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Effect of thermal annealing in air on scintillation properties of LuAG and LuAG:Pr

Research Article

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Abstract: Pure and Pr-activated $Lu_3Al_5O_{12}$ (LuAG) crystals have been grown by the Czochralski method. In order to improve the scintillation properties, several samples have been annealed in air. Various annealing temperatures and periods of time have been tested to determine optimal conditions in the way of scintillation yield and energy resolution enhancement. The largest increase of yield of LuAG:Pr (17%), accompanied by a distinct decrease of resolution, has been observed after annealing at 1100°C for 48 h. On the contrary, in case of undoped LuAG no significant changes following thermal annealing have been noticed.

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Keywords: LuAG • praseodymium • scintillator • thermal annealing • Czochralski method

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1. Introduction

Rare-earth-activated wide bandgap oxide crystals are widely used in the field of ionizing radiation detection due to the fast and parity-allowed *d*-*f* transitions of rare earth ions. $Lu_3Al_5O_{12}$:Pr has a potential as a modern scintillator characterized by excellent energy resolution of 4.6% (at 662 keV), high density of 6.7 g/cm^3, fast response of 20 ns, and low scintillation non-proportionality of around 8% in the range from 17 to 1274 keV [1–4]. Although the light yield of around 19000 ph/MeV is not the best parameter of this material, one observes an increase of about 30% of the value just by heating the sample to ~180°C. This feature is associated with a (thermally dependent) weakening of the role of electron traps in the energy transfer between the LuAG host and the Pr^{3+} activator ions [3, 5]. Based on this fact an increase of room temperature yield of LuAG:Pr also seems to be possible, wherein thermal annealing is one of the most promising and quite simple methods to achieve this goal.

In this paper we show and discuss the impact of air-annealing on the scintillation performance of LuAG:Pr. By

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means of pulse height measurement we study several series of polished cube and plate samples, some of which have been previously annealed in air for 24-144 h at temperatures between 700 and 1400°C. In addition we compare the results with those obtained for undoped LuAG samples treated in the same way, trying to determine tentatively the physical processes lying behind all the observed features.

2. Materials and experiment

Two single crystals of $Lu_3Al_5O_{12}$ (one pure and one activated with praseodymium) with boule diameters of 2" were grown by the Czochralski method by Furukawa Co. Ltd., Japan, on purpose of this research. Details about the growth technology are presented in [6]. The concentration of Pr^{3+} ions in LuAG:Pr was determined as 0.2 mol% by the ICP (inductively coupled plasma) technique. 6 x 6 x 6 mm^3 cube and 6 x 6 x 1 mm^3 plate samples were cut from the boules and mechanically polished. After the preliminary confirmation of scintillation yield uniformity by pulse height measurements (separately within the cubes and within the plates), several samples of each size were annealed in air inside a resistance heating furnace with vacuum-tight system using one of the six following annealing conditions: 48 h/700°C, 24 h/1100°C, 48 h/1100°C, 72 h/1100°C, 144 h/1100°C, and 48 h/1400°C. The heating and cooling rates in the annealing cycle were equal to 100°C/h.

A typical set-up consisting of an Inel XRG3D X-ray generator with a Cu-anode tube operated at 45 kV and 10 mA, an ARC SpectraPro-150 monochromator, and a Hamamatsu R928 photomultiplier (PMT) was used to record room temperature X-ray excited emission spectra. The spectra were not corrected for the spectral sensitivity of the detection part.

Pulse height spectra necessary to determine photoelectron yields and energy resolutions were collected at room temperature under 662 keV gamma excitation from a Cs-137 source. The pulsed output signal from a Hamamatsu R2059 photomultiplier 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.

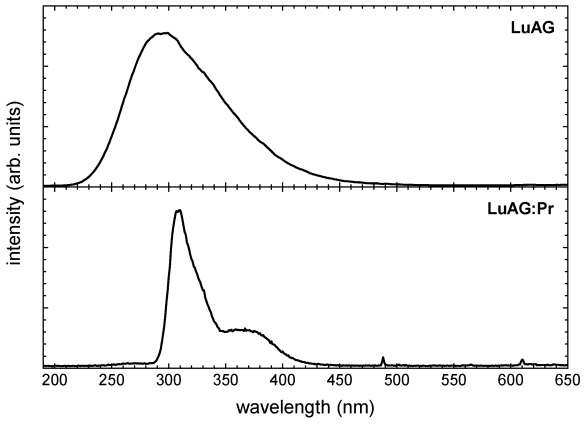

Figure 1. Radioluminescence spectra of LuAG and LuAG:Pr.

Since we had at our disposal 3 cubes and 3 plates of each series of LuAG and LuAG:Pr (84 samples in total), for a better accuracy of the data we recorded pulse height spectrum of each cube at least 3 times (*i.e.* with 3 different sides of the cube stuck with Viscasil to the PMT window). Likewise, we measured pulse height spectra of each plate twice (*i.e.* from both sides of the plate). In this way for each series of samples we obtained 9 or 6 values of photoelectron yield and energy resolution (for cubes or plates, respectively). The spreads within such sets of values were lower than the 5% accuracy of a single yield/resolution determination, hence for clarity of the data presentation we show the highest yields and lowest resolutions observed for each series.

3. Results and discussion

Representative radioluminescence spectra of pure and Pr activated LuAG are presented in Fig. 1. It is evident that the host emission, clearly apparent in case of LuAG, gives place in LuAG:Pr to the praseodymium strong *d-f* (below 450 nm) and weak *f-f* (above 450 nm) luminescence, the former of which is crucial for the fast scintillation of this material.

From all of the collected pulse height spectra some typical examples of cubes and plates from both series (LuAG and LuAG:Pr) are presented in Figs. 2–5. All of the spectra are shown in comparison to the non-annealed samples. The samples from Figs. 2 and 3 (a cube and a plate) were annealed in air at 1100°C for 48 h and seem to display the highest increase of yield so far. Also, one can note an improvement of energy resolution to the value of 5.3% which is nearly the same as observed previously using a

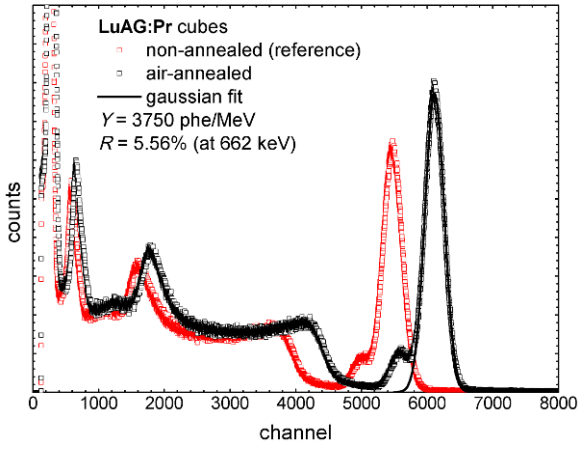

Figure 2. A Cs-137 pulse height spectrum of the prominent LuAG:Pr cube (cut from a ⌀2" boule and annealed in air at 1100°C for 48 h) in comparison to a non-annealed sample.

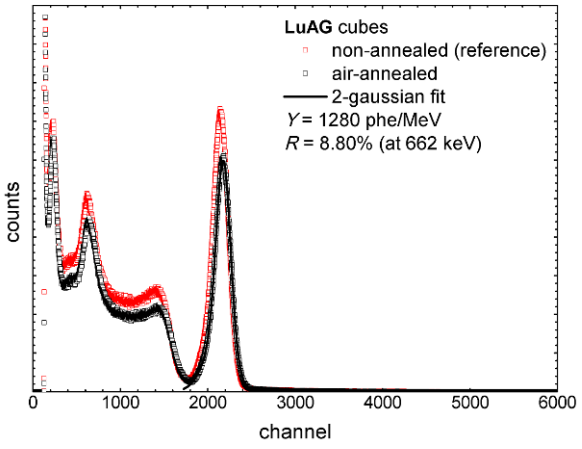

Figure 4. A Cs-137 pulse height spectrum of typical LuAG cube (cut from a ⌀2" boule and annealed in air at 1100°C for 72 h) in comparison to a non-annealed sample.

