based elpasolite scintillation crystals

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ABSTRACT

Elpasolite scintillators play an important role in radiation detection and imaging. Novel Tl-based elpasolite scintillators such as Ce-doped Tl_2LiYCl_6 (TLYC) have been developed as excellent Tl-based dual mode gamma and neutron detectors. This paper presents a successful high yield growth and γ-ray characterization of large diameter (1-inch to 1.5-inch diameter) single, crack-free, and transparent TLYC crystals at Fisk University. Energy resolution of 4.2% (FWHM) at 662 keV and light yield of 26,000 photons/MeV are measured. As-processed and hermetically packaged TLYC samples are characterized for their gamma-ray energy resolutions, light yields, non-proportionality behaviors and decay times. Successful growth of 1-inch diameter $(Cs,Tl)_2LiLaBr_6$:Ce crystals are also shown. The best result is obtained when the content of Cs^+ is larger than Tl^+. Energy resolution of 3.4% (FWHM) at 662 keV is measured for $(Cs,Tl)_2LiLaBr_6$:Ce for 75% Cs-to-25% Tl ratio.

1. Introduction

Demand for high density, fast decay time and high detection efficiency 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 LaX_3 [1], CeX_3 [2] and Cs_2AX_5 [3], 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 europium doped SrI_2, with a light yield as high as 110,000 ph/MeV and moderate density of 4.55 g/cm^3, has also shown the potential of alkaline metal halide scintillators [4].

New cubic-structured scintillation materials, like recently discovered elpasolite family, with composition A_2BLnX_6; where A and B are alkali metal ions, Ln is lanthanide ion, and X is halogen ion, hold promise for scintillator materials due to their excellent energy resolution, high light output, proportionality, and toughness. The isotropic nature of the cubic elpasolites leads to minimal thermo mechanical stresses during single-crystal solidification during melt growth and eliminates the problematic light scattering at the grain boundaries [5]. Recent elpasolite scintillators, such as Cs_2LiYCl_6:Ce (CLYC) [6–8], $Cs_2LiLaBr_6$:Ce (CLLB) [9–11], and Tl_2LiYCl_6:Ce (TLYC) [12,13], have been recently favored by many researchers due to their good properties and they are currently in early production stages. TLYC was grown as a thallium analogue to CLYC, where replacing Cs ion with Tl ion leads to a higher density and a higher effective atomic number [12,13]. Besides having a better detection efficiency, TLYC has a lower melting point, higher photo fraction, higher light yield, shorter decay time constants compared to CLYC [13].

While favorable properties of TLYC raise its status to an almost ideal scintillator, issues surrounding the growth of elpasolite crystals, especially large (≥1-inch) diameter growth, are still a concern for TLYC as well. Growing elpasolite crystals usually requires binary compounds as starting materials, including dopants. Reactions between these binaries create undesirable additional phases in the melt and, eventually, crystal. Hence incongruency in melt grown elpasolite crystals is an issue. When the growth is incongruent, the growth yield is low, which increases the overall production cost. Elimination of these additional phases can be accomplished if the crystal grower knows the behavior of these phases, usually with the aid of phase diagrams. Elpasolite scintillators also depend on dopants to create the necessary energy levels to promote or improve scintillation. Non-uniformity in dopant distribution causes dissimilar scintillation performance from different parts of the crystal boule, which decreases the number of useable crystal parts. All these detrimental factors not only decrease growth yield, but they also influence the overall cost to produce elpasolite scintillators. Most of elpasolite crystals like TLYC are also hygroscopic, thus requiring proper handling procedures and hermetic packaging to preserve the crystals.

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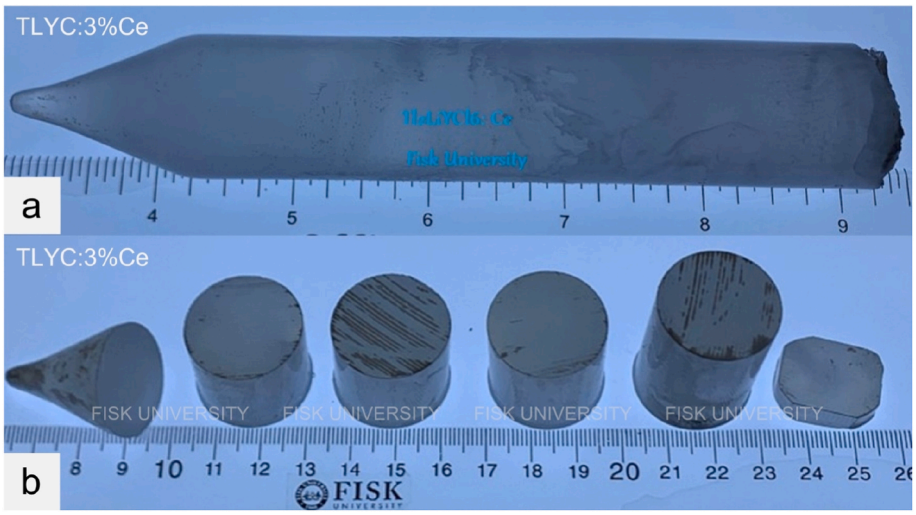

Fig. 1. (a) 1-inch diameter TLYC crystal boule from the initial growth run. (b) As-cut and as-lapped crystal samples of the boule in (a).

Another Tl-based elpasolite crystal $Tl_2LiLaBr_6$:Ce (TLLB), based off its Cs-analogue CLLB, has also been considered [14]. CLLB has a slight advantage over CLYC for its higher light yield, better energy resolution, and much shorter decay time constants. Like CLYC, due to neutron sensitive elements in the matrix, CLLB is a dual-mode γ-n scintillation detector, also capable of pulse height discrimination (PHD) and pulse shape discrimination (PSD) [10,11]. Because of these favorable properties of CLLB, its Tl-analogue TLLB has been considered. Unlike CLLB, however, TLLB is not congruent when grown by melt (as seen in Fig. 1 in [14]). To avoid non-congruence issue, Cs–Tl mixed cation elpasolites $(Cs,Tl)_2LiLaBr_6$:Ce are being considered.

In this paper describes the crystal growth of Tl-based elpasolite scintillators at Fisk University. The main objective of the successful high yield growths of 1-inch and 1.5-inch diameter Ce-doped Tl_2LiYCl_6 (TLYC) elpasolite scintillators, 1-inch diameter new mixed cation elpasolites $(Cs,Tl)_2LiLaBr_6$:Ce are presented. Initial packaging efforts of TLYC crystals at Fisk University are also reported. Growth and scintillation characterization results, like energy resolution, relative light yield data, non-proportionality data and luminescence decay time, will be described in the following sections.

2. Experimental methods

Stoichiometric amounts of binary compounds TlCl, LiCl, YCl_3 and $CeCl_3$ (amounting to 3-wt%), all with 4 N purity, were used as the starting materials for growing TLYC. Binary compound CsCl (4 N) was also used when growing mixed cation elpasolite $(Cs,Tl)_2LiLaBr_6$:3%Ce. The growth process started with material purification using the zone refining technique. Purified TLYC starting materials were loaded into a pre-cleaned baked quartz ampoule in an inert atmosphere glove box, then dehydrated and sealed under high vacuum. Two-zone vertical Bridgman furnaces were utilized to grow 1-inch and 1.5-inch (inner)

