Bridgman growth and site occupation in LuAG:Ce scintillator crystals

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LuAG:Ce single crystals with various activator concentrations were grown by the vertical Bridgman technique. Characterization of crystals was done in terms of actual doping level, macroscopic defects and degree of non-equivalent substitutions by Lu for Al in octahedral lattice sites. Scintillation measurements were performed using 2 × 2 × 8 mm3 shaped samples with Ce concentration in the range 0.05–0.55 at%. Essential improvement of performance was demonstrated in samples containing ≥0.2 at% of Ce; the light yield measured in LuAG:Ce (0.55 at%) was about 26000 ph/MeV, or close to that of LSO.

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1. Introduction

Scintillation of Ce3+-doped lutetium–aluminum garnet Lu3Al5O12 (LuAG:Ce) was reported in the middle of nineties [1]. As compared with other garnet-type scintillator hosts, e.g. Y3Al5O12 (YAG) or Gd3Sc2Al3O12 (GdSAG), LuAG has a higher density (6.73 g/cm3) and a higher effective Z number (62.9) that is important for most applications. The reported scintillation light yield of LuAG:Ce [1,2] was however significantly lower than the light yield of YAG:Ce (20 000 ph/MeV) [3] or GdSAG:Ce (16 000 ph/MeV) [4], even when measured in thin (1 mm) samples. In comparison with oxide scintillators belonging to other structural groups, such as LSO [5] or LuAP [1,6], LuAG:Ce seemed even less promising due to its relatively lower density and slower decay (∼60 ns). Due to these reasons this Ce3+-doped garnet scintillator was considered as not very much attractive for further development. It should be noticed that, in comparison with other Ce3+-doped garnets, no strong differences had been detected in spectral locations of Ce3+ associated absorption bands, Stoke’s shift or defect-related absorptions, which could be readily responsible for the low light yield. At least two factors should however be taken into account when comparing this garnet host with other aluminum garnets, i.e. (a) high intrinsic disorder coming from large amount of non-equivalent substitutions by the rare-earth ion (Lu) in octahedral lattice sites normally occupied by Al3+ [7,8] (dodecahedral sites of rare-earth aluminum garnets are occupied by the rare-earth ion, octahedral sites – preferentially by Al and tetrahedral sites – by Al) and (b) low distribution coefficient of Ce3+ ions resulting from size difference between Ce3+ and Lu3+ ions. The former seems important, as the existence of traps bringing slow decay components has been explained by the occurrence of Lu in octahedral sites [9]. The latter factor complicates preparation of concentrated crystals, while maintaining high optical quality; possibly for this reason the scintillation characteristics of LuAG:Ce reported so far were measured only in lightly (∼0.1 at%) doped crystals grown in majority of cases by Czochralski technique.

The present studies were initiated by the needs of development and optimization of LuAG:Ce fibers for high energy calorimetry [10,11]. In this application crystalline fibers are required with good scintillation parameters in terms of luminosity and decay time; these parameters are in many cases dependent on crystal composition, more especially the activator concentration, as it is the case for some other scintillators, e.g. LuAP:Ce [6] or LuAG:Pr [12]. The micro-pulling and the vertical Bridgman techniques were applied to grow LuAG:Ce with various Ce concentrations for detailed studies of scintillation potential of this material. The results have shown for the first time that the light yield of LuAG:Ce can be considerably improved, if the Ce3+ concentration is ≥0.2 at%. Comparison of scintillation parameters of LuAG:Ce grown by the two methods (Bridgman and micro-pulling) is given in Ref. [11]. This paper expands on the
work in Ref. [11] giving the details of single crystal growth of LuAG:Ce by the vertical Bridgman method, as well as material characterization including impurity incorporation, site occupation by Lu, and shortly, some optical and scintillation properties relative to Ce concentration.

2. Experimental

Single crystals of LuAG:Ce were grown by the vertical Bridgman method the details of which can be found in Refs. [13,14]. The starting oxides Lu₂O₃, Al₂O₃ and CeO₂ of at least 99.99% purity were melted in molybdenum containers under an enclosed Ar/H₂ (85/1 vol%) atmosphere; the melting point of LuAG is about 2060 °C. The concentration of Ce in the melt (C₀) in different runs was 0–1.5 at%. Translation rates of 0.8–1.5 mm/h were applied depending on the cerium concentration in starting melts; for C₀ > 1.2 at% it was selected in between 0.8 and 0.9 mm/h to avoid deterioration of the crystal quality at the last growth stages due to continuously increasing doping level.

Most of the crystalline defects occurring in melt-grown garnets were revealed and understood several decades ago to meet the technological demands created by laser applications [14,15]. Among those, facets, growth striations, solid and gas bubble inclusions, voids and dislocation arrays are the most detrimental.

Single crystals of LuAG:Ce were grown along the ⟨1 0 0⟩ crystallographic axis using 2 cm long seeds of the crucible diameter cut from un-doped LuAG, which were placed in the bottom of the molybdenum tubes. As for many other garnet-type crystals grown in the Bridgman geometry, the freezing isotherm of LuAG:Ce is convex towards the melt as revealed by growth striations. The ⟨2 1 1⟩ and ⟨1 1 0⟩ facets in garnets grown along the ⟨1 0 0⟩ direction are restricted to crystal peripheral regions where the interface shape is most convex [16]. Several single-phase and light-scatter-free crystals up to 618 × 80 mm² with facets located within a narrow peripheral ring were obtained under the applied experimental conditions. Since facets introduce strain and refractive index variation, the samples for scintillation measurements were cut from the central strain-free parts of the boules. A few examples of LuAG:Ce are shown in Fig. 1.

Typical configuration of facets in a cross-section viewed under crossed polarizers is given in Fig. 2 showing also that the central part of the sample is strain-free.

The chemical formulae reflecting site occupation preference by constituent ions in dodecahedral [c], octahedral [a] and tetrahedral (d) lattice sites of this garnet host are usually written as [Lu₃][Al₂₋ₓLuₓ](Al₃)O₁₂, where y is in the range 0.01–0.05; the ensuing lattice constant change is in the range 11.907–11.923 Å [8]. For the Ce-doped crystal the formula is written as [Lu₃₋ₓCeₓ][Al₂₋ₓLuₓ](Al₃)O₁₂, where y varies with x, as shown in the next sections. An excess of Lu₂O₃ was added to the melts to compensate the octahedral site occupancy by Lu and thus to

Fig. 1. Examples of LuAG:Ce crystals and shaped elements.

Fig. 2. Configuration of facets in a cross-section of LuAG:Ce (diameter 16 mm, d=2 mm) viewed under crossed polarizers.
avoid second phase precipitation: either Lu$_2$Al$_5$O$_{12}$/Al$_2$O$_3$ or Lu$_2$Al$_5$O$_{12}$/Lu$_2$O$_3$ depending on the melt composition [8].

It should be noted that garnets grown in molybdenum crucibles contain Mo$_{3^{+}}$ ions located in octahedral lattice sites; the concentration of Mo$_{3^{+}}$ in LuAG grown by the vertical Bridgman technique estimated by ESR is $3 \times 10^{17}$ ions/g [17]. Mo$_{3^{+}}$ ions in concentrations of about 10–20 ppm were recently revealed also in LuAG grown by the Czochralski technique from molybdenum crucibles [18]. Possible role of trace amounts of Mo$_{3^{+}}$ upon performance of LuAG:Ce will be investigated on the next stage of our studies using thermoluminescence methods.

To determine the solid solubility limit of Ce$_{3^{+}}$ in LuAG:Ce single-phase polycrystalline powders with different Ce$_{3^{+}}$ contents up to 7 at% were prepared by multi-step solid-state reactions at 1200 °C in air followed by heat treatments at 1600 °C in Ar/H$_2$ (85/15 vol%) atmosphere.

