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Advances in the scintillation performance of LuYAP:Ce single crystals

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Abstract

In the last years, there has been an effort to study and improve the performance of cerium doped $Lu_{0.7}Y_{0.3}AlO_3$ crystals. Since the first grown boules produced with the Czochralski technique, significant progress has been made in the crystal growth process that has resulted in larger crystal ingots and in important improvements of the scintillation properties. In this study, the results in light yield, energy resolution and decay time will be presented from the first studied batches, grown in the pre-production phase, as well as from crystals of the mass production. The optical characteristics such as transmission and absorption spectra were investigated and important correlations with the scintillation properties will be pointed out. The pixels produced in large quantities are going to be implemented in several small animal PET scanners and therefore the observed consistency of the scintillation properties is of great importance for the performance of these devices.

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1. Introduction

In the last years an important progress in the development of new inorganic scintillators and better understanding of the energy resolution of

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scintillation detectors has taken place. Cerium-doped orthoaluminates like YAP:Ce [1], LuAP:Ce [2,3] and mixed LuYAP:Ce [4,5] crystals are scintillators with high light yield, fast decay time and high density (with the exception of YAP). For these reasons the Crystal Clear Collaboration [6] decided in the beginning of the year 2000 to start an ambitious program of technology development of LuAP:Ce crystals in collaboration with the Bogoroditsk Techno Chemical Plant in Russia. In our study, we have looked at the possibility to reduce the amount of lutetium in an attempt to simplify the crystal growth and to reduce the production cost of the crystals. One obvious candidate to substitute to lutetium is yttrium, as the scintillation properties of YAP:Ce are well known.

In 2001 and 2002 the pre-production phase of the $Lu_{0.7}Y_{0.3}AP$ crystal took place and the results of the crystals produced at that time have been reported [7,8]. Although being at an early stage of development, the scintillation properties including light yield and in particular energy resolution were very promising.

In this new study, we report the results of a similar study based on a large amount of crystals grown in mass production in the last year. We have investigated the scintillation characteristics of over 200 boules of LuYAP:Ce with a diameter of 25 mm and a length of 150–180 mm. About 50 of them were cut into 10,000 pixels, each $2 \times 2\,mm^2$ $\varnothing$ with 8 or 10 mm length. The results are compared to the results from the pre-production phase.

The pixels are going to be implemented in several small animal ClearPET™ scanners in phoswich geometry together with LSO:Ce. Therefore homogenous scintillation properties, e.g. light yield, energy resolution and decay time, are mandatory.

2. Experiment

We used the Czochralski technique to grow more than 200 cerium-doped LuYAP single crystal boules. The lutetium amount in the melt was fixed to 70%. The cerium concentration in the melt was 0.3%. The main difficulty for the growth of large size and high-quality crystals relies on the fact that due to the very narrow region of the perovskite phase in the phase diagram a very high precision in the stoichiometry of the starting raw material is needed. Strong requirements are set on the precision of the heating system which should be able to control the temperature in any part of the melt in a range smaller than $\pm 3\,^{\circ}C$.

From the mass produced crystals five batches of crystals were delivered until now. The delivery time of the batches, number of produced pixels and dimension of the samples are given in Table 1. From the indicated batches (*) 10 samples were randomly chosen and their scintillation properties were investigated. Note that the length of the studied pixels differ, which impacts the light yield and energy resolution measured in vertical position.

For the light yield measurements, each pixel was wrapped with several layers of Teflon tape to get the highest possible light output and coupled with one of its large faces (horizontal position) to the center of a XP2020Q photomultiplier by means of silicon grease (Rhodorsil silicone pâte 4). In foresight on the later use of the crystals in a PET scanner, energy spectra were measured using a ^{137}Cs source with the small side of the crystal facing the PMT (vertical position). The number of photoelectrons per energy unit (phe/MeV) was measured by comparing the position of the 662 keV full energy peak from the ^{137}Cs source

Table 1
Delivery time, number of pixels and dimensions of the pixels of the studied LuYAP crystals

