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Intrinsic scintillators: $TlMgCl_3$ and $TlCaI_3$

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ABSTRACT

Two intrinsic scintillators $TlMgCl_3$ and $TlCaI_3$ with excellent energy resolution and fast scintillation decay are presented. Crack-free transparent crystals were successfully grown by the Bridgman method. The scintillation light yields of $TlMgCl_3$ and $TlCaI_3$ are approximately 30,600 ph/MeV and 42,200 ph/MeV, respectively. Their energy resolutions at 662 keV are 3.7% for $TlMgCl_3$ and 6.2% for $TlCaI_3$. The scintillation decay times of $TlMgCl_3$ are 46 ns, 166 ns, and 449 ns. The scintillation decay times of $TlCaI_3$ are 62 ns, 200 ns, and 1.44 μs. Under X-ray irradiation, the emission of $TlMgCl_3$ is between 300 nm and 540 nm with the peak at 409 nm. $TlCaI_3$ has a broad emission band between 300 nm and 750 nm. Due to their excellent scintillation properties, these two scintillators can be developed for gamma-ray detection. Additionally, $TlMgCl_3$ is non-hygroscopic.

1. Introduction

Global nuclear nonproliferation applications highlight the importance of radiation detection technologies. Scintillators are ones of the most widely used radiation detectors, and there is a continuing need for new materials with superior properties. The key criteria for an ideal scintillator include high scintillation light yield, fast scintillation decay, exceptional energy resolution, high effective atomic number, favorable emission wavelength, mechanical robustness, and low cost [1].

In the past few decades, metal halide scintillators have attracted the most attention due to their proper bandgap for luminescence dopants, high optical transparency, and low cost. NaI:Tl and CsI:Tl were the earliest metal halide scintillators [2,3], and have been widely used as industrial benchmarks. Other binary halides with higher light yield and better energy resolution, such as SrI_2:Eu [4,5], $CeBr_3$ [6,7] and $LaBr_3$:Ce [8] have been developed as the new generation of radiation detectors. Ternary halides with high light yield such as Eu-doped $CsBa_2I_5$ [9,10] or $LiSr_2I_5$ [11] have also been reported as promising scintillators.

This work focused on two intrinsic halide scintillators, $TlMgCl_3$ and $TlCaI_3$. This work expands on our research of Li-based ternary compositions [11], however, Tl ions are used instead of Li ions. Both $TlMgCl_3$ and $TlCaI_3$ have high effective atomic numbers (Z_{eff} ($TlMgCl_3$) = 70, Z_{eff} ($TlCaI_3$) = 65) and moderately high densities (ρ ($TlMgCl_3$) = 4.43 g cm^{-3}, ρ($TlCaI_3$) = 4.73 g cm^{-3}). These properties contribute to a high stopping power, indicating that these crystals are excellent photon absorbing materials. Moreover, unlike many halide materials, these compositions do not require a dopant. An earlier study on $TlMgCl_3$ has also been reported [12]. Material synthesis, crystal growth, and scintillation properties of both materials are discussed in the following sections.

2. Experimental procedures

For each growth, a 10 mm inner diameter quartz ampoule was cleaned in aqua regia to remove organic impurities from the ampoule, and then it was thoroughly rinsed with deionized water. The ampoules were subsequently annealed at 1000 °C for eight hours. Stoichiometric amounts of starting materials with 4N purity (obtained from Sigma Aldrich and APL Engineered Materials) were loaded into the clean quartz ampoules (TlCl and $MgCl_2$ for $TlMgCl_3$; TlI and CaI_2 for $TlCaI_3$). The loading procedure was conducted inside a glove box under inert Ar gas atmosphere to avoid degradation of starting materials due to contact with air and/or moisture. The Ar gas went through a filtration system prior to being circulated inside the glove box. The environment inside the glove box renders the use of a desiccant unnecessary. The ampoule was subsequently sealed under high vacuum (approximately 10^{-6} Torr), and the crystal was grown in a single zone furnace by the vertical Bridgman method, with a growth rate of 15–20 mm/day. The starting growth temperatures were 700 °C for $TlMgCl_3$ and 610 °C for $TlCaI_3$. After solidification, the ampoules were subjected to a cooling rate of 50–75 °C/day. Crack-free transparent crystal boules were retrieved after growth. These samples were then sliced, and subsequently polished inside the glove box under inert Ar(g) atmosphere. Crystal specimens of $TlMgCl_3$ and $TlCaI_3$ are shown in

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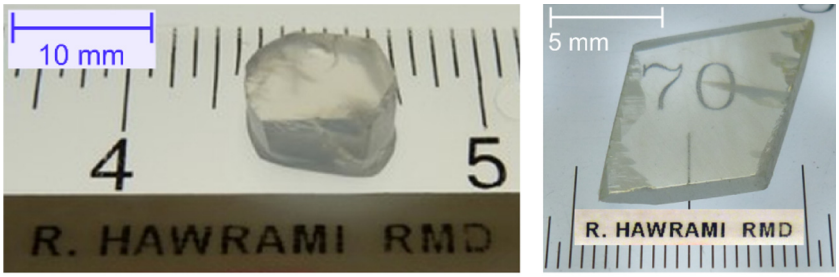

Fig. 1. Polished pieces of (a) $TlMgCl_3$ (~11 × 9 × 4 mm^3) and (b) $TlCaI_3$ (~8 × 7 × 0.5 mm^3) for evaluation. Visible cracks and/or delamination on the specimens were induced during processing.

Fig. 1a and b, respectively. Visible cracks and/or delamination in the specimens were induced during processing. $TlMgCl_3$ is non-hygroscopic, while $TlCaI_3$ is sensitive to moisture. Therefore, processing $TlCaI_3$ inside the glove box was especially imperative to avoid material degradation.

The emission spectra were recorded by exciting a specimen with X-ray radiation from a Philips X-ray generator at power settings of 40 kV and 20 mA. The scintillation light was then passed through a McPherson 0.2-m monochromator and detected with a cooled C31034 photomultiplier tube (PMT). Because of small sample sizes, in lieu of being enclosed in a hermetic packaging, each sample was placed in oil inside a quartz cup (wrapped with Teflon tape), with a flat quartz window, for measurements. Scintillation pulse height spectra were measured by coupling each sample to a Hamamatsu R6233-100 photomultiplier tube (PMT) and recording the response to various sources of gamma rays, namely ^{22}Na, ^{57}Co, ^{133}Ba, ^{137}Cs, and ^{241}Am. The light yield was calculated by comparing the ^{137}Cs full energy peak position to the position of the peak from spectra collected with NaI:Tl (1 in. right cylinder) while taking into account of the quantum efficiency of PMT. The non-proportionality was calculated based on the relative light yield at various gamma-ray energies. To determine the scintillation decay time profile, an ADC converter was used to digitize pulses collected at the PMT output and appropriate multi-exponential decay functions were fitted to the averaged digitized waveforms.

3. Results and discussions

3.1. Radioluminescence spectra

The X-ray excited radioluminescence spectrum of $TlMgCl_3$ is shown in Fig. 2(a). $TlMgCl_3$ has a broad peak from 300 mm to 540 mm, and the central peak position locates at approximately 409 nm. The emission can be attributed to the self-trapped exciton (STE) emission. Such broad emissions have been previously reported in other intrinsic halide scintillators such as Cs_2HfCl_6 [13]. Fig. 2(b) shows the X-ray excited emission spectrum of $TlCaI_3$, showing a broader emission range between 300 and 750 nm. Two overlapping emission spectra appear to be present. The main peak occurs at 533 nm, while the secondary peak occurs at 460 nm, possibly corresponding to Tl emission. The origin of the emission peak at 533 nm is still under investigation.

3.2. Scintillation light yield and energy resolution

The scintillation light yield and energy resolution was measured on one 11 × 9 × 4 mm^3 $TlMgCl_3$ sample and one 8 × 7 × 0.5 mm^3 sample of $TlCaI_3$, as shown in Figs. 3 and 4, respectively. For $TlMgCl_3$ the scintillation light yield was measured at 30,600 ph/MeV with the energy resolution of 3.7% at 662 keV, while $TlCaI_3$ gives the light yield of 42,200 ph/MeV with the energy resolution of 6.2% at 662 keV. With further purification of the raw materials and growth parameter optimization, crystal quality, light yield and resolution are expected to improve. A barely visible peak below the Tl X-ray escape peak can be observed in Fig. 4. The origin of this peak is yet to be determined at this point, however, the peak could be due to interactions with secondary phases that might have formed during the crystal growth. Also note the Compton-to-peak ratio for both spectra, which is comparable to that of the reference crystal, a $\phi 1'' \times 1''$ NaI:Tl.

3.3. Non-proportionality

The non-proportionality of $TlMgCl_3$ and $TlCaI_3$ were measured using different sources of gamma-rays. The data, along with NaI:

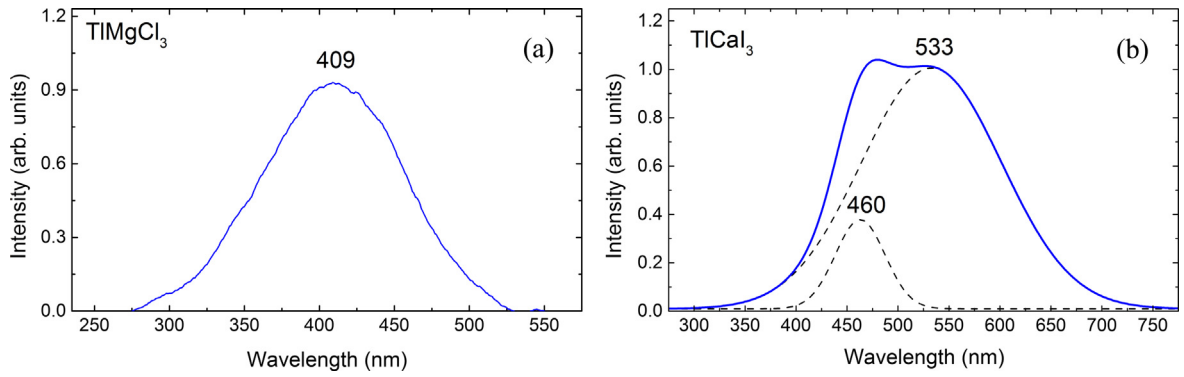

Fig. 2. Emission spectra from X-ray excitation, of (a) $TlMgCl_3$, with the emission band peaking at about 409 nm, and (b) $TlCaI_3$, with a broad emission band between 300 nm and 750 nm.