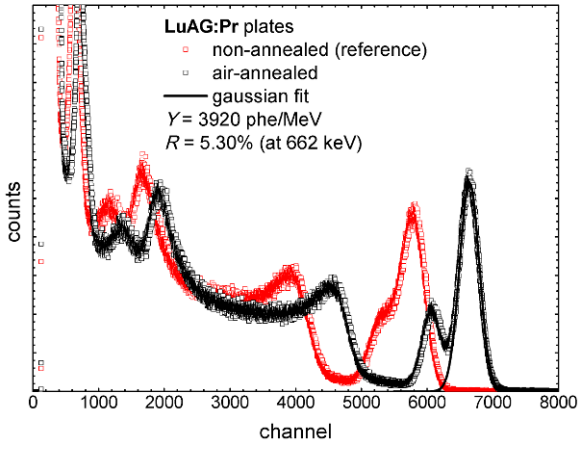

Figure 3. A Cs-137 pulse height spectrum of the prominent LuAG:Pr plate (cut from a ⌀2" boule and annealed in air at 1100°C for 48 h) in comparison to a non-annealed sample.

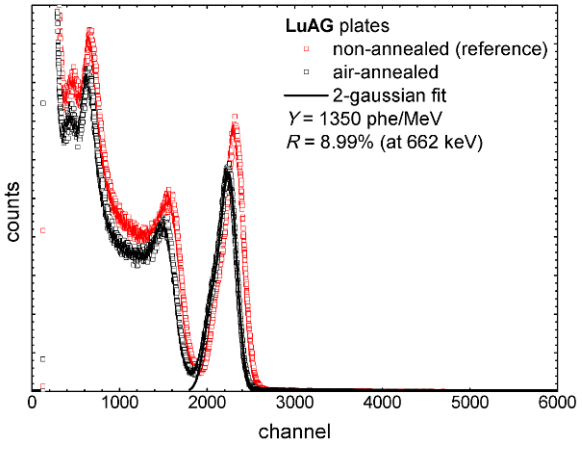

Figure 5. A Cs-137 pulse height spectrum of a typical LuAG plate (cut from a ⌀2" boule and annealed in air at 1100°C for 72 h) in comparison to a non-annealed sample.

much better PMT [3]. The enhancement is visible in the pulse height spectrum itself, wherein the escape peak is clearly separated from the photopeak (Fig. 3), unlike in the reference spectrum of a non-annealed sample. The situation is completely different for undoped LuAG. Typical pulse height spectra are shown in Figs. 4 and 5. The samples presented therein were annealed at 1100°C for 72 h. First of all, one observes a much lower photoelectron yield compared to LuAG:Pr, accompanied by a deterioration of energy resolution (see Tables 1, 2). This can be expected due to absence of activating ions. Secondly, the undoped crystals differ from the Pr-activated ones with respect to their response to annealing. To discuss these discrepancies we plot the values of photoelectron yield and energy resolution against annealing time (Figs. 6 and 7) and against temperature of annealing (Figs. 8 and 9).

In case of LuAG:Pr (Figs. 6 and 8) we can easily notice that the annealing in air at 1100°C for 48 h is the optimal thermal treatment that results in both increase of light yield and decrease of energy resolution. Neither the prolongation of time nor the increase of temperature above the favorable conditions enhances these scintillation parameters. On the other hand, there appears to be very little (if any) influence of the annealing on undoped LuAG. Moreover, at temperatures above 1100°C annealing tends to reduce the scintillation performance of LuAG in terms of both yield and resolution.

There is a number of cases reported in literature, concerning such scintillators as LuAG:Ce and LPS:Ce [8–10], where annealing of the crystals in air leads to a decrease

Table 1. Parameters obtained from the experiment for Pr-activated crystals (*Y* - photoelectron yield, *R* - energy resolution at 662 keV; the accuracy of yield and resolution determination is below 5%.)

	cubes			plates		
annealing conditions	*Y* (phe/MeV)	*Y* (%)	*R*(%)	*Y* (phe/MeV)	*Y* (%)	*R*(%)
none	3210	100	6.29	3410	100	6.93
48 h, 700°C	3370	105	5.93	3610	106	5.34
24 h, 1100°C	3280	102	6.11	3560	104	5.32
48 h, 1100°C	3750	117	5.56	3930	115	5.28
72 h, 1100°C	3720	116	5.60	3900	114	5.27
144 h, 1100°C	3720	116	5.52	3870	113	5.32
48 h, 1400°C	3650	114	5.61	3890	114	5.27

Table 2. Parameters obtained from the experiment for undoped crystals (*Y* - photoelectron yield, *R* - energy resolution at 662 keV; the accuracy of yield and resolution determination is below 5%.)

	cubes			plates		
annealing conditions	*Y* (phe/MeV)	*Y* (%)	*R*(%)	*Y* (phe/MeV)	*Y* (%)	*R*(%)
none	1260	100	8.85	1370	100	7.66
48 h, 700°C	1360	108	8.75	1470	107	8.49
24 h, 1100°C	1250	99	8.82	1340	98	9.09
48 h, 1100°C	1310	104	8.84	1390	101	9.01
72 h, 1100°C	1280	102	8.81	1350	99	8.99
144 h, 1100°C	1230	98	9.07	1350	98	9.17
48 h, 1400°C	1180	94	10.03	1270	93	9.43

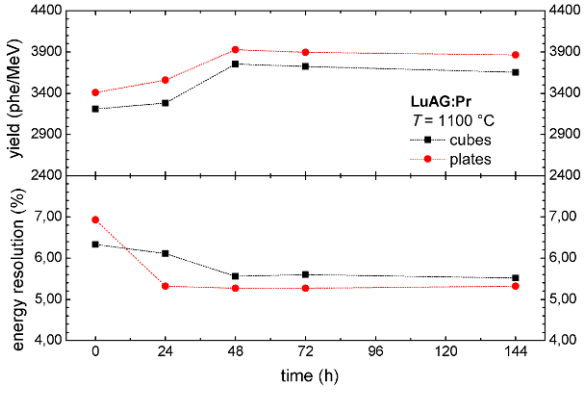

Figure 6. Photoelectron yield and energy resolution of Pr-activated LuAG (using best achieved values) as functions of annealing time (annealing temperature 1100°C).

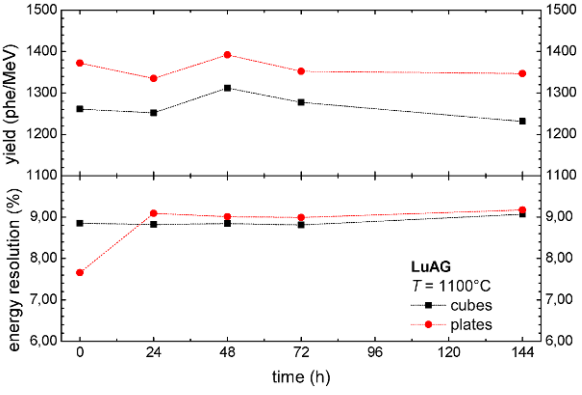

Figure 7. Photoelectron yield and energy resolution of undoped LuAG (using best achieved values) as functions of annealing time (annealing temperature 1100°C).