Batch	Delivery time	# of pixels	Size (mm^3)
Pre-production 1	Feb 2002	14	$2 \times 2 \times 10$
Pre-production 2	March 2002	15	$2 \times 2 \times 10$
Pre-production 3	May 2002	16	$2 \times 2 \times 10$
Batch P1	Feb 2003	1500*	$2 \times 2 \times 8$
Batch P2	April 2003	3100	$2 \times 2 \times 10$
		100*	$2 \times 2 \times 8$
Batch P3	May 2003	2300*	$2 \times 2 \times 8$
		1900	$2 \times 2 \times 10$
Batch P3+	June 2003	101*	$2 \times 2 \times 10$
Batch P4	Aug 2003	210*	$2 \times 2 \times 10$

with that of the single photoelectron peak. For calculating the light yield of the scintillator (ph/MeV), the integral quantum efficiency QE = 25% was used (LuYAP). The natural background spectrum from the crystal was not subtracted.

The scintillation time profiles under γ-excitation from a ^{22}Na source were measured using the single photon counting method originated by Bollinger and Thomas [9] with XP2020Q photomultipliers to detect single photons.

Absorption spectra from the near infrared up to the ultraviolet (UV) domain were measured using a Lambda 900 Perkin Elmer UV/VIS/NIR spectrometer.

Transmission measurements were performed in a wavelength region ranging from 250 to 600 nm using the CERN made spectrophotometer. The transmission was measured in transversal and longitudinal direction respective to the crystal.

3. Results

3.1. Density

The crystals grown in the pre-production exhibited a lower density than expected. A composition of 70% Lu and 30% Y corresponds to a density equal to 7.44 g/cm^3. Unfortunately a lower density equal to around 6.50 ± 0.09 g/cm^3 was found. In the beginning several successive crystallizations were necessary due to miscellaneous problems (bad seeding, crucible leaks, etc.). Each time a strong evaporation of oxides occurred, which disturbed the necessary balance between Lu_2O_3 and Y_2O_3. In addition cation vacancies were produced in the lattice, which tend to decrease the density. The result of this is a shift of composition of the crystal components in the melt leading to a decrease in density. This problem has been understood and was corrected during the prototype production. The improvement in densities over all studied batches is illustrated in Fig. 1. Note that the latest batch of delivered pixels P4 only consists of samples with around 7.17 g/cm^3 density.

There seems to be an interesting correlation between the light yield and the density as shown in

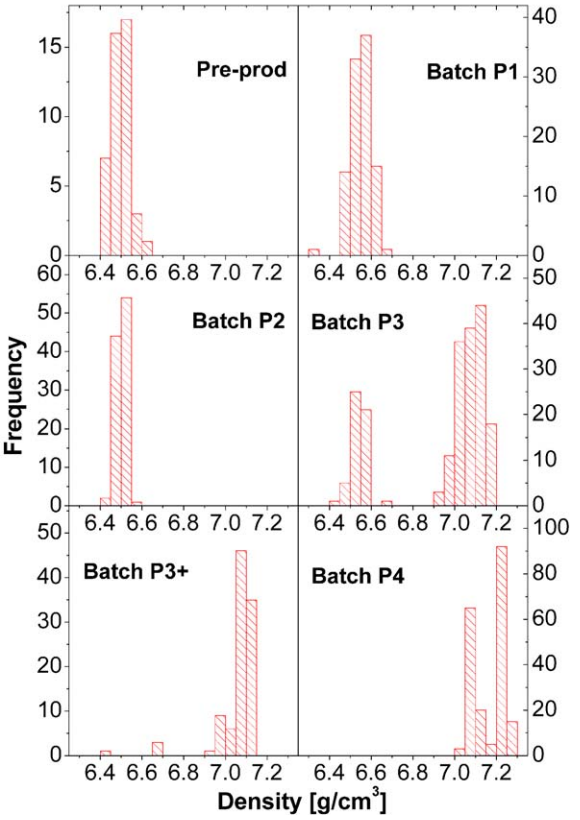

Fig. 1. Summary of the measured density for all the studied LuYAP samples. Note that there is an improvement in the density from batch P1 to batch P4.