The lattice constant values of both single crystals (in samples cut from various crystal portions and with specified Ce content) and reacted powders were measured by X-ray diffraction (DRF-2.0 diffractometer; CuK$_\alpha$) with an accuracy of 0.001 Å. The quality of single crystals was inspected in optically polished 0.5 and 2 mm thick plates and with Ce$_{3^{+}}$ concentration up to about 0.7 at% using high-resolution microscopes. Absorption spectra were measured in the range 200–800 nm at 300 K (Specord M40 spectrophotometer). Scintillation parameters were measured in 2 × 2 × 8 mm$^3$ samples with estimated Ce$_{3^{+}}$ concentration; the samples were cut from two boules grown from melts with initial Ce concentration equal to 0.8 and 1.2 at%. Measurements were done in both transversal (h = 2 mm) and longitudinal (h = 8 mm) setups using 662 keV γ-rays emitted from a $^{137}$Cs source and a XP2020Q photomultiplier.

### 3. Results and discussion

#### 3.1. Ce$^{3^{+}}$ concentration

Due to a low distribution coefficient (k) the concentration of Ce$_{3^{+}}$ ions, as expected, gradually increases over the length of LuAG:Ce crystals evidenced visually by the color variation from green to yellow due to strong intensity increase and broadening of Ce$_{3^{+}}$ associated absorption bands with increase in the concentration (Fig. 3); FWHM for the band peaking at 347 nm shown in this figure is increasing from 20.34 (g = 0.35) to 21.50 (g = 0.91). It is known that the longitudinal impurity distribution in garnets grown by Bridgman is well described by the normal freeze equation [14,19] evidencing complete mixing of the melts. One of the possible reasons initiating flow and solute transfer in this configuration, where the melt is the coolest at the interface, has been described as due to upward motion of gas bubbles [14,21]. Numerous small-size gas bubbles are trapped during melt preparation and conserved in the saturated liquid; segregation of gaseous impurity occurs during the liquid–solid transition leading to increase in the size of gas bubbles and their subsequent motion towards the top driven by the buoyancy force. This motion initiates convective flows and also a direct mass transfer through the surfaces of gas bubbles.

The dependence between impurity concentration and absorption coefficient for relatively low (< 1%) impurity concentrations follows the Beer law; to specify the slope it is necessary to determine the impurity concentration by a direct method. If the distribution coefficient of added impurity is known, then its concentration distribution over the crystal length can be calculated using the normal freeze equation [19]; the impurity concentration in a selected sample can then be estimated by its location in the boule. The absorption coefficient variation with impurity concentration can be further plotted to obtain the required dependence.

The relationship between Ce$_{3^{+}}$ concentration and absorption coefficient at 347 nm in LuAG:Ce was obtained by correlating the measured absorption coefficients at 347 nm with calculated concentrations in crystal portions with specified fraction (g) of the crystallized melt (Fig. 4). The value k = 0.06 was taken in calculations based on reported data for LuAG:Pr ([k = 0.06–0.065 [12]) and close radii of Ce$_{3^{+}}$ and Pr$_{3^{+}}$ ions [20]. The absorption was measured in nine samples cut from selected positions over the crystal length marked on the calculated distribution curve (Fig. 4); the values of absorption coefficients against the g-values were then plotted, as shown in the inset. The obtained relationship between Ce$_{3^{+}}$ concentration and absorption coefficient at 347 nm can be used for concentration estimations in other samples with high relative accuracy. The absolute accuracy is acceptable too, since e.g., the difference in concentration values determined using plots based on distribution curves calculated for k = 0.06 and 0.05 is less than 10% (for the Ce$_{3^{+}}$ concentration range up to 0.4 at%).
Concluding this section it should be mentioned that melt preparation under high vacuum restricts solute convective flow, as shown for several host–impurity systems [14], and can be applied to increase the fraction of the boule with a high and more uniform doping concentration.

