



# Effects of Ca<sup>2+</sup> co-doping on the scintillation properties of LSO:Ce

M.A. Spurrier<sup>1</sup>, C. L. Melcher<sup>1</sup>, P. Szupryczynski<sup>1,2</sup>, K. Yang<sup>1</sup>, A. A. Carey<sup>2</sup>,

<sup>1</sup>Scintillation Materials Research Center, University of Tennessee, Knoxville, Tennessee, USA

<sup>2</sup>Siemens Medical Solutions Molecular Imaging, Knoxville, Tennessee, USA

**Abstract** Lu<sub>2</sub>SiO<sub>5</sub>:Ce (LSO) is a widely used scintillator in positron emission tomography, with well-known scintillation properties including light yield of ~30,900 photons/MeV, an emission peak near 420 nm, and a decay time of ~43 ns. We have found that both the light output and decay time may be improved by a combination of optimized crystal growth atmosphere and co-doping with divalent cations such as Ca. Scintillation light output of ~38,800 photons/MeV has been achieved, as well as scintillation decay time as short as 31 ns with no long components. Possible explanations of the underlying mechanism are being explored.

## Introduction



Advances in the quality and performance of LSO:Ce have been made since its introduction in the early 1990s, with significant improvement in the scintillation light output though little change in decay time. Recent work has focused on methods to further increase average light yield while shortening decay time.

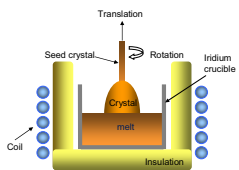


Various researchers have previously investigated the effect of additional dopants on both the crystal growth behavior and the scintillation properties of a number of scintillators, such as PbWO<sub>4</sub> and LuAlO<sub>3</sub>. It is known that doping these materials with aliovalent ions can reduce the concentration of intrinsic point defects.

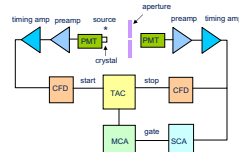


In this work we report the results of doping LSO:Ce crystals with Ca<sup>2+</sup> ions with concentrations in the initial starting materials in the range of 0.1 – 0.4 at%. In contrast to work reported by others who used lower Ca concentrations, we observed significant changes in light output and particularly decay time.

## Procedures



The Czochralski technique was used to grow LSO:Ce and LSO:Ce:Ca from 60 mm diameter x 60 mm tall iridium crucibles that were inductively heated by an 8 kHz power supply. The flowing atmosphere was ~ 0%, 0.7%, and 0.15% oxygen in bulk nitrogen, monitored continuously by a residual gas analyzer. The purity of the starting materials was at least 99.99%. The boules were 32 mm in diameter and ~ 100 mm long.



Scintillation decay times were measured by the time-correlated single photon technique originated by Bollinger and Thomas.

Absolute scintillation light output was measured with a Hamamatsu R2059 photomultiplier tube. Crystals were coupled to the tube with Dow Corning Q2-3067 optical couplant and covered with Tetratex TX3104 PTFE membrane to enhance the light collection efficiency. A 1.0 μCi <sup>22</sup>Na excitation source was used to supply 511 keV gamma rays, and the source was placed directly on top of the Tetratex membrane. The integral quantum efficiency was 24.1% for the Hamamatsu R2059 PMT with respect to the LSO emission spectrum. The light output measurement was reproducible to within +/-3%.

## Results

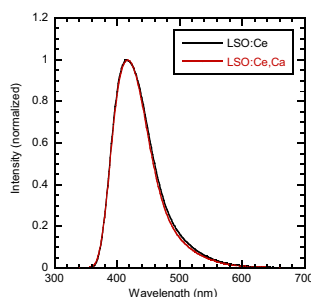


Fig. 1. Radioluminescence emission spectra of LSO:Ce and LSO:Ce:Ca crystals excited with 30 keV x-rays.