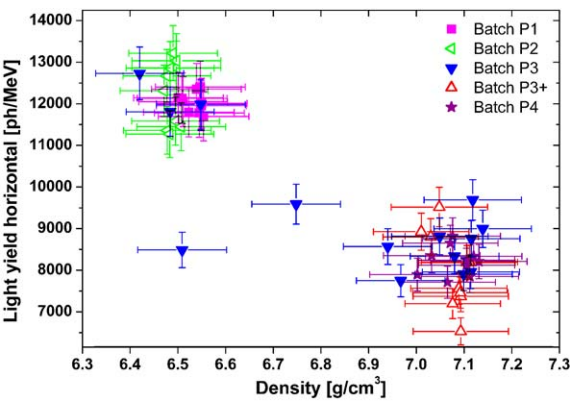

Fig. 2. Correlation between the light yield in horizontal position and the measured density of the samples.

Fig. 2. The higher the light yield, the lower the density. The reason for this correlation has to be clarified. Nevertheless, in the latest delivery there are a certain number of crystals with high density and high light yield.

3.2. UV and visible spectroscopy

The absorption spectrum contains a sequence of five bands in the ultraviolet region. These bands are assigned to Ce^{3+} 4f–5d bands. On the low-wavelength side, an absorption tail can be seen in the spectrum, which does not originate from Ce^{3+} 4f–5d transitions. This additional absorption tail is more enhanced for crystals produced in mass production than for the pre-produced pixels as shown in Fig. 3. The presence of this additional tail leads to a reduction in light yield, especially when measuring in vertical position, and thus also to a deterioration of the energy resolution.

A graph showing the transmission curves for LuYAP crystals grown in pre-production and mass production is given in Fig. 4. The transmission measurements confirmed the results from the absorption. All the crystals produced in mass production (batches P1 to P3+) exhibited a higher cut-off wavelength und thus a more intense self-absorption. The transmission at 365 nm for the mass-produced crystals is only 60% compared to

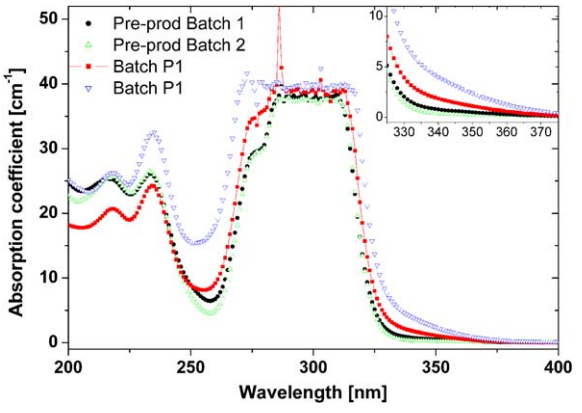

Fig. 3. Comparison between the absorption spectra measured for selected samples from the pre-production and the mass production phase (batch P1). The inset shows the enlarged region from 325 to 375 nm.

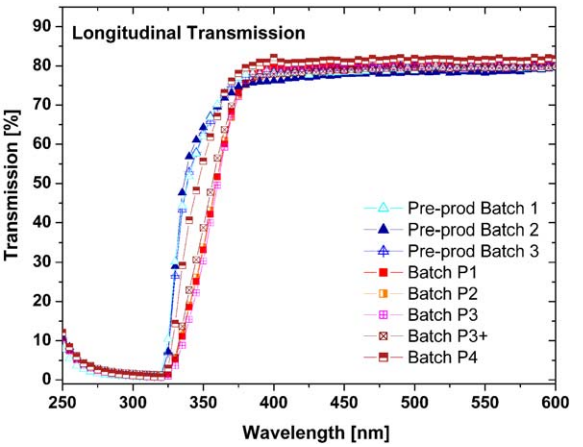

Fig. 4. Comparison of transmission spectra for selected samples from all the studied batches. Note the shift in the cut-off wavelength between the pre-produced and the mass produced pixels.

