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The effect of co-doping on the growth stability and scintillation properties of LSO:Ce

M.A. Spurrier[1], P. Szupryczynski[1,2], H. Rothfuss[1,2], K. Yang[1], A.A. Carey[2], C. L. Melcher[1],
[1]Scintillation Materials Research Center, University of Tennessee, Knoxville, Tennessee, USA
[2]Siemens Medical Solutions Molecular Imaging, Knoxville, Tennessee, USA

Abstract Lutetium oxyorthosilicate (LSO) is a well-known scintillator that is widely used for gamma-ray detection in Positron Emission Tomography (PET) as well as in other applications. LSO is typically doped with 0.05 – 0.5% Ce while controlling other impurities at low levels, but recent research has begun to explore the manner in which various co-dopants may influence scintillation properties. We have found that some co-dopants, particularly Ca, have a desirable impact on scintillation, leading to improvements in both light yield and decay time that are related to co-dopant concentration. However, it has been observed that in concentrations high enough to optimize scintillation properties some of these co-dopants can have a pronounced negative effect on the growth stability in Czochralski growth systems. We have observed acentric growth shortly after reaching full diameter despite no obvious change in thermal gradients or convective flow. Visual observations of the liquid meniscus suggest that Ca co-doping significantly reduces surface tension; one possible explanation is that the resulting enhanced Marangoni flow is responsible for the unstable growth behavior. Fortunately, we have found that an additional co-dopant can be used to restore adequate surface tension and thus stabilize growth with no negative impact on the scintillation properties of the crystal. To date, the most effective co-dopant for this purpose is Zn, when introduced in concentrations greater than that of Ce and Ca.

Introduction

The development of cerium doped Lu_2SiO_5 (LSO) in the early 1990s represented a significant advance in inorganic scintillators for medical imaging. With its 7.4 g/cm^3 density, high light yield, and fast (~43ns) decay time, LSO is widely regarded as the best material available for positron emission tomography. LSO went into large-scale commercial production in the late 1990s; since that time there has been a significant effort by the authors and others to advance the state of the art of LSO growth.

Considerable work has been done in recent years by a number of researchers on the use of co-doping to improve the scintillation properties or growth of various inorganic scintillators, including doping of gallium garnets with divalent elