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Scintillation characterizations of $Tl_2LiLuCl_6$: Ce^{3+} single crystal

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ABSTRACT

We report the growth and scintillation characterization of $Tl_2LiLuCl_6$ single crystals, developed from the melt using two-zone vertical Bridgman technique, while doped with 0.5, 1, 3 and 5 mol% Ce concentration. X-ray-induced emission spectra shows Ce^{3+} emission ranging from 370 to 540-nm wavelength. Energy resolution, light yield and decay time of the grown samples are measured under γ-ray excitation at room temperature. Energy resolution of 5.6% FWHM with 27,000 ± 2700 ph/MeV light yield is found for 1mole% Ce-doped sample. For the same dopant concentration, three decay components are also observed. Variation of scintillation properties is observed as a function of dopant concentration in the material. It will provide excellent detection efficiency for X- and γ-rays due to its high effective Z-number and density. It is expected that such scintillator will be a potential detector for the medical imaging techniques.

1. Introduction

New inorganic scintillation materials with enhanced scintillation performance are needed for the detection of X-rays, γ-rays and neutron in various applications: industrial inspection, dosimetry, medical imaging, high-energy physics, homeland security, basic research in condense matter and nuclear physics, and oil exploration [1]. The performance of a scintillation detector strongly depends on the light yield, energy resolution, decay time, density and effective Z-number [2]. In different applications, where neutron detection is involved, lithium- and gadolinium-contained scintillation detectors, due to their high-interaction cross-section, are usually the best choice. Similarly, for X- and γ-rays detection, high effective Z-number and density compounds are necessary. Therefore, many new compounds in the form of a single crystal have been discovered and their scintillation properties reported. Among these, Ce^{3+}-doped single crystals are interesting and have shown excellent scintillation properties [3]. Elpasolite crystal structure provides an ideal environment for incorporating rare-earth ions [4]. We tried different rare-earth ions, such as Y, Gd, and Lu ions, in order to discover new high-density and high-effective-Z-number scintillation materials for the aforementioned applications.

Recently, we have discovered and reported new Tl-based alkali halide elpasolites [5–7], since Tl possesses high Z-number (81) and density (11.85 g/cm^3). Among these scintillators, $Tl_2LiGdCl_6$: Ce^{3+} [5] and Tl_2LiYCl_6: Ce^{3+} [6] show excellent scintillation performance, including good energy resolutions of 4.8% FWHM and 4.6% FWHM with 58,000 ph/MeV and ~31,000 ph/MeV light yields, respectively, under the γ-ray excitation. Cs_2LiYCl_6: Ce^{3+} scintillator has recently been proposed for thermal neutron detection. However, its major drawback is its low density (ρ = 3.3 g/cm^3) and low effective Z-number (Z_{eff} = 45) [8]. After the replacement of Cs by Tl ion in Cs_2LiYCl_6 and doped with Ce^{3+}, significant improvement in the density and effective Z-number is observed. Comparing with the commercially available scintillators such as $LaBr_3$: Ce^{3+} (Z_{eff} = 46.9), NaI:Tl (Z_{eff} = 50.8), CsI:Tl (Z_{eff} = 54.1), SrI_2: Eu^{2+} (Z_{eff} = 50.3), and $CeBr_3$ (Z_{eff} = 47.6), the photoelectric conversion efficiency and stopping power of our Tl-based halide elpasolites will be higher due to their high effective Z-number. In addition, these lithium (Li) - and gadolinium (Gd)-contained halide elapsolites can be used as a future neutron detectors.

In the present study, we investigated the scintillation properties of our newly grown Ce-activated $Tl_2LiLuCl_6$ (TLLC) scintillation material. Scintillation properties were studied under X- and γ-ray excitation at room temperature. Substitution of Gd and Y by Lu ion in the Tl-based alkali halide elpasolites enhanced the Z_{eff} and density of TLLC, compared with $Tl_2LiGdCl_6$: Ce^{3+} and Tl_2LiYCl_6: Ce^{3+} crystals.

2. Experimental technique

2.1. Crystal growth

$Tl_2LiLuCl_6$: Ce^{3+} single crystals of various Ce-concentrations were grown by two-zone vertical Bridgman technique. Starting

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materials (TlCl, LiCl, $LuCl_3$ and $CeCl_3$ of ~5 N purity powders) from Sigma-Aldrich or Alfa-Aesar were weighed in ultra-dry argon purged glove box, having moisture and oxygen level less than 5 ppm. Weighing powder was loaded in ultra-clean quartz ampoule with an inner diameter of 8 mm. Loaded quartz ampoule with the powder were sealed with an Oxy-propane torch under dynamic vacuum of $\sim 10^{-7}$ Torr. After sealing, all the ampoules were lowered into two-zone vertical Bridgman chamber with the help of a synchronous motor. Temperature of the furnace was raised to 570 °C, i.e. 40 °C higher than the melting point of TLLC. A temperature gradient of 10 °C/cm was achieved by adjusting the upper- and lower-zone temperatures of the Bridgman furnace. During the crystal growth process, the rate of growth was maintained at 10–12 mm/day. Finally, the grown samples were transparent while small size samples with dimensions of $\sim\phi 8 \times 1$ mm^3 were cut and polished for the scintillation characterization. Fig. 1 shows pictures of the as grown samples of TLLC: Ce^{3+} single crystals.