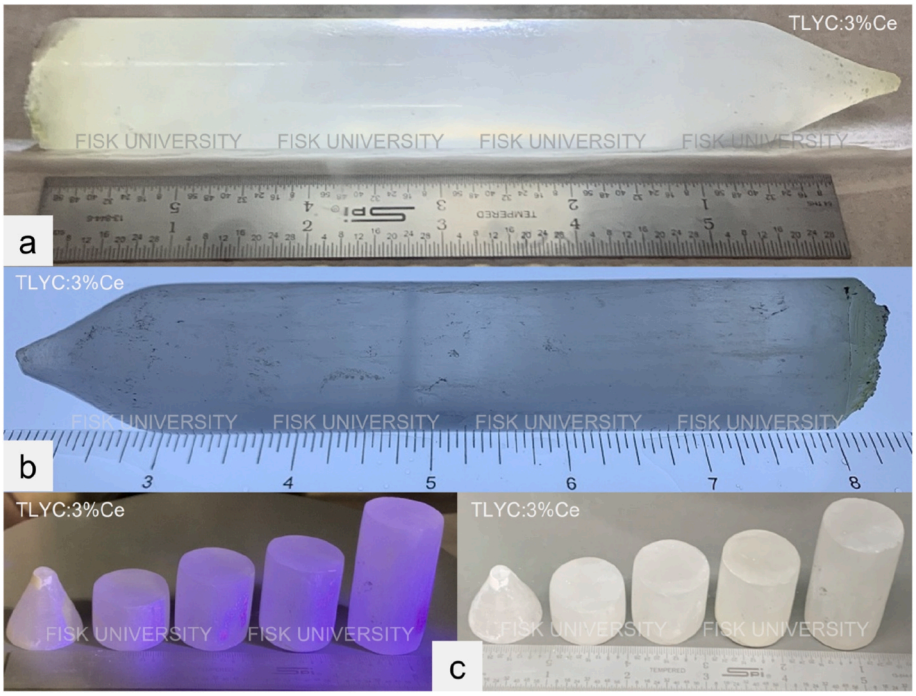

Fig. 2. (a) The second 1-inch diameter TLYC crystal boule and (b) the third 1-inch diameter TLYC crystal boule, both grown at Fisk University. (c) As-cut and as-lapped samples of different crystal lengths (left: under UV light, right: under ambient light condition) from the boule in (b).

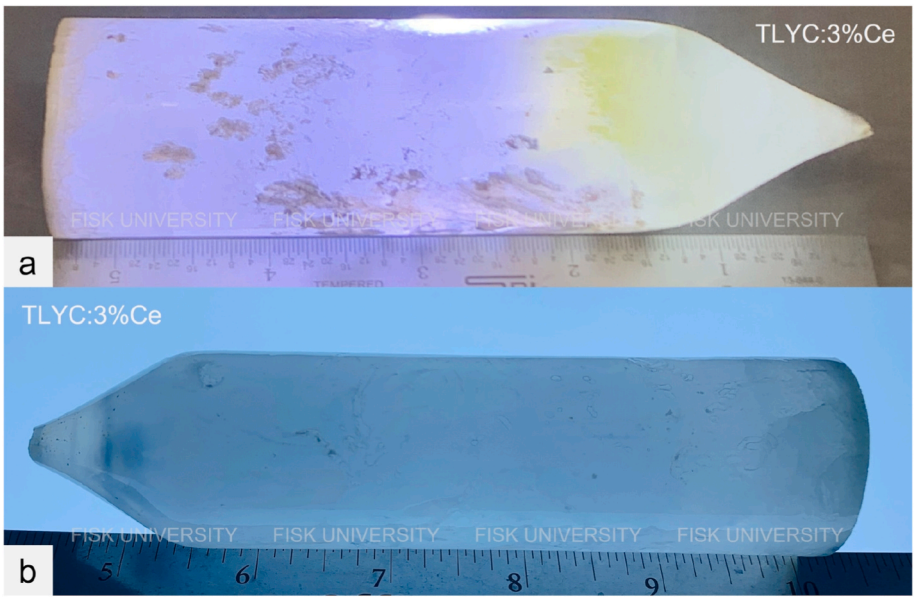

Fig. 3. (a) 1st growth of 1.5-inch diameter TLYC crystal. (b) 2nd growth of 1.5-inch diameter TLYC crystal.

diameter TLYC as well as 1-inch $(Cs,Tl)_2LiLaBr_6$: 3%Ce crystals. For $(Cs,Tl)_2LiLaBr_6$: 3%Ce compounds, growth of three Cs-to-Tl ratios were examined.

After growth the boules underwent post-growth processing, which includes cutting, lapping, and polishing. After processing each sample was characterized, first in mineral oil in a Teflon-lined quartz cup and second in a hermetic packaging can. Using silicone optical grease, either the oil cup or the hermetic can was coupled to a R6231-100 Hamamatsu super bi-alkali photomultiplier tube (PMT) connected to standard nuclear instrument module (NIM) equipment. Energy resolution, relative light yield data, and non-proportionality data were measured and will be compared to smaller-diameter samples. To obtain luminescence decay time information, signals from the PMT anode were recorded with a CAEN DT5720C digitizer and the waveforms were analyzed offline.