3.2. Site occupation

The degree of non-equivalent substitution on the octahedral lattice site by Lu, \([\text{Lu}_{O}]\), was estimated by comparison of the measured lattice constant in concentration series of reacted polycrystalline powders and single crystals with those calculated for the zero concentration of Lu in these sites using the empirical formula [22] and ionic radii from [20] \((0.977 \text{ Å} \text{ and } 1.14 \text{ Å}, \text{ respectively, for } \text{Lu}^{3+} \text{ and } \text{Ce}^{3+} \text{ in } 8\text{-fold coordination}; 0.53 \text{ Å} \text{ for } \text{Al}^{3+} \text{ in } 6\text{-fold coordination}; 0.39 \text{ Å} \text{ for } \text{Al}^{3+} \text{ in } 4\text{-fold coordination})\). The results of measurements (including the actual \(\text{Ce}^{3+}\) concentration) are given in Table 1 and shown graphically in Fig. 5. The measured lattice constant is increasing with actual \(\text{Ce}^{3+}\) content in both single crystal and reacted powder series; the slopes of the dependences, as expected, are very different confirming that the solubility of Lu in octahedral sites increases with the temperature. The above results indicate also that more Lu enters octahedral sites as the concentration of \(\text{Ce}^{3+}\) entering the dodecahedral sites increases. The maximum concentration of \(\text{Ce}^{3+}\) measured in facet-free regions in the studied single crystal series is 0.72 at\%. The solid solubility limit of \(\text{Ce}^{3+}\) in polycrystalline \(\text{LuAG:Ce}\) prepared under the applied conditions \((1600 \text{ °C}, \text{Ar}/\text{H}_{2})\) is about 5 at\%. For comparison, the reported solid solubility limit of \(\text{Ce}^{3+}\) in polycrystalline \(\text{YAG:Ce}\) prepared at 1450 °C under reducing atmosphere is about 6 at\% [23].

Using the data for single crystal and powder samples given in Table 1 the degree of deviation from stoichiometry, i.e. the degree of substitution on the octahedral site by Lu, was calculated using the relationship

\[
y = 2\Delta a/1.615(r_{\text{Lu}}^{VI} - r_{\text{Ce}}^{VI}) \Delta a = \alpha(\exp) - \alpha(\text{cal}) \quad [24]
\]

and ionic radii from [20]. The relationship [24] was derived for gallium garnets but it is applicable to aluminum garnets as well, since a good agreement was obtained between the measured unit cell constants and those calculated by applying the empirical formula [22] to the composition \((\text{Lu}_{3-x} \cdot \text{Ce}_x)_2\text{[Lu}_6\text{Al}_{12-x} - y\text{Al}_2\text{O}_{12}]\), where \(\text{Ce}_x\) is the measured concentration of \(\text{Ce}^{3+}\), and \(\text{Lu}_x\) is the degree of Lu substitution on the octahedral site estimated from the relationship [24].

