Crystal growth and characterization of LuAG:Ce:Tb scintillator

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ABSTRACT
To investigate the possibility of Tb\(^{3+}\) → Ce\(^{3+}\) energy transfer, we grew single crystals of Lu\(_{5}\)Al\(_{5}\)O\(_{12}\):Ce co-doped with Tb\(^{3+}\) using both the micro-pulling-down method and the conventional Czochralski technique. Compositional and phase homogeneity, growth defects, and crystallographic properties were studied. Visible non-uniformity of dopants distribution in the radial direction was observed in the micro-pulling-down grown crystals. Underlying luminescence processes were evaluated by measuring luminescence properties under photo-, X- and gamma-rays excitation at room temperature. © 2009 Elsevier B.V. All rights reserved.

1. Introduction

One of the major applications for single crystal scintillators is in medical imaging, such as positron emission tomography and X-ray computed tomography, where scintillator crystals are used as detectors for gamma or X-rays [1]. High detection efficiency can be achieved by using materials with high density and high atomic number. Fast 5d → 4f luminescence of Ce\(^{3+}\) with distinctive decay time of 20–60 ns is usually exploited to provide an efficient emission at room temperature. Ce-doped Lu\(_{5}\)Al\(_{5}\)O\(_{12}\) (LuAG:Ce) is a well-known scintillator that exhibits desirable physical and scintillation properties [2,3]. A promising approach to enhance the luminescence efficiency of selected Ce\(^{3+}\)-doped scintillators by co-doping with isovalent Tb\(^{3+}\) has been reported [4–7]. The crystal field of LuAG is also strong enough to shift the host-sensitive 5d levels of Ce\(^{3+}\) to a position where Tb\(^{3+}\) → Ce\(^{3+}\) energy transfer becomes possible [8].

In the current research, we focus on developing a highly efficient scintillator material that makes use of Tb\(^{3+}\) to Ce\(^{3+}\) energy transfer. Two different crystal growth techniques, micro-pulling-down (µ-PD) method and the Czochralski method, were used to produce single crystals of LuAG:Ce co-doped with Tb\(^{3+}\). The µ-PD method is known as a fast and economical solution for materials screening [9]. In this work, the µ-PD method was used to determine optimal dopant concentrations, whereas the Czochralski technique was used for producing crystal boules of high quality and optimized composition.

2. Experimental procedure

The micro-pulling-down and the Czochralski techniques were used for the LuAG:Ce:Tb crystal growth. Starting materials were at least 99.99% pure Lu\(_{2}\)O\(_{3}\), Al\(_{2}\)O\(_{3}\), CeO\(_{2}\) and TbO\(_{7}\) powders. Raw powders were mixed in stoichiometric ratio. Table 1 lists nominal concentrations of Ce and Tb in LuAG:Ce:Tb crystals and the method of crystal growth.

We followed the standard crystal growth procedure for µ-PD growth experiments [9]. The crystals were grown from a 0.16 mm iridium crucible. The crucible had a square-shaped 4 × 4 mm nozzle and a ~0.1 mm capillary for melt supply from crucible volume to the melt meniscus. A 30 mm long iridium after-heater was used to support crucible and provide suitable thermal gradient. Crucible with loaded powder mixtures was heated inductively by using a RF generator. Temperature ramping was done for 2 h from room temperature RT to the melting point of LuAG, which was determined by visual observations of the melt droplets, appeared on the nozzle bottom. Solid/liquid interface was monitored in real time by using a CCD camera. Crystal growth was initiated with LuAG seed crystal oriented along the [1 1 1] axis. With a seed touching the melt meniscus, the growth system was kept for about 1 h to bring it to equilibrium. Crystal growth was begun with a pulling rate of 0.05 mm/min. After the crystal reached the full diameter of 4 mm, pulling rate was increased and then held constant at 0.15 mm/min. These numbers were experimentally found as the optimal pulling rates for the square-shaped crystals of complex oxides. Crystal cooling down was done for 2 h. During cooling down process the position of the crystal was below the after-heater zone. Czochralski Cyberstar Oxypuller growth furnace was used to grow LuAG:Ce 1%:Tb 3% boule of 30 mm diameter and 100 mm length. Iridium pin was used as a seed to initiate the crystallization. In all experiments, the flowing gas atmosphere was...
3.1. Crystal growth

3. Results and discussion

3.2. Optical and scintillation characterization

Table 1

<table>
<thead>
<tr>
<th>Growth method</th>
<th>Concentration of Ce, at%</th>
<th>Concentration of Tb, at%</th>
</tr>
</thead>
<tbody>
<tr>
<td>µ-PD</td>
<td>0.3</td>
<td>0.3</td>
</tr>
<tr>
<td>µ-PD</td>
<td>0.3</td>
<td>3</td>
</tr>
<tr>
<td>µ-PD</td>
<td>1</td>
<td>3</td>
</tr>
<tr>
<td>µ-PD</td>
<td>1</td>
<td>10</td>
</tr>
<tr>
<td>Cz</td>
<td>1</td>
<td>3</td>
</tr>
</tbody>
</table>

central part of the crystals had better uniformity and quality. However, peripherals of the crystals were produced from the melt that contained excess of Ce and Tb dopant ions due to their lower segregation coefficient. Rejected dopant ions can modify melt composition in the vicinity of the crystal surface. Finally, the surface part of the crystals was produced from considerably non-stoichiometric melt that had considerable excess of dopants. This melt had relatively lower melting point and formed two phases: a garnet phase and a secondary phase. Similar effect was observed earlier and it was well illustrated in [11]. As a result, the rim of the cross-sectioned samples appeared much brighter on the cathodoluminescence images which display regions of inhomogeneous luminescence and reveal that concentration of Tb and Ce is higher near the side surface of the crystals, Fig. 3. Moreover, BSE images demonstrate secondary phase inclusions that are identified as not completely reacted Al2O3 and CeO2. Note that these phases were not detected by the XRD measurements.

3.2. Optical and scintillation characterization

Photoluminescence spectra under 450 nm light excitation of LuAG:Ce:Tb show intense and broad emission band around 510–530 nm due to 5d→4f radiative transitions of Ce3+, whereas selective excitation of Tb3+ ions at 320 nm results in superposition of Ce3+ broad band emission with a four-line spectrum from Tb3+ with a dominating line at 545 nm due to 5D4→7Fj (j=6, 5, 4, 3) transitions of Tb3+ ion [8], Fig. 4. As the nominal concentration of Tb is increased, the characteristic Tb3+ emission prevails over the Ce3+ emission and the dominant peak shifts to the longer wavelength. Excitation spectra of the luminescence monitored at 545 nm consist of multiple bands. Peaks with maxima at 345 and 450 nm can be ascribed to Ce3+ excitation bands and peaks at 270, 320 and 370 nm can be ascribed to Tb3+. Fig. 4[12,13]. Photoluminescence spectra of LuAG:Ce:Tb are shown in Fig. 5. Characteristic Tb3+ four-line emission features point to the fact that Tb3+ is involved in the scintillation process. Higher emission intensity of the Cz-grown sample with respect to the µ-PD grown crystals can be explained by more uniform distribution of the constituents in the crystals that originates from different crystal manufacturing methods.

Photoluminescence and scintillation decay spectra are shown in Fig. 6. The data from photoluminescence decay profiles under 345 nm LED excitation, which correspond to the absorption band of Ce3+, can be fitted with a single-exponential decay function with a ~44 ns time constant. It is very similar to previously observed 5d→4f Ce3+ photoluminescence decay in LuAG lattice [13]. The luminescence decay under 314 nm light excitation (absorption band of Tb3+, as well as 370 nm) consists of two exponential components: ~60 and 100–120 ns. Note that a very slow component with a lifetime of µs–ms related to 4F9/2→4I15/2 transitions of Tb3+[5,6] was not observed.
The scintillation time profile consists of a single-exponential rise with \( \tau = 20 \) ns time constant and double exponential decay with a major component of \( \tau = 50 \) ns, which is likely due to \( \text{Ce}^{3+}\) 5d\(-\)4f emission, Fig. 6. As the nominal concentration of Tb is increased, the decay time components decrease from 55 to 48 ns and from 432 to 300 ns, which may be due to interactions between \( \text{Ce}^{3+} \) and \( \text{Tb}^{3+} \) ions [13]. No photopeaks were resolved in gamma-ray excited pulse height spectra for either Cz or \( \mu\)-PD grown LuAG:Ce:Tb crystals, and no improvement was obtained as a result of annealing at 1500 °C in air or nitrogen. One possible explanation for absence of gamma-ray photo-peak is that the majority of LuAG:Ce:Tb scintillation light is emitted through slow (on the order of ms) \( \text{Tb}^{3+} \) luminescence, which is too slow to be integrated by the pulse processing electronics in our data acquisition system.

TSL glow curves of the Cz-grown LuAG:1% Ce, 3% Tb crystal display intense broad peaks below RT, Fig. 7. Similar features have previously been ascribed to the existence of shallow electron traps.
Moreover, additional thermoluminescence peaks are present above RT: a small peak at 330 K and a broad band with a maximum at 520 K. The TSL curves indicate that incorporation of Tb$^{3+}$ ions into LuAG:Ce may result in the formation of additional trapping states. These traps can also interact with LuAG:Ce point defects, which are known to be responsible for degraded scintillation performance of LuAG:Ce [14,15]. The first order kinetic model provided by Randall and Wilkins [16] was used to calculate trap parameters such as energy, frequency factor and lifetime. Calculated detrapping time at RT from the 330 K peak-related trap in Cz-grown LuAG:Ce 1%:Tb 3% is about $2 \times 10^3$ s.

X-ray afterglow of the same sample can be described by two-exponential decay function with a main component of 1 s, Fig. 8.

### 4. Summary

Despite the sharp increase in dopants concentration near the surface of the LuAG:Ce:Tb crystals grown by the $\mu$-PD, the bulk of the crystal volume is rather uniform. Refinement of growth conditions may possibly have certain improvements in this aspect.

Emission and excitation spectra, as well as radioluminescence spectra, show superposition of Ce$^{3+}$ and Tb$^{3+}$ bands with dominant peak at $\sim$545 nm. Scintillation kinetics consists of a rise stage ($\sim$25 ns) and a decay stage with major component of $\sim$50 ns, which is likely due to 5d$\rightarrow$4f emission of Ce$^{3+}$. Decrease
of both fast and slow decay components with increasing nominal Tb concentration may point to interaction between Ce\(^{3+}\) and Tb\(^{3+}\) during the luminescence processes. It turns out that the luminescence excitation efficiency of Ce\(^{3+}\) through Tb\(^{3+}\) is fairly low and the bulk LuAG:Ce:Tb crystals fail to demonstrate efficient Tb\(^{3+}\) → Ce\(^{3+}\) energy transfer. Unlike bulk crystals, LuAG:Ce:Tb single crystalline films grown by the liquid phase epitaxy have been reported to have fewer crystal point defects, particularly anti-site defects [17], so the light output there increased greatly due to Tb\(^{3+}\) co-doping [7]. Defects of different nature can be originated in bulk crystal samples (both μ-PD and Cz) as a consequence of some variations in local distributions of Ce and Tb; therefore defect distribution can be localized close to the crystal surface. They can be the reason for the population of deep electron and hole traps and can decrease the light output. The difference in the defect structures can also have an effect on the afterglow.

References