73% for the pre-produced samples and for batch P4. This has a strong influence on the light yield measured in vertical position. The additional absorption band is reduced for the latest batch of crystals P4. For these crystals the transmission curve is in between the curves measured for the pre-produced samples and for batches P1 to P3+.

3.3. Light output

For the mass production, certain crystal growth parameters were changed to produce larger ingots. Thus a change in the scintillation properties from the pre-production to the mass produced pixels is expected. Fig. 5 shows the evolution of the light yield (ph/MeV) of all studied crystals in horizontal and vertical position for the three pre-production batches and the crystals produced in the mass production phase.

Note that the first 3 batches of the mass production (batches P1–P3) contain pixels with 8 mm length. For pixels with the same density (compare pre-production to batches P1 and P2) the light yield (horizontal) increased from 7500 to 12,300 ph/MeV. This corresponds to an increase of 64%. From batches P2 to P3 the light yield decreases steadily but the density increases as

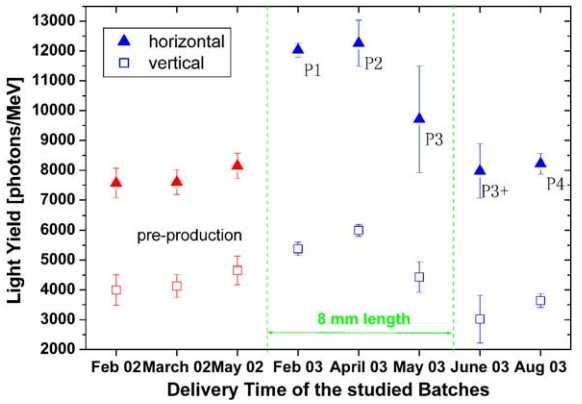

Fig. 5. Evolution of the light yield in vertical (square) and horizontal (triangle) position of the studied LuYAP pixel over the time of production. (The bars indicate the standard deviation.)

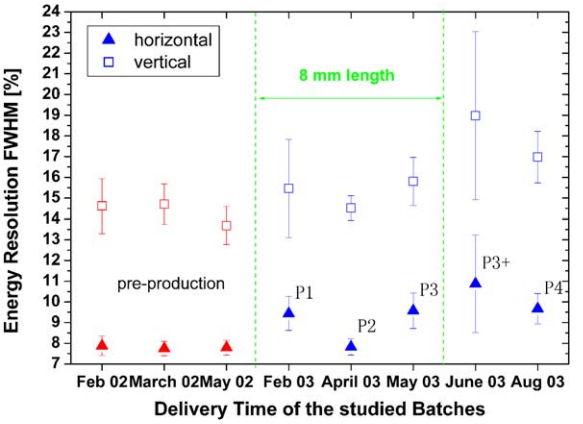

Fig. 6. Evolution in the energy resolution (FWHM for Cs-137) measured in vertical (square) and horizontal (triangle) position of the studied LuYAP samples. (The bars indicate the standard deviation.)

mentioned in Section 3.1. In vertical position, the higher light yield values found for batches P1–P3 reflect the reduced crystal length (8 mm), compared to the other batches. The light yield ratio between vertical and horizontal position, measured for the 10 mm samples, varied from 57% (pre-production) to 33% (batch P3+). The reason for this lower ratio for the batches produced in mass production is the additional absorption band at the wavelengths of the emission (see Fig. 4).

The last batch of delivered pixels P4 exhibits only crystals with high density (7.1 g/cm^3) and the scintillation properties are comparable to the pre-production phase. The additional absorption tail was reduced and so the light yield in vertical position has improved compared to batch P3+. Note that for P4 the spread in light yield, given as the standard deviation over the 10 selected samples, is only 4.2% in horizontal and 6.3% in vertical position. This clearly shows that over the time of development, crystals of good quality and homogenous scintillation properties were achieved.