**Table 1**

<table>
<thead>
<tr>
<th>Composition</th>
<th>(a_0 ) (Å) (measured)</th>
<th>(a_0 ) (Å) (calculated)</th>
<th>(\Delta a_0)</th>
<th>(y\text{Lu}<em>6\text{Al}</em>{12-x} \cdot \text{Lu}_x\text{Al}<em>2\text{O}</em>{12})</th>
<th>(\text{Lu}_x) (at %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Single crystals</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(\text{LuAG} \cdot \text{off facet})</td>
<td>11.914</td>
<td>11.9078</td>
<td>0.0062</td>
<td>0.0233</td>
<td>1.165</td>
</tr>
<tr>
<td>(\text{LuAG} \cdot \text{on facet})</td>
<td>11.922</td>
<td>11.9078</td>
<td>0.0142</td>
<td>0.0533</td>
<td>2.665</td>
</tr>
<tr>
<td>(\text{LuAG}:\text{Ce}(0.25 \text{ at%}) \cdot \text{off facet})</td>
<td>11.925</td>
<td>11.9068</td>
<td>0.0163</td>
<td>0.0612</td>
<td>3.06</td>
</tr>
<tr>
<td>(\text{LuAG}:\text{Ce}(0.42 \text{ at%}) \cdot \text{off facet})</td>
<td>11.931</td>
<td>11.9094</td>
<td>0.0216</td>
<td>0.0811</td>
<td>4.055</td>
</tr>
<tr>
<td>(\text{LuAG}:\text{Ce}(0.5 \text{ at%}) \cdot \text{on facet})</td>
<td>11.938</td>
<td>11.9097</td>
<td>0.0283</td>
<td>0.1062</td>
<td>5.31</td>
</tr>
<tr>
<td>(\text{LuAG}:\text{Ce}(0.72 \text{ at%}) \cdot \text{off facet})</td>
<td>11.937</td>
<td>11.9105</td>
<td>0.0265</td>
<td>0.0995</td>
<td>4.975</td>
</tr>
<tr>
<td>(\text{LuAG}:\text{Ce}(0.86 \text{ at%}) \cdot \text{on facet})</td>
<td>11.953</td>
<td>11.911</td>
<td>0.042</td>
<td>0.1576</td>
<td>7.88</td>
</tr>
<tr>
<td>Reacted powders</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(\text{LuAG})</td>
<td>11.908</td>
<td>11.9078</td>
<td>0.0002</td>
<td>0.0007</td>
<td>0.035</td>
</tr>
<tr>
<td>(\text{LuAG}:\text{Ce}(0.5 \text{ at%}))</td>
<td>11.911</td>
<td>11.9097</td>
<td>0.0013</td>
<td>0.0049</td>
<td>0.245</td>
</tr>
<tr>
<td>(\text{LuAG}:\text{Ce}(1 \text{ at%}))</td>
<td>11.912</td>
<td>11.9116</td>
<td>0.0004</td>
<td>0.0015</td>
<td>0.075</td>
</tr>
<tr>
<td>(\text{LuAG}:\text{Ce}(2 \text{ at%}))</td>
<td>11.917</td>
<td>11.9153</td>
<td>0.0017</td>
<td>0.0064</td>
<td>0.32</td>
</tr>
<tr>
<td>(\text{LuAG}:\text{Ce}(4 \text{ at%}))</td>
<td>11.926</td>
<td>11.9228</td>
<td>0.0032</td>
<td>0.012</td>
<td>0.6</td>
</tr>
</tbody>
</table>

The difference between the lattice constants of un-doped \(\text{LuAG}\) prepared by melt-growth and solid state reactions is 0.006 Å (Table 1). Taking zero for the concentration of Lu in octahedral sites in the un-doped reacted powder, the octahedral occupancy by Lu in the facet-free region of the un-doped single crystal is 1.165 at\%. In fact, some small amount of Lu does enter the octahedral sites in un-doped \(\text{LuAG}\) reacted powder but its effect upon the lattice constant, in comparison to that introduced by \(\text{Ce}^{3+}\) doping, is negligibly small. Fig. 6 shows the estimated octahedral occupancy \((y)\) by Lu in reacted powder and single crystal series as a function of the \(\text{Ce}^{3+}\) concentration. The concentration of octahedral Lu in the most concentrated single crystal, LuAG:Ce \(0.72\text{ at%}\), is about 5 at\%. In the reacted powder LuAG:Ce \(4\text{ at%}\) the octahedral concentration of Lu is only 0.6 at\%.

3.3. Facets

The \(\text{Ce}^{3+}\) concentration in \(\text{LuAG:Ce}\) measured on \((2 1 1)\) facets is by some 20% higher than in adjacent facet-free regions, as it is the case for some other rare-earth doped garnets (e.g. \(\text{YAG:Nd}\) [25]) and resulting from dissimilar growth mechanisms on singular and atomically rough interfaces [26]. The difference...
between the lattice constant measured on \{2 1 1\} facets and facet-free regions in un-doped LuAG is 0.008 Å (Table 1).

Fig. 7 shows a fragment of the X-ray powder diffraction photograph (reflection 664 from CuKα emission) taken from an un-doped LuAG containing both facetted and facet-free regions. Two reflections each with Kα1 and Kα2 splitting are seen, which correspond to the same family of planes but with dissimilar interplane distances. The lattice constant measured on \{2 1 1\} facets is larger than that of the un-facetted regions (\(d_{a/\alpha} = 6.7 \times 10^{-4}\)); this value is by a factor of 5 larger, as compared with \(d_{a/\alpha} = 1.3 \times 10^{-4}\) reported for YAG and Gd3Ga5O12 (GGG) [27], suggesting a larger magnitude of strain.