of concentration of oxygen-vacancy-related traps. It is suggested therein that oxygen vacancies act as electron traps competing with the Ce^{3+} luminescence centers, decreasing in turn the overall yield. At first, we could expect that LuAG:Pr provides a similar case. Since electron traps have already been recognized to decrease the scintillation yield of this material [5], they could be related to oxygen vacancies and their role would be weakened just by decreasing their concentration by thermal annealing in air. However, the results of our parallel studies [7] prove that the real mechanism of the enhancement is much more complicated. Although a similar improvement to that upon air-annealing can be achieved using an atmosphere of pure oxygen (O_2), which could indeed seem plausible that the presence of oxygen in the annealing atmosphere is responsible for the positive effects, we note that the

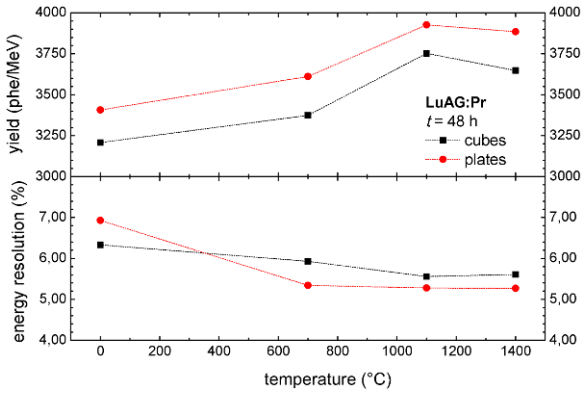

Figure 8. Photoelectron yield and energy resolution of Pr-activated LuAG (using best achieved values) as functions of annealing temperature (annealing time 48 h).

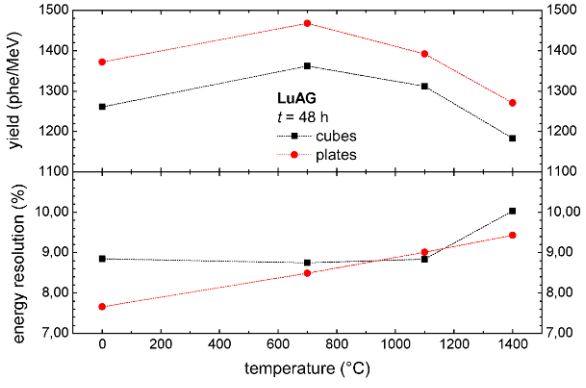

Figure 9. Photoelectron yield and energy resolution of undoped LuAG (using best achieved values) as functions of annealing temperature (annealing time 48 h).

annealing in pure argon (Ar) terminates at an enhancement of yield and resolution with a comparable magnitude. Two possibilities should be thus considered. Either there is a single, not yet identified, common mechanism for the annealing in air, O_2, and Ar, or there are two different mechanisms: an unknown, explaining the argon-induced improvement, and an oxygen-related, associated with the improvement following the annealing in air and oxygen [7]. One fact that seems to be certain is that the annealing is a process that reduces the concentration of electron traps inside LuAG:Pr. Preliminary results of thermoluminescence studies [7], as well as the negligible effect of annealing on the undoped LuAG crystals, strongly support such explanation.

4. Conclusions

The conducted research indicates that the largest increase of photoelectron yield of LuAG:Pr and improvement of its energy resolution occurs when the process of annealing in air is conducted for 48 hours at 1100°C. We attribute the enhancement to a decreased concentration of electron traps which improves the energy transfer to the Pr^{3+} luminescence centers. The lack of similar response in undoped LuAG to the annealing process seems to provide for this explanation, since there are less defects in the crystal structure because of the absence of the praseodymium ions. There also seems to be room for further fine-tuning of the annealing procedure, as the curves of the scintillation parameters as functions of the annealing conditions clearly have maxima that can be determined much more precisely.

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