2.2. Equipment

Emission spectra of TLLC crystals under X-ray excitation were obtained at room temperature. Investigated sample were irradiated with an X-ray tube (DRGEM. Co.) using a tungsten anode, operating at 50 kV and 1 mA. The emission spectra were measured by utilizing a spectrometer (QE65000 fiber optic spectrometer), made by Ocean Optics. Pulse-height spectra were measured with a Hamamatsu R6233 photomultiplier tube (PMT) at room temperature. Polished sample crystals were wrapped in several layers of 0.1-mm-thick UV reflecting Teflon tape except one face which was coupled directly with the entrance window of the PMT using refractive index matching optical grease. After irradiation with γ-rays from a ^{137}Cs source, the analog signals, produced in the crystal, were shaped with a Tennelec TC 245 spectroscopy amplifier and were fed into a 25-MHz flash analog-to-digital converter (FADC). A software threshold was set to trigger an event by using a self-trigger algorithm on the field programmable gate array (FPGA) chip on the FADC board. The FADC output was recorded into a personal computer by using a USB2 connection, and the recorded data was analyzed with a C++ data analysis program [9].

For the decay-time spectra measurement, TLLC: Ce^{3+} crystals were optically-coupled with the PMT (Hamamatsu R6233) and irradiated by 662 keV γ-rays from a ^{137}Cs source. PMT signals were fed into a 400-MHz FADC. The sample pulse is fabricated by FADC every 2.5 ns for duration up to 64 μs so that one can fully reconstruct each photoelectron pulse [10]. From the recorded pulse shape information, the decay time of TLLC: Ce^{3+} was obtained.

3. Scintillation properties

3.1. Crystal analysis

TLLC, having a tetragonal crystal structure, was reported by Mayer et al. [11]. It has *P4/nbm* space group with lattice constants a = 10.145 Å and c = 10.251 Å. The volume and density of the unit cell are obtained as 1055.0 Å^3 and 5.06 g/cm^3, respectively. Effective Z-number of this material is found to be 71.

3.2. Spectroscopy

X-ray-induced luminescence spectra of the Ce-activated TLLC single crystals are displayed in Fig. 2. Lutetium (Lu^{3+}) and cerium (Ce^{3+}) ions have the same oxidation state, +3, therefore, the former may be replaced with the latter. In TLLC single crystal, Ce^{3+} ion captures hole from the valence band and become Ce^{4+} (Ce^{3+} + hole → Ce^{4+}), and then an electron, from the conduction band, recombines with the Ce^{4+} and subsequently scintillation light is emitted (Ce^{4+} + e^- → Ce^{3+*}, Ce^{3+*} → Ce^{3+} + photon). The emission is attributed to the parity allowed $5d \rightarrow 4f$ transition of the Ce^{3+} ion, i.e. transition from the lowest *5d* level to $^2F_{5/2}$ and $^2F_{7/2}$ levels of the $4f^1$ configuration [12]. The emission spectra are not identical and show a shift towards higher-wavelength regions with the increase of Ce-concentration in the host. For 0.5 and 1mol% Ce-concentrations, broad emission bands are located between 370 and 540 nm, peaking at 428 nm. While 3 and 5 mol% Ce

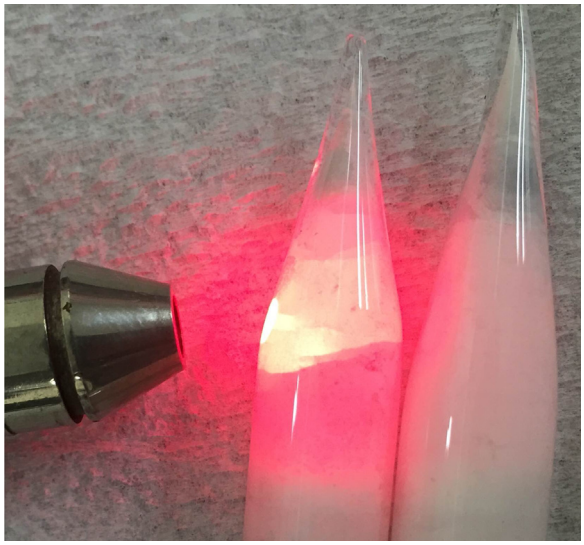

Fig. 1. A photograph of the as grown samples of TLLC single crystals.

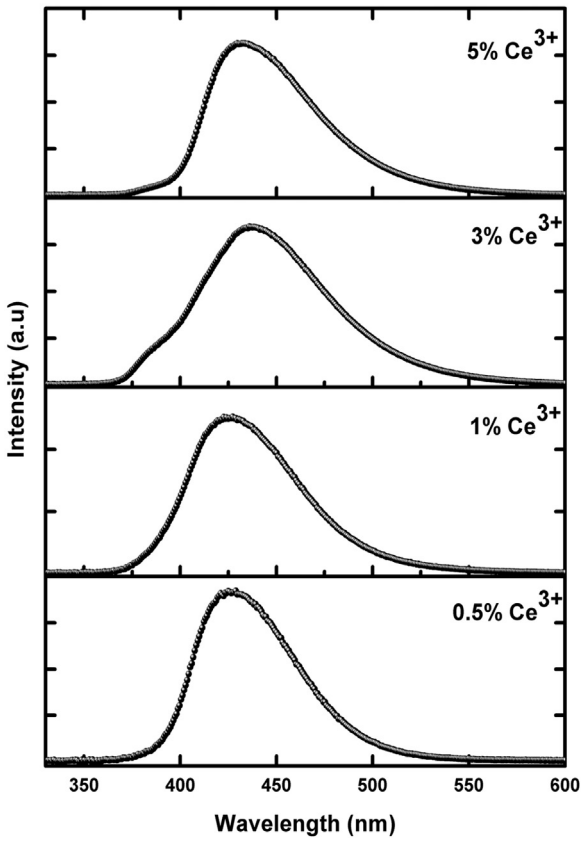

Fig. 2. X-ray-excited emission spectra at room temperature of TLLC: x Ce^{3+} (x=0.5%, 1%, 3%, and 5%).