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W.W. Moses and S.E. Derenzo

Life Sciences Division
Lawrence Berkeley Laboratory
University of California
Berkeley, California 94720

A. Fyodorov and M. Korzhik

Institute for Nuclear Problems
Minsk, Republic of Belarus

A. Gektin and B. Minkov

Institute for Single Crystals
Kharkov, The Ukraine

and

V. Aslanov

SCITEC RI&NC
Minsk, Republic of Belarus

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$LuAlO_3$:Ce – A HIGH DENSITY, HIGH SPEED SCINTILLATOR FOR GAMMA DETECTION*

W. W. Moses[§], S. E. Derenzo[§], A. Fyodorov[†], M. Korzhik[†], A. Gektin[◊], B. Minkov[◊], and V. Aslanov[¶],
[§]Lawrence Berkeley Laboratory, University of California, Berkeley, CA 94720,
[†]Institute for Nuclear Problems, Minsk, Republic of Belarus,
[◊]Institute for Single Crystals, Kharkov, The Ukraine,
and [¶]SCITEC RI&NC, Minsk, Republic of Belarus

Abstract

We present measurements of the scintillation properties of cerium doped lutetium aluminum perovskite, $LuAlO_3$:Ce, a new dense (ρ=8.34 g/cm^3) inorganic scintillator. This material has a 511 keV interaction length and photoelectric fraction of 1.1 cm and 32% respectively, which are well suited to gamma ray detection. In powdered form with 0.5% cerium concentration, the scintillation light output is estimated to be 9,600 photons/MeV of deposited energy, the emission spectrum is a single peak centered at 390 nm, and the fluorescence lifetime is described by the sum of 3 exponential terms, with 60% of the light being emitted with a 11 ns decay time, 26% with a 28 ns decay time, and 13% with a 835 ns decay time. Single crystals contaminated with ≈10% lutetium aluminum garnet ($Lu_3Al_5O_{12}$) have significantly altered scintillation properties. The light output is 26,000 photons/MeV (3.2 times that of BGO), but the decay time increases significantly (1% of the light is emitted with a 10 ns decay time, 15% with a 245 ns decay time, and 85% with a 2010 ns decay time) and the emission spectrum is dominated by a peak centered at 315 nm with a secondary peak centered at 500 nm. The short decay lifetime, high density, and reasonable light output of $LuAlO_3$:Ce (the perovskite phase) suggest that it is useful for applications where high counting rates, good stopping power, good energy resolution, and fast timing are important. However, it is necessary to grow single crystals that are uncontaminated by the garnet phase to realize these properties.

1. INTRODUCTION

A number of cerium doped lutetium oxide scintillators have recently been developed, including LSO (Lu_2SiO_5:Ce) [1], LOP ($LuPO_4$:Ce) [2], and LuAG ($Lu_3Al_5O_{12}$:Ce) [3, 4]. These materials tend to exhibit the three qualities most desired for gamma detection scintillators: high density and effective atomic number (thus the ability to absorb and detect gamma rays in a relatively short distance), high scintillation light yield (thus the ability to accurately measure the gamma ray energy), and short decay time (thus the ability to operate at high counting rates and to provide accurate timing pulses).

In this work we continue the examination of cerium doped lutetium oxide scintillators by evaluating the scintillation properties of cerium doped lutetium aluminum perovskite $LuAlO_3$, the lutetium analog of YAP, a scintillator known for its high light output and short decay time, albeit relatively low density and atomic number [5]. By analogy, we refer to this material as LuAP, noting that lanthanum aluminum perovskite is frequently referred to as LAP. LuAP has previously been suggested as a scintillation material [6] and some of its scintillation properties have previously been reported [7]. Another group also reports on this material's scintillation properties in this issue [8].

The material properties of LuAP make it quite attractive as a gamma detection scintillator. Its density is 8.34 g/cc — higher than that of LSO (7.1 g/cc), LuAG (6.9 g/cc), or LOP (6.2 g/cc). This gives it an attenuation length and photoelectric interaction for 511 keV gamma rays of 1.1 cm and 32% respectively. It is not hygroscopic, is relatively hard (estimated hardness is 8.5 Mho) and free of cleavage planes, so is relatively easy to cut and polish. Its melting point of 1960° C is similar to that of LOP (1947° C) and significantly lower than that of LSO (2150° C), and is sufficiently low that it can be grown in molybdenum crucibles rather than the more expensive iridium crucibles.

2. MATERIALS

Samples were prepared in both powder and single crystal form. All samples were formed from the melt in molybdenum crucibles from starting materials of unknown purity. The cerium fraction in the starting material was 0.5%–2.0% (quoted as a mole fraction of the lutetium concentration), but the segregation coefficient is low (approximately 0.4) due to the large size mismatch between the cerium and lutetium ions, so the fraction of cerium in the resulting samples was 0.2%–0.8%. Samples were analyzed by x-ray diffraction to verify the composition of the material, and as some samples contained material in the garnet phase ($Lu_3Al_5O_{12}$), x-ray diffraction was also used to estimate the perovskite / garnet ratio.

3. MEASUREMENTS WITH LuAP POWDER

The most crystallographically pure sample is available only as a powder. This sample is colorless and is estimated to contain less than 2% garnet phase. Although a single crystal sample of this material is not available, accurate measurement of its decay time and emission spectrum and an estimate of its luminosity are made using pulsed x-ray excitation [9].

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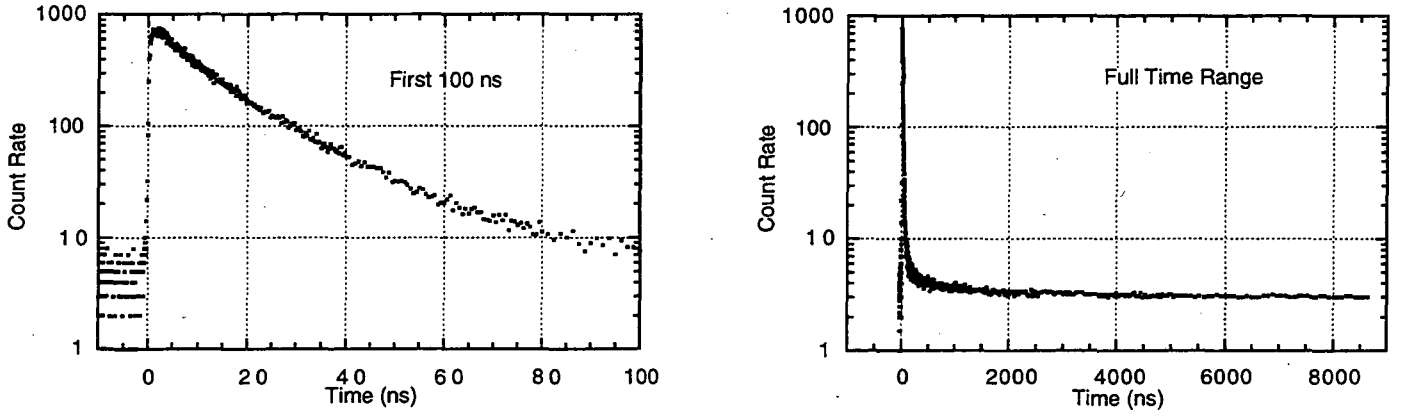

Figure 1: Decay time spectrum of LuAP powder excited by pulsed x-rays. The plot on the left shows the first 100 ns of decay. The plot on the right shows the full time range over which data was collected, showing that there is no long (>1 μs) component.

The scintillation decay time is measured with the delayed coincidence method [10]. A powdered sample is placed in a quartz cuvette (5 mm outer diameter, 1 mm wall thickness), irradiated with a brief (120 ps fwhm, 100 khz repetition rate) pulse of x-rays, and the resulting fluorescent emissions detected with a sapphire windowed microchannel plate photomultiplier tube. A time to digital converter (TDC) measures the time between the x-ray pulse and the detected scintillation photons in 78 ps bins, and the result read into a computer. The instrumental response (*i.e.* the x-ray pulse width convolved with the impulse response of the time measurement system) was measured to be 410 ps fwhm [11]. A plot of the acquired data is shown in Figure 1.

