Scintillation yield enhancement in LuAG:Pr crystals following thermal annealing

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Effects of thermal annealing in various atmospheres of Czochralski-grown Lu3Al5O12:Pr (LuAG:Pr) crystals on their scintillation yield and energy resolution are discussed. It is shown that annealing in argon, air, or oxygen at 1373 K for 48 h is a simple way of achieving a ten-off percent increase of yield together with an improvement of energy resolution. High temperature thermoluminescence measurements indicate significant reductions of trap concentrations in the annealed crystals compared to the "as grown" ones, which correlates well with the observed yield increase. A simple model is proposed to predict further available yield enhancement in LuAG:Pr upon thermal annealing.

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1. Introduction

Praseodymium activated lutetium aluminum garnet, Lu3Al5O12:Pr (LuAG:Pr), was first studied as a potential heavy and fast scintillator by Nikl et al. [1]. Initial reports on LuAG:Pr used to assert its high density of 6.7 g/cm² and fast scintillation decay time of 20 ns [1,2]. Further papers highlighted its very good energy resolution below 5% (at 662 keV), low yield non-proportionality of 10% (17–1274 keV), and minor internal light losses [3,4]. All these features rendered LuAG:Pr a promising material for several applications, including the newly developed PEM (positron emission mammography) device for medical diagnostics [5].

Although the observed absolute light output of LuAG:Pr, close to 19,000 ph/MeV [3] at optimal praseodymium concentration, was undoubtedly a weaker point of the material, it clearly seemed to leave some room for improvement. A distinct sidelite could be noticed within the thermal dependence of yield, showing an increased yield of LuAG:Pr at 450 K by almost 40% compared to room temperature [3]. The follow-up studies attributed this feature to the existence of shallow electron traps and their temperature-dependent contribution to the host-to-ion energy transfer in LuAG:Pr, based on a consecutive capture of charge carriers at praseodymium ions [6]. Regardless of the origin of these traps it became clear that efforts should be made to reduce their concentration with a view to increasing the scintillation yield of LuAG:Pr.

An overview of defects likely to occur in RE₃Al₅O₁₂ hosts was presented by Stanek et al. [7]. They indicated the formation of three types of so-called antisite defects, namely Al₃ (RE₃Al₅O₁₂), and fusing oxygen atoms. In their explanation electron traps associated with these vacancies, a significant concentration was to be anticipated only if the formation of voids and oxygen vacancies, a significant concentration was to be anticipated only if the formation of voids and oxygen (RE₃Al₅O₁₂) crystals. The former authors noticed a strong increase of luminescence intensity of LPS:Ce annealed in air at 1373 K, which they ascribed to a process of vacancy filling by di- oxygen vacancies. In their explanation electron traps associated with these vacancies competed for electrons with Ce³⁺ ions and thereby decreased the scintillation yield, hence a lower concentration of the vacancies could give rise to a higher yield. The latter authors tested, beside air, the atmosphere of nitrogen, but the impact of annealing in N₂ on yield of LPS:Ce was negligible. Zhong et al. [12,13] reported the creation of oxygen vacancies during...
the growth of LuAG:Ce crystals by the Czochralski method. They annealed their crystals in air at 1473 K for 40 h and observed a significant reduction of their concentration via high temperature thermoluminescence measurements. Interestingly, they failed to attain any scintillation yield enhancement in LuAG:Ce upon annealing, either in air or in mixed H₂ + N₂ atmosphere.

In this paper we describe the effects of thermal annealing in various atmospheres on the basic scintillation properties of LuAG:Pr crystals, i.e. their scintillation yield, energy resolution, and intrinsic light losses. The results of comparative pulse height and high temperature thermoluminescence measurements, performed on “as grown” and annealed LuAG:Pr samples, are analyzed quantitatively in order to determine an optimal annealing atmosphere and to assess further potential for yield increase.

2. Materials and experiment

A Ø3-inch boule of Lu₃Al₅O₁₂:Pr was grown by the Czochralski method by Furukawa Co. Ltd., Japan. The concentration of Pr³⁺ ions in the crystal was determined to fall between 0.22 and 0.24 mol%. Details about the growth technology can be found in [2]. 6 × 6 × 6 mm³ “cube” and 6 × 6 × 1 mm³ “plate” samples were cut from the boule and left unpolished. Some of the samples were annealed at 1373 K for 48 h inside a resistance heating furnace with a vacuum-tight system in one of the four following atmospheres: 100% Ar, 98% Ar + 2% H₂, 100% O₂, and air. The heating and cooling rate in the annealing cycle was equal to 100 K/h.

Pulse height spectra necessary to determine photoelectron yields and energy resolutions were collected at room temperature under 662 keV gamma excitation from a ¹³⁷Cs source. The pulsed output signal from a Hamamatsu R2059 photomultiplier (PMT, 1500 V high voltage) was processed by a Canberra 2005 integrating preamplifier, a Canberra 2022 spectroscopy amplifier (2 μs shaping time), and a multichannel analyzer. Positions of so-called photopeaks in the spectra, corresponding to full energy scintillations, were used to evaluate the yields of particular samples, expressed as numbers of photoelectrons released from the PMT photocathode per an unit (1 MeV) of energy deposited in the crystal. To improve light collection efficiency the samples were coupled to the quartz window of the PMT with Viscasil grease and covered with several layers of Teflon tape. We point out that higher values of energy resolution (>6.7%) obtained with the Hamamatsu R2059 PMT compared to those observed with the Hamamatsu R1791 PMT (~5% [3]) are probably related to a different dynode structure in these PMTs (R1791 is optimized for gamma spectroscopy). The lack of polishing of the currently studied samples may also deteriorate their resolution.

Thermoluminescence (TL) glow curves were recorded using a Risoe TL/OSL-DA-12 reader. Prior to the beta irradiation from a ⁹⁰Sr/⁹⁰Y source the samples (plates) were annealed by heating to 107°C for 4 h inside a resistance heating furnace with a vacuum-tight system in one of the four following atmospheres: 100% Ar, 98% Ar + 2% H₂, 100% O₂, and air. The heating and cooling rate in the annealing cycle was equal to 100 K/h.

3. Results and discussion

Two examples of pulse height spectra of LuAG:Pr are shown in Fig. 1. The values of photoelectron yield and energy resolution of all the studied samples, derived from their spectra, are listed in Table 1 and illustrated in Fig. 2. It is clear that, regardless of the atmosphere, annealing improves both yield and resolution of LuAG:Pr. The magnitude of enhancement is similar upon annealing in 100% Ar, air, or 100% O₂. Only the mixed 98% Ar + 2% H₂ atmosphere is less effective, but still induces an improvement.

One can also notice that higher increases of yield involve larger samples (cubes, up to 17%) compared to the smaller ones (plates, up to 6%). This observation suggests that internal light losses in the crystals have been reduced by annealing. Indeed, the values of a so-called loss coefficient based on the “2K” model [14,15] indicate that annealing in 100% Ar, air, or 100% O₂ abates the internal losses more than twice (Table 1). This turns out to be an additional positive effect of annealing, which is of importance for maintaining sufficient yield with increasing crystal size. In particular, it should be considered to anneal LuAG:Pr pixels prepared for PET [16] or PEM [5].

The whole set of recorded glow curves of LuAG:Pr is presented in Fig. 3. The curves reveal the existence of at least three traps peaking at about 370, 530, and 580 K. A fourth peak above 650 K can be observed only in case of the non-annealed sample and the Ar/H₂-annealed one. Clearly annealing in 100% Ar, air, or 100% O₂ effectively reduces the concentration of carriers captured by the fourth trap. The positions of the three aforementioned peaks do

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**Table 1** Parameters describing the basic properties of the studied LuAG:Pr samples (Y – photoelectron yield, R – energy resolution at 662 keV, μ – loss coefficient, S – area under the glow curve between 300 and 750 K; the accuracy of yield and resolution determination is below 5%).

<table>
<thead>
<tr>
<th>Annealing atmosphere</th>
<th>Cubes</th>
<th>Plates</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Y (phe/MeV)</td>
<td>Y (%)</td>
</tr>
<tr>
<td>None</td>
<td>2870</td>
<td>100</td>
</tr>
<tr>
<td>100% Ar</td>
<td>3310</td>
<td>115</td>
</tr>
<tr>
<td>98% Ar + 2% H₂</td>
<td>3120</td>
<td>109</td>
</tr>
<tr>
<td>Air</td>
<td>3360</td>
<td>117</td>
</tr>
<tr>
<td>100% O₂</td>
<td>3360</td>
<td>117</td>
</tr>
</tbody>
</table>

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not move upon annealing, the slight shifts are only caused by non-ideal heat transfer between the crystal and the heating plate [17]. The basic trap parameters, i.e. trap depths $E$ and frequency factors $s$, have been derived from a fit based on the classic first-order model of Randall and Wilkins [18], performed with the GlowFit software [19], and they are figured out in Table 2. The glow curve of the $O_2$-annealed plate has been chosen for the fit, shown in Fig. 4, as it seems to be hardly affected by the non-ideal heat transfer.