3.4. Energy resolution

The energy resolution of the 662 keV peak of ^{137}Cs was found to be around 7.75% in horizontal geometry and around 14% in vertical position for all pre-produced crystals. The mass produced pixels exhibited an energy resolution of around 8–10% in horizontal and 14–16% (8 mm pixels) in vertical position. Fig. 6 gives the average value (plus standard deviation) for the energy resolution from the studied batches. The low light yield (vertical) found for batch P3+ (10 mm length) results in an inferior energy resolution. As noted before, for the latest batch P4 a better energy resolution (9.67 ± 0.73)% was found due to the reduction of the additional absorption tail.

3.5. Light pulse shape

The decay time constants were derived by fitting the measured curve with a sum of two exponential functions. Both time constants were obtained from the best fit of the total light pulse shape. For LuYAP the fast component has a decay time constant of around 25 ± 1 ns and is followed by a slower component, with $\sim 250 \pm 25$ ns decay time constant. A slight decrease for both decay time components can be found over the studied batches. The intensity of the fast component decreased from 56% to 40%. One reason for the more intense slow component might be that an absorption and reemission occurs. The evolution of the decay time components and relative

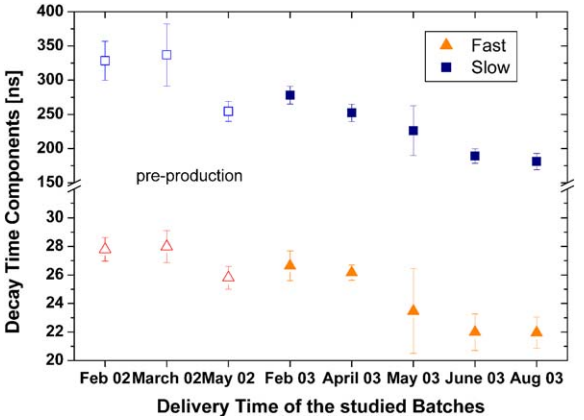

Fig. 7. Decay time components of the studied LuYAP samples. (The bars indicate the standard deviation.)

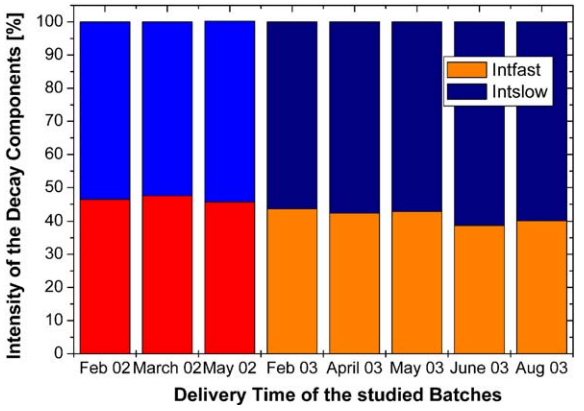

Fig. 8. Summary of the intensity of the decay time components for the LuYAP samples.

intensities over the studied batches from the pre-production and mass production is illustrated in Figs. 7 and 8.

4. Discussion and conclusion

Significant progress and a large effort from the Crystal Clear Collaboration has been made in the development of Lu(Y)AP, which has led to the stabilization of a production line of $Lu_{0.7}Y_{0.3}AP$ crystals in large quantities. The consistency of the scintillation properties has improved in the last 2 years of R&D and the problem with the density of the crystals produced in the pre-production phase is clarified. In the latest batch the samples have a density of 7.1 g/cm^3, a light yield of 8200 ph/MeV and a energy resolution of around 9.6% FWHM. The spread in light yield and energy resolution is very small (standard deviation of 4.2% and 7.4%, respectively) thus the scintillation properties are very homogenous. The studied crystals are going to be implemented in combination with LSO (phoswich) in several small animal PET scanners presently under construction by the collaboration. Further work is going on along three directions:

1. The suppression of the additional absorption band to increase the light yield measured in vertical position. The first success in the reduction of the absorption tail is reflected in the reduced cut-off wavelength of batch P4.
2. The increase of the lutetium content in the melt leading to crystals with even higher stopping power.
3. The increase of the diameter of the ingots.

We are confident to reach these aims in the next years of research and development.

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