The data was fit to a constant background plus the sum of three exponential decay components. This fit yields decay times of 11 ns (60% of the emitted light), 28 ns (26% of the light) and 834ns (13% of the light). A "long" component was searched for by adding a fourth exponential decay component to the mathematical model and refitting, but this did not improve the fit to the data.

The emission spectrum, shown in Figure 2, is collected by exciting the sample with x-rays, passing the scintillation light through a monochromator, and counting single photons with a cooled photomultiplier tube. The wavelength dependence (200 – 600 nm) of the quantum efficiency for this monochromator / photomultiplier tube combination was determined using a calibrated light source (NIST traceable) and used to correct the data. The emission is centered at 390 nm, and drops to less than 10% of its peak value at 340 and 450 nm.

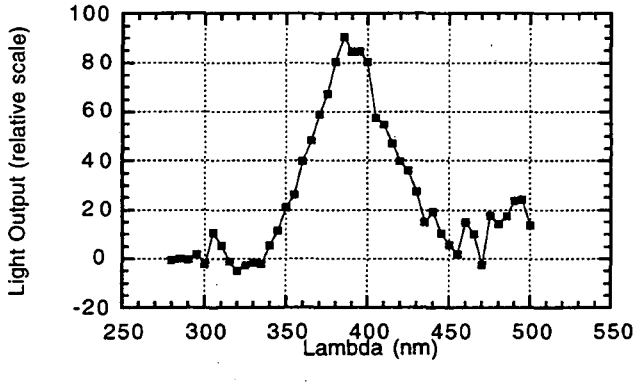

Figure 2: Emission spectrum (corrected for the wavelength dependence of the monochromator and photomultiplier tube quantum efficiency) of powdered $LuAlO_3$:Ce.

To estimate the total light output, similarly prepared powdered samples of LuAP and YAP were exposed to a ^{57}Co source and the resulting fluorescent emissions counted with a photomultiplier tube. As the LuAP count rate is 60% that of the YAP count rate and the absolute luminosity for YAP is 16,000 photons per MeV of deposited energy [5], we estimate the luminosity of LuAP to be 9,600 photons/MeV.

4. Measurements with Crystalline Samples

Encouraged by the scintillation properties of LuAP powder, we attempted to grow large single crystals of this material. Two major obstacles lie in the way of successful crystal growth: the tendency of the material to crack while cooling and the fact that there is a garnet phase of lutetium aluminum oxide that co-crystallizes with the desired perovskite phase. The first obstacle is overcome by adding a gadolinium co-dopant to stabilize the crystal lattice. The second obstacle has not yet been overcome by this group (although others report LuAP crystals 2 cm in diameter and 5 cm long [8]) and so all crystalline samples of LuAP measured contain 5%–10% LuAG. The garnet has a pronounced green color with an intensity that varies spatially within the crystals, suggesting non-uniform garnet concentration. Crystals have been grown in three basic geometries: "flake" (0.15 mm thick with irregularly shaped boundaries with 3–5 mm typical dimension), "plate" (1 mm thick quasi-rectangular solids with 5–10 mm typical dimensions) and "solid" (quasi-rectangular solids with 3–7 mm typical dimensions).

The decay time spectra of all crystals are measured with the apparatus and method described in Section 2, and the spectra (and fits) for four of the samples are shown in Figure 3. The decay spectra are virtually identical for all crystalline samples and is significantly different for these crystalline samples than for the powdered sample. The fast (11 ns) component that previously dominated the spectrum is virtually non-existent and the spectrum is instead dominated by a 2 μs component.

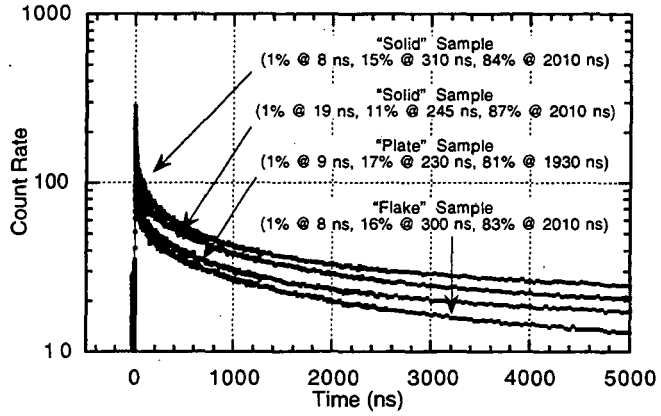

Figure 3: Decay time spectra for four LuAP crystals excited with pulsed x-rays.