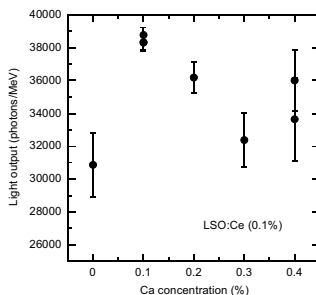


Fig. 2. Light output as a function of the Ca concentration in the initial starting materials

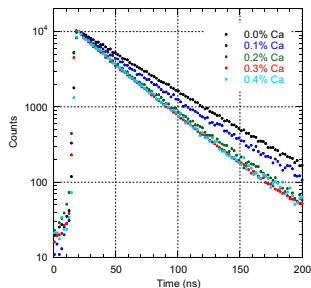


Fig. 3. Scintillation decay of LSO:Ce crystals with 0.1, 0.2, 0.3, and 0.4% Ca doping. All samples had single exponential decays with no long components.

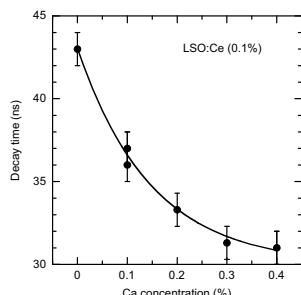


Fig. 4. Decay time as a function of Ca concentration in the melt.

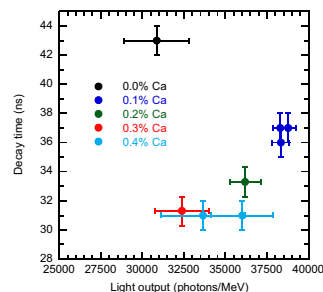


Fig. 5. Decay time vs. light output for crystals doped with 0.1% Ca.

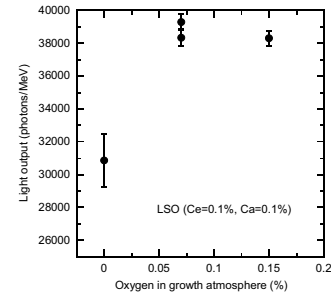


Fig. 6. Light output for crystals grown with various amounts of oxygen in the growth atmosphere

Ca concentration (%)	Light output (photons/MeV)	Decay time (ns)
0.0	30900	43.0
0.1	38800	36.7
0.2	36200	33.3
0.3	32400	31.3
0.4	34800	31.0

Light output and decay time values are the average of multiple samples

## Discussion

We have found that co-doping LSO:Ce with relatively high concentrations of Ca<sup>2+</sup> can simultaneously improve light yield and shorten decay time, in contrast to the results of previous studies of lower doping levels. The relationship between scintillation decay time and Ca concentration is sufficiently well-defined that for the first time it is possible to tune the decay time of these crystals as they are grown, opening up new possibilities for cost-effective manufacture of phoswich and time-of-flight detectors.

While it is clear that co-doping with Ca<sup>2+</sup> can be used to significantly improve LSO:Ce scintillation properties, further work is needed to unambiguously identify the role of Ca<sup>2+</sup> in the scintillation process.

With respect to decay time, Suzuki et al. found that the two Ce sites in LSO:Ce have individual decay times of 32 and 54 ns, and it is perhaps noteworthy that the fastest Ca doped crystals have decay times comparable to the faster of the two Ce sites. However, it is not obvious why Ca would affect the relative populations of the two Ce sites. With respect to light output, it is possible that Ca<sup>2+</sup> compensates for oxygen vacancies that would otherwise diminish light output by trapping electrons in competition with Ce. This possibility is supported by the importance of an oxygen-containing growth atmosphere. To fully explain our results, Ca would need to perform both of the above functions. A further possibility is that the presence of Ca suppresses an as yet unidentified trapping center, although unless Ca interacts preferentially with only one of the two cerium sites such a phenomenon would seem to primarily pertain to increased light output rather than faster decay time.