Due to its being hygroscopic, packaging of TLYC crystals were done inside an inert atmosphere glove box. To remove moisture from their surfaces, the packaging parts were placed in vacuum in the antechamber of the glove box for a period up to 24 h. Custom aluminum containers were fabricated in house at Fisk University to accommodate different sizes and shapes of the crystals. Two types of optical glass, quartz and sapphire, were utilized. After a final polish, each crystal was wrapped with a Teflon tape and Gore Teflon pad as reflectors. One face of the crystal was open for mounting to the optical glass using silicone optical grease pad as coupling. The aluminum container was then hermetically sealed.

For x-ray radioluminescence, an x-ray tube source providing <30 keV x-rays was used, and emission was collected by a fiberoptic-coupled Ocean Optics spectrometer, employing a silicon CCD readout. Emission spectra were collected for $(Cs,Tl)_2LiLaBr_6$: 3%Ce compounds. X-ray excited emission spectra of TLYC with different doping concentration were previously published in [15].

3. Results and analysis

After producing pure starting materials using in-house purification methods and a few initial growth runs, we managed to successfully grow a 1-inch diameter TLYC, as shown in Fig. 1a. The crack-free boule exhibits single crystallinity and uniform translucency from the first-to-freeze (tip) to last-to-freeze section. The boule was cut with a diamond wire saw to different crystal lengths. Shown in Fig. 1b are the as-cut and as-lapped crystal samples. As shown in Fig. 1a the crystal was translucent.

Because the TLYC compound is hygroscopic, further purification of raw materials was employed to remove O_2 and OH^-. Two more TLYC growth runs were conducted, with the resulting boules exhibiting better transparency than the first boule. Fig. 2a and b shows the second and third TLYC boules grown at Fisk University. Similar to the first boule, both TLYC crystal boules were single and crack-free. The boule in Fig. 2b

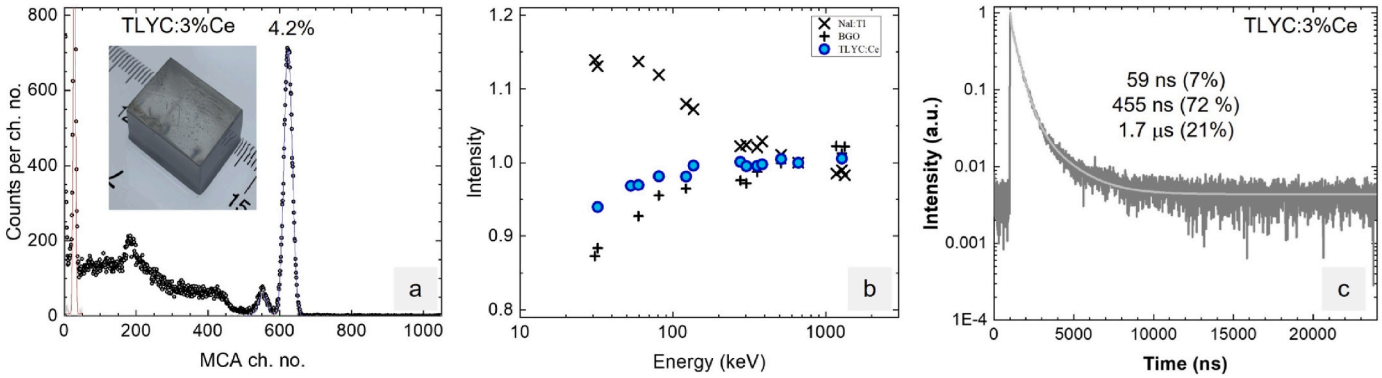

Fig. 4. (a) ^{137}Cs spectrum collected with a TLYC sample. Energy resolution of 4.2% (FWHM) was measured. (b) Comparison of light yield non-proportionality between TLYC, NaI:Tl, and BGO. (c) Decay time profile with decay constants of 59 ns (7%), 455 ns (72%), and 1.7 µs (21%) was measured.

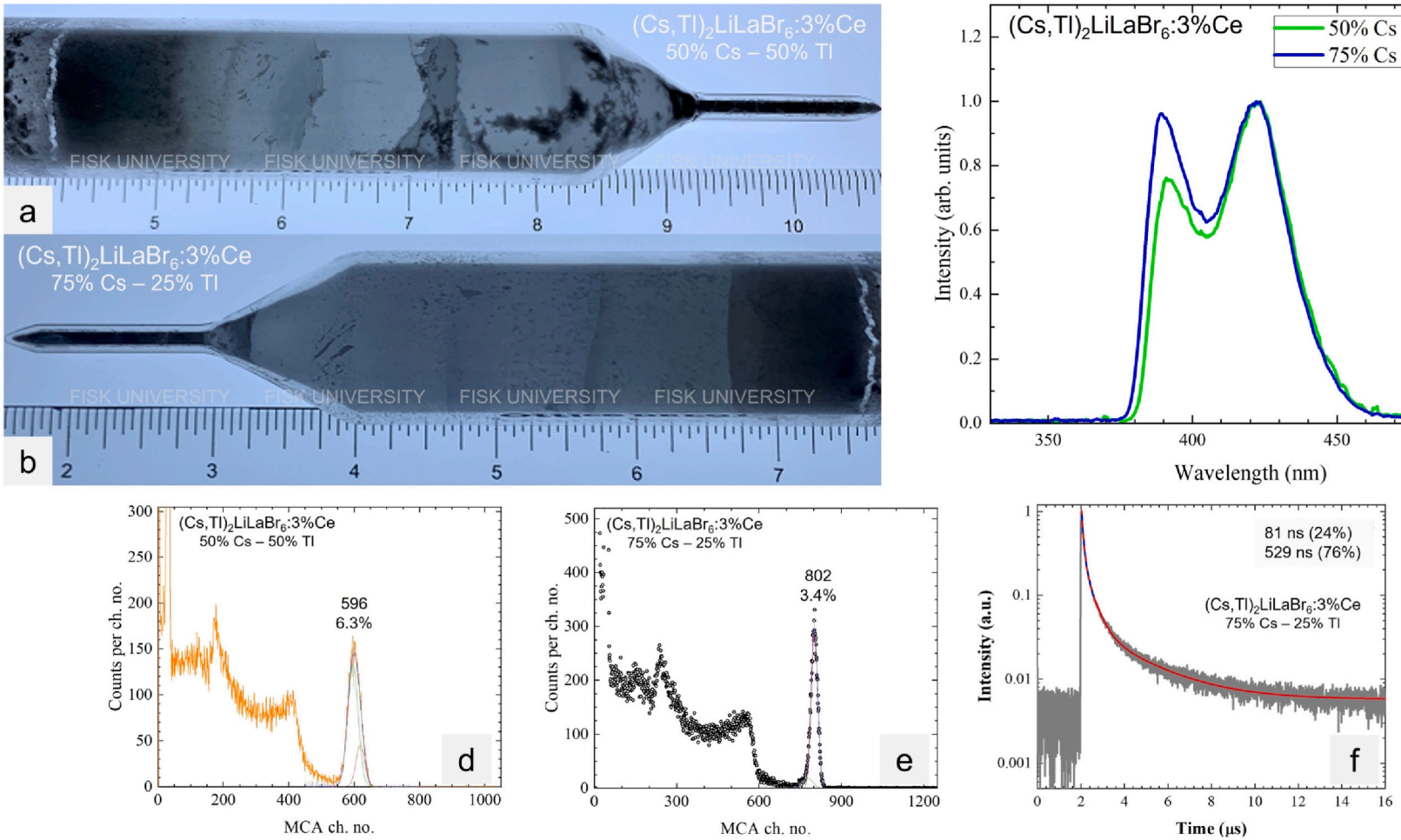

Fig. 5. (a) 1-inch diameter boule of $(Cs,Tl)_2LiLaBr_6$:Ce with 50% Cs-to-50% Tl ratio. (b) 1-inch diameter boule of $(Cs,Tl)_2LiLaBr_6$:Ce with 75% Cs-to-25% Tl ratio. (c) X-ray radioluminescence spectra for of $(Cs,Tl)_2LiLaBr_6$:Ce with 50% Cs-to-50% Tl and 75% Cs-to-25% Tl ratios, respectively. (d) ^{137}Cs spectrum collected with a sample from the boule in (a). (e) ^{137}Cs spectrum collected with a sample from the boule in (b). (f) Decay time profile for $(Cs,Tl)_2LiLaBr_6$:Ce with 75% Cs-to-25% Tl ratio.

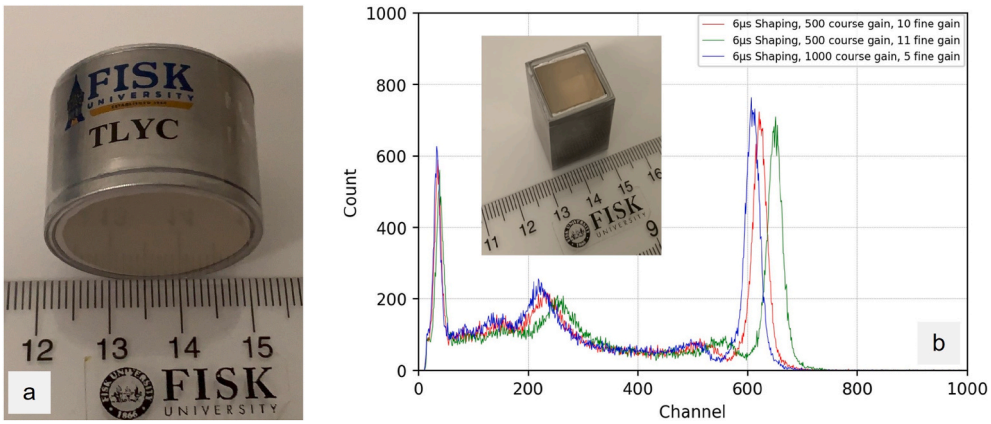

Fig. 6. (a) Packaged TLYC crystals. (b) ^{137}Cs spectra collected by a packaged TLYC with quartz window, on photomultiplier tube and with different amplifier gain settings.

was sliced with a diamond wire saw, using mineral oil as a lubricant and moisture-protectant. Fig. 2c shows the cleaned, as-cut 1-inch diameter samples in order from the first to last-to-freeze sections (the tip, 0.5-inch, 1-inch, 1.5-inch and 2-inch-long samples) under UV light (left) and ambient light condition (right).

The scale-up to 1.5-inch diameter TLYC is shown in Fig. 3. While the initial 1.5-inch diameter boule, shown as irradiated with a UV light in Fig. 3a, was single, crack-free, and with good transparency, it shows some yellow residue due to excess of chlorine and/or organic impurities left-over from the purification process. With better purification and a tweak in the furnace temperature profile, another single, crack-free, and transparent 1.5-inch diameter TLYC crystal was successfully grown and re-produced, as shown in Fig. 3b.

A TLYC sample from the first boule (Fig. 1a) was finely polished and characterized. Fig. 4a shows a ^{137}Cs spectrum collected with the sample, with an energy resolution of 4.2% (FWHM) at 662 keV. Good peak-to-Compton ratio is exhibited, and the calculated light yield is about 26,000 photons/MeV. Comparison of the non-proportionality behavior between TLYC, NaI:Tl, and BGO is shown in Fig. 4b. Good linearity is observed for photon energy above 60 keV. Decay time constants of 59 ns (7%), 455 ns (72%), and 1.7 μs (21%) was measured (Fig. 4c).

$(Cs,Tl)_2LiLaBr_6$: 3%Ce compounds, grown to avoid non-congruence issue in TLLB, were grown with three different Cs-to-Tl ratios. Shown in Fig. 5a is a 1-inch diameter boule of $(Cs,Tl)_2LiLaBr_6$:3%Ce with 50% Cs–50%Tl ratio, and in Fig. 5b a 1-inch diameter boule of $(Cs,Tl)_2LiLaBr_6$:3%Ce with 75%Cs-to-25%Tl ratio. While the 50%-to-50% composition grew a single and crack-free boule, its performance as a scintillation detector was less than satisfactory. X-ray radioluminescence spectra for both samples are shown in Fig. 5c. Both emission spectra feature a peak around 390 nm and another peak around 422 nm. ^{137}Cs spectrum collected with a sample from the 50%Cs-to-50% Tl boule resulted in an energy resolution of 6.3% (FWHM) at 662 keV (Fig. 5d), which is less than expected for a CLLB-type compound. The 50%Cs-to-50%Tl grown boule also shows a dark last-to-freeze section (Fig. 5a), which may be due to thallium being pushed up during the growth. Because of this reasoning, the amount of thallium was reduced for the next growth to 75%Cs-to-25%Tl. The boule in Fig. 5b, which is a 1-inch diameter $(Cs,Tl)_2LiLaBr_6$:3%Ce with 75%Cs–25%Tl ratio, has a better crystallinity, besides being single and crack-free. ^{137}Cs spectrum collected with a sample from the 50% Cs-to-50% Tl boule resulted in an energy resolution of 3.4%, which is as good as CLLB (Fig. 5e). The decay time profile for $(Cs,Tl)_2LiLaBr_6$:3%Ce with 75% Cs-to-25% Tl ratio is shown in Fig. 5f, with decay constants of 81 ns and 529 ns

Fig. 6a shows a hermetically packaged 1-inch diameter TLYC crystal packaged at Fisk University. Fig. 6b shows three ^{137}Cs spectra, collected at University of Surrey with a TLYC crystal packaged with a quartz window (inset) on a photomultiplier tube and with different amplifier gain settings, all spectra resulting in energy resolution of 4.6% (FWHM) at 662 keV. While the investigation to TLYC crystal packaging is still in its initial stages at Fisk University, the current results were encouraging and showed that there was a little difference in detector performance (in terms of energy resolution) between bare TLYC crystal and packaged TLYC crystal.

4. Conclusions

In this paper we presented successful growth and scintillation performance of high quality and well performing one-inch diameter 3 wt-% Ce-doped Tl-based elpasolite Tl_2LiYCl_6 (TLYC) as well as the scale up to 1.5-inch diameter crystals with same performance as the one-inch crystals. The successful growth of the 1.5-inch diameter TLYC single crystals is reported for the first time. Also presented is the one-inch diameter growth and performance of mixed $(Cs,Tl)_2LiLaBr_6$:3%Ce elpasolite dual mode scintillator crystals. To grow high quality elpasolite crystals with a high growth yield, the purity of the starting materials is paramount, as impurities may form extraneous crystal phases that can reduce scintillation performance as well as lower growth yield. The successful growth of mixed cation compounds $(Cs,Tl)_2LiLaBr_6$: 3%Ce shows the possibility of growing congruent TLLB-based compounds, with the best result obtained with larger Cs^+ content than Tl^+. Because elpasolite crystals grown from melt like $(Cs,Tl)_2LiLaBr_6$:Ce can have multi phases present in the melt, which cause incongruency, and non-uniformity in dopant distribution, more sample analysis per crystal boule are needed to better address these growth issues. As noted in Introduction, addressing and remedying these growth problems can increase growth yield, increase crystal size, and in turn decrease production cost. The performance of TLYC as a dual mode γ-n detector has been shown previously [12,13,15]. Characterization of TLYC and $(Cs,Tl)_2LiLaBr_6$:3%Ce crystals grown at Fisk University as dual-mode gamma-neutron detectors will be reported in the near future.

CRediT authorship contribution statement

R. Hawrami: Conceptualization, Methodology, Validation, Formal analysis, Investigation, Resources, Writing – original draft, Writing – review & editing, Visualization, Supervision, Project administration, Funding acquisition. **E. Ariesanti:** Validation, Formal analysis, Investigation, Writing – original draft, Writing – review & editing, Visualization. **A. Burger:** Resources, Supervision. **P. Sellin:** Resources, Visualization, Supervision.

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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