Since the traps detected in TL of LuAG:Pr can be regarded as deep ($E = 0.746–1.51$ eV), they are expected to decrease the room temperature (RT) scintillation yield. Such conclusion is based on the so-called single-trap model [20], which has already been applied for LuAG:Pr [6], assuming that the prompt consecutive capture of charge carriers, followed by their radiative recombination at $Pr^{3+}$ ions, constitutes the main route for the host-to-ion energy transfer in this material. Besides there is a delayed, trap-mediated route for the energy transfer due to the participation of the traps. Since the $Pr^{3+}$ ions are likely to capture valence band holes promptly and efficiently [21], we suppose that these traps are electron traps. The trap lifetime $\tau$ is described by the classic Arrhenius formula:

$$\frac{1}{\tau} = s \exp \left( \frac{E}{k_BT} \right)$$

($E$ – trap depth, $s$ – frequency factor, $T$ – temperature, $k_B$ – the Boltzmann constant), whereas the dependence of the scintillation yield $Y$ on the trap lifetime $\tau$ is given by the expression [20]:

$$Y = Y_{tf} \left( a + b \frac{\tau_{rad}}{\tau} \left( 1 + \frac{\tau}{\tau_{rad}} \left( \exp \left( \frac{2.35\tau_{sh}}{\tau} \right) - 1 \right) \right) \right)$$

($Y_{tf}$ – yield of a trap-free material, $a$ and $b$ – relative contributions from the direct and trap-mediated scintillation components, respectively ($a + b = 1$), $\tau_{rad}$ – radiative lifetime of the $Pr^{3+}$ ions, $\tau_{sh}$ – shaping time).

In order to investigate the effect of annealing on thermoluminescence and, consequently, scintillation yield of LuAG:Pr, we start with a comparison of the areas under the recorded glow curves (Table 1). We note that the smallest areas under the glow curves are observed in case of the crystals annealed in 100% Ar, air or $100% O_2$, i.e. in these atmospheres that have caused the yield increase. Since it is a distinct correlation, we tentatively try to describe it quantitatively, limiting the attention to RT (at which the yields have been measured so far). We have already presumed that at RT the trap-mediated component is stored in traps, hence the RT yield may be expressed as:

$$Y_{RT} = aY_{tf} = (1 - b)Y_{tf}$$

The magnitude of the trap contribution is reflected by the area under the glow curve. In the simplest approach we assume a direct proportionality $b = kS$, where $S$ denotes the area and $k$ is a coefficient. In this way we obtain a linear relation:

$$Y_{RT} = (1 - kS)Y_{tf} = -kY_{tf}S + Y_{tf}$$

which we employ to fit a straight line in Fig. 5, displaying the RT yields of the non-annealed and annealed LuAG:Pr plates. Even such unsophisticated attitude clearly shows that there is room for improvement and the yield of LuAG:Pr could be further enhanced if it was possible to completely get rid of the traps peaking at 370,
530, and 580 K. We note that although for 1 mm thick plates an increase of yield to $Y_{TF} = 3970 \text{ phe/MeV}$ would mean a profit of “only” 12% compared to non-annealed samples, in case of larger samples like 6\(\times\)6 mm\(^3\) cubes studied herein or 2.1\(\times\)2.1\(\times\)15 mm\(^3\) pixels used in PEM [5] the enhancement would be much more significant.

4. Conclusions

The results presented in this paper indicate that thermal annealing, mostly in 100% Ar, air, or 100% O\(_2\), can be successfully utilized to improve the scintillation performance of LuAG:Pr by increasing its scintillation yield and decreasing its energy resolution. The observed enhancement seems to be related to the reduction of charge trap concentrations in the annealed crystals, even though the current attention has been limited to the traps revealed by high temperature measurements. Better optical properties of the annealed crystals, reflected by lower internal light losses, are also of importance.

At this stage it is impossible to determine the mechanisms that stand for the reduction of trap concentrations. Although in case of annealing in air or 100% O\(_2\) one could suspect the process of vacancy filling by diffusing oxygen atoms [9], it would not explain a similar improvement achieved upon annealing in 100% Ar. It seems that there is either a different mechanism associated with annealing in argon, or even one common mechanism, in which high temperature plays a major role regardless of the ambient atmosphere.

For a more precise evaluation, low temperature TL glow curves should be recorded on non- and annealed samples. Various annealing temperatures and periods of time are also worth to be examined thoroughly. Preliminary results of the latter research have already been obtained and will be reported elsewhere.

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References


Fig. 5. Photoelectron yield of LuAG:Pr plates as a function of TL response (the orange open square related to the Ar/H\(_2\)-annealed sample has not been taken into account in the linear fit).