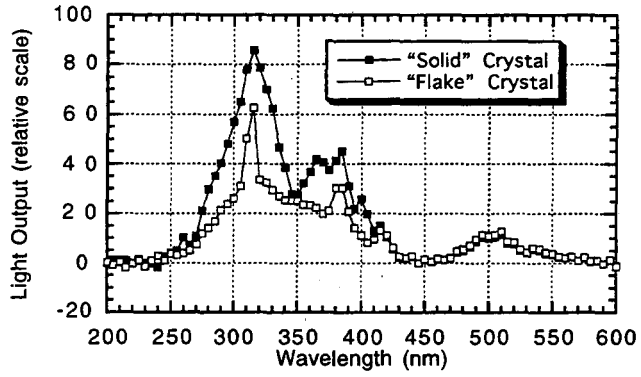

Figure 4: Emission spectrum (corrected for the wavelength dependence of the monochromator and photomultiplier tube quantum efficiency) of two LuAP crystals.

The emission spectra of two crystals (one "plate" and one "solid") are measured with the same apparatus and method described in Section 2 and the spectra shown in Figure 4. Due to the range of emission wavelengths, each spectrum is a composite of three data sets: one with a grating blazed for 300 nm emissions (data range 200–400 nm), one with a grating blazed for 500 nm (350–450 nm), and one with the 500 nm blaze grating and a 380 nm cutoff filter (400–600 nm). The three data sets are corrected for the wavelength dependence of the detection apparatus quantum efficiency, and the wavelength ranges overlap to provide a consistency check. The emission spectra observed in the crystals is significantly different than that of the powder and differ quantitatively between the two crystals. Their emission spectrum is dominated by a broad peak centered near 315 nm, additional emissions between 350 and 390 nm, and a small peak centered near 500 nm, rather than a single peak centered at 390 nm.

The scintillation light yield is measured for all crystals by polishing their surfaces, wrapping them with Teflon tape to provide a reflective coating, coupling them to a quartz windowed Hamamatsu H-3177 photomultiplier tube (spectral range 200–600 nm), and exciting with 511 keV photons. The resulting output is amplified with a 5 μs shaping time and digitized. The position of the photopeak is recorded for each sample, as well as for a similarly prepared 3 mm cube of BGO

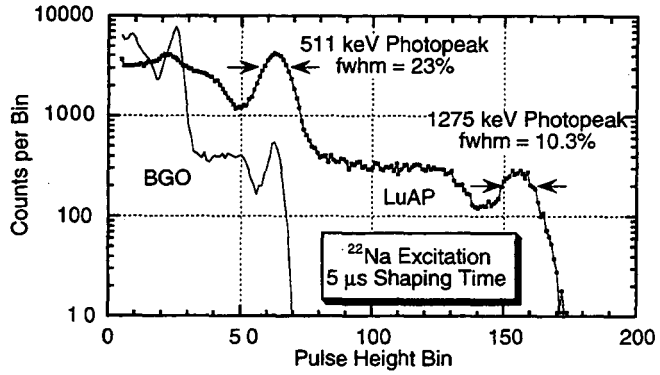

Figure 5: Pulse height spectra for LuAP and BGO crystals excited with 511 and 1275 keV gamma rays (5 μs shaping time).

(bismuth germanate or $Bi_4Ge_3O_{12}$). Photopeaks are observed for all samples, with the pulse heights for the LuAP/LuAG crystals ranging from 1.3 times the light output of BGO (for one of the "plates") to 3.2 times the light output of BGO (for one of the "flakes"). Using the value of 8,200 photons/MeV for the light output of BGO [12], this corresponds to light output for these LuAP / LuAG crystals ranging from 10,300 photons/MeV to 26,000 photons/MeV.