It should be mentioned that LuAG, in comparison with YAG, exhibits a higher tendency for crack formation during crystal cooling despite close values of thermal coefficients of the expansion (8.8 \(\times\) \(10^{-6}\) and 8.9 \(\times\) \(10^{-6}\) K\(^{-1}\) for LuAG and YAG, respectively [28]). Among the principal sources responsible for facet strain, segregation of oxygen vacancies and octahedral occupancy by rare-earth ions were considered as the most likely [27,29].

3.4. Optical and scintillation properties

Transmission spectra of LuAG:Ce in the range 470–540 nm are given in Fig. 8 and show high transparency in the range of emission, > 510 nm. Fig. 9 shows the relation between the cut-off wavelength [6] for the longer wavelength shoulder of the Ce\(^{3+}\) associated absorption band peaking at 450 nm (derived from transmission spectra) and the Ce\(^{3+}\) concentration in LuAG:Ce. The emission spectra for the same series under excitation at \(\lambda_{exc} = 450\) nm are shown in Fig. 10 (for better comparison the spectra are normalized to their respective maximum values). The wavelength of maximum emission moves with increase in the Ce\(^{3+}\) content from \(\lambda_{MaxEm} = 512\) nm (C = 0.08 at\%\) to \(\lambda_{MaxEm} = 533\) nm (C = 0.55 at\%). The excitation bands broaden with increase in the Ce\(^{3+}\) concentration, as it is the case for absorption bands. The change in the maximum emission wavelength has been taken into account in calculations of the light yield values since the quantum efficiency of the photomultiplier strongly depends on the wavelength. The quantum efficiency for LuAG:Ce is only 5–6%, as compared to 22% for LSO. In the photoluminescence set-up the incident light was directed at a low angle to excite only the surface in order to avoid possible absorption effects. To correct the quantum efficiency the emission spectra were taken into account...
but similar results were obtained even when the average value was taken.

In scintillation studies $2 \times 2 \times 8 \text{ mm}^3$ samples optically polished on all sides were used. Fig. 11 shows the light yield figures measured in the horizontal set up ($h=2 \text{ mm}$), which increase from 17722 to 25714 ph/MeV with increase in the Ce concentration from 0.05 to 0.55 at%; the energy resolution figures are also given in the figure. In the vertical set up ($h=8 \text{ mm}$) the respective figures for the light yield increase from 12036 to 18130 ph/MeV. The light yield ratio reflecting the degree of losses due to self-absorption measured in these samples is in the range 1.1–0.4 at% in un-doped LuAG to about 4 at% in LuAG:Ce (0.5 at%). The solid solubility limit of Ce$^{3+}$ in LuAG:Ce prepared by solid state reactions (1600 °C, Ar/H$_2$ atmosphere) was found to be about 5 at%.

Evaluation of the scintillation potential of LuAG:Ce with Ce$^{3+}$ concentration in the range 0.05–0.55 at% has demonstrated that LuAG:Ce containing 0.2 at% or more of Ce$^{3+}$ ions is a highly competitive scintillator displaying light yield about 26 000 ph/MeV or close to that of LS0:Ce. The timing performance of LuAG:Ce does not show any noticeable dependence on the Ce$^{3+}$ concentration.

4. Conclusions

Concentrated single crystals of LuAG:Ce (0.05–0.7 at%) were developed using the vertical Bridgman technique. The relationship between Ce$^{3+}$ concentration and absorption coefficient at 347 nm was established and used for estimation of Ce$^{3+}$ concentration in samples fabricated for scintillation measurements. It was found that the degree of non-equivalent substitution on the octahedral lattice sites by Lu increases from about 1.1 at% in un-doped LuAG to about 4 at% in LuAG:Ce (0.5 at%). The solid solubility limit of Ce$^{3+}$ in LuAG:Ce fabricated by solid state reactions (1600 °C, Ar/H$_2$ atmosphere) was found to be about 5 at%.

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