A 3x5x7 mm^3 "solid" crystal is exposed to the 511 keV and 1275 keV gamma rays from ^{22}Na, and the resulting pulse height spectrum shown in Figure 5 along with a similar spectrum obtained with the BGO sample. The position of the photopeaks indicate that this sample has 2.5 times the light output of BGO (or 20,500 photons/MeV), and the widths of the 511 and 1275 keV photopeaks are 23% and 10% fwhm respectively. This resolution is representative for the crystals measured, and is significantly worse than expected based on photon counting statistics. However, the optical quality of the crystal is far from perfect (a portion of the crystal has significant green coloration and there is internal cloudiness in another region), and so the light collection efficiency is likely to be spatially dependent, thus degrading the photopeak width.

5. Measurements of LuAP / LuAG Mixtures

All three of the major scintillation decay characteristics – the decay time, emission spectrum, and light output – of LuAP are significantly different in the crystal samples than they are in the powdered sample. The difference can partially be ascribed to the increased abundance of the garnet phase in the crystalline samples, as cerium doped LuAG is also known to scintillate [3, 4]. To determine the role that LuAG plays, we have done some further examination of powders of cerium doped LuAG and 90% LuAP contaminated with 10% LuAG.

The decay time spectra and fits for LuAP, LuAG, and 90% LuAP / 10% LuAG are acquired with the apparatus and methods described in Section 2, and are displayed in Figure 6. The major conclusion to be drawn from these measurements is that the decay time of the 90% LuAP / 10% LuAG powder (and the crystal samples measured in Section 3) is virtually identical to that of the LuAG powder, indicating that scintillation proper-

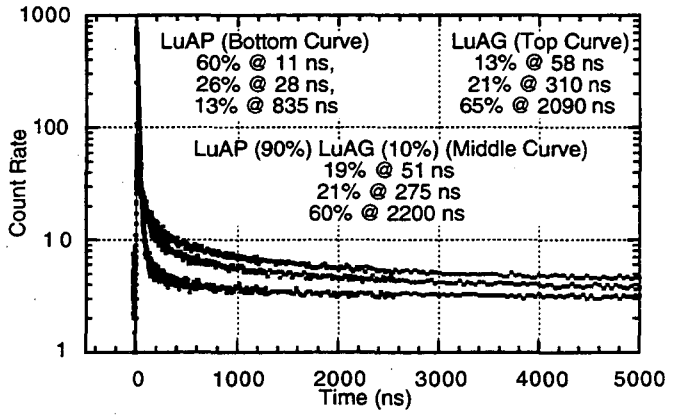

Figure 6: X-ray excited decay time spectra of cerium doped LuAP, LuAG, and 90% LuAP contaminated with 10% LuAG.

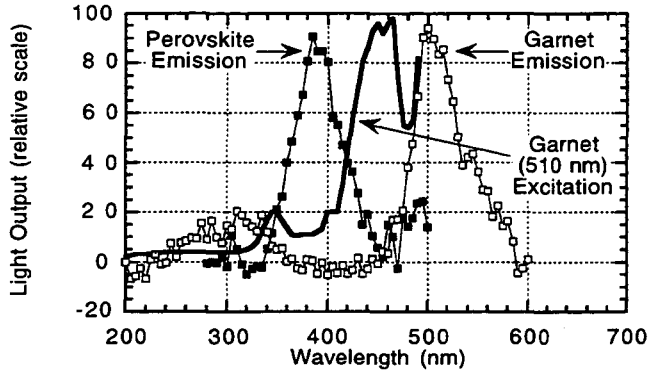

Figure 7: Emission spectra of LuAP and LuAG (corrected for the wavelength of the monochromator and photomultiplier tube quantum efficiency), as well as the excitation spectrum of the 500 nm emission line of LuAG.

ties of the mixed phase samples are dominated by the garnet phase, even when it is present in only 10% concentration.

The x-ray excited emission spectrum of LuAG powder is measured with the method and apparatus in Section 3 (*i.e.* 3 configurations covering 3 spectral ranges), and shown in Figure 7. It is significantly different than the emission spectrum of LuAP powder (also shown in Figure 7) and the crystal spectra shown in Figure 4, with the dominant peak centered at 500 nm and lesser emissions near 300 nm. Figure 7 also shows the excitation spectrum of the 500 nm emission line of the powdered LuAG sample (*i.e.* the intensity of the 500 nm emissions as a function of optical excitation wavelength).

There is significant overlap between the emission spectrum of the perovskite and the excitation spectrum of the garnet, implying that perovskite emissions will be absorbed and re-emitted by the garnet. This further implies that the decay kinetics for the mixed compounds (the 90% LuAP / 10% LuAG powder and the crystals) will be dominated by the slower of the two emissions (the garnet, in this case), which is observed. However, it also suggests that the emission spectrum for these materials would also be identical to the garnet emission, which is not observed. This is particularly puzzling as the dominant emissions in the crystal samples are

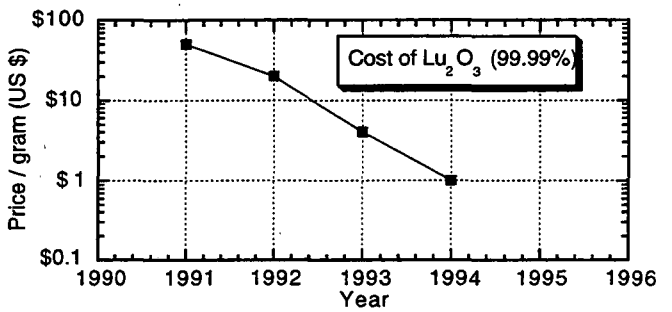

Figure 8: Cost of 99.99% pure lutetium oxide versus time.

near 315 nm, which is a shorter wavelength (and higher energy) than either of the primary LuAP or LuAG emissions!

It is possible that the gadolinium dopant added to prevent cracking of the crystals may participate in the scintillation process — the narrow line at 315 nm observed in the emission spectrum of one of the crystal samples in Figure 4 is characteristic of forbidden 4f-4f' transitions in gadolinium. However, significant broad band emissions are also observed in this region, and these are not characteristic of gadolinium.

There is hope that the peculiar scintillation properties of these mixed perovskite / garnet phase cerium doped lutetium aluminates will become of academic interest only. Another research group reports in this issue that a large (2 cm diameter by 5 cm long) boule of LuAP has been grown via the Czochralski method that is relatively free of garnet contamination [8]. The scintillation decay time and emission spectrum of this crystal agree with our measurements of the powdered LuAP sample in addition to the high light output (>26,000 photons/MeV) observed in the mixed phase crystals.

6. Cost of Lutetium

While there is concern that lutetium based scintillators are impractically expensive due to the high cost of lutetium, we believe that there is potential for lutetium to become inexpensive. Figure 8 plots the price of 99.99% pure Lu_2O_3 for the past few years. While the initial cost is quite high ($50/g), there is a steady reduction in cost with time mainly due to supplies in China and the former Soviet Union becoming available. While it is impossible to extrapolate this curve to the "ultimate" cost, recent trends are quite encouraging.

One common hypothesis is that lutetium is expensive due to its rarity, and lutetium is frequently described as the rarest of the rare earth elements. It is actually the second rarest (thulium is slightly less abundant), but it is not particularly rare. In fact, its elemental abundance in the earth's crust is the same as iodine, and it is more abundant than cadmium, mercury, and bismuth combined [13]. Raw materials containing reasonably high concentrations of lutetium are available, especially in the tailings of mozanite ores (which contain many rare earth elements) that have been processed to extract some of the other elements. Thus, we do not see any fundamental reason for lutetium to be expensive, and hypothesize that the previous high price was largely due to lack of industrial demand.

7. CONCLUSIONS

Lutetium aluminum perovskite doped with 0.04% cerium has the potential to become an outstanding scintillator for gamma ray detection due to its high density (8.34 g/cm^3), short decay time (11 ns and 28 ns main components), and high light output (>26,000 photons/MeV). In addition, its emission wavelength, centered at 390 nm, is convenient for readout with glass–windowed photomultiplier tubes and its 1960° C melting point is low enough that relatively inexpensive crucibles can be used for crystal growth. Care must be taken during growth to avoid contamination by the garnet phase, as this lengthens the primary decay time to 2 μs and shifts the primary emission peak to 315 nm, but large, clear crystals have been grown by the Czochralski method, indicating that contamination free growth is possible. Finally, we believe that the cost of lutetium, which historically has been high, is dropping rapidly and that lutetium based scintillators need not be expensive due to the cost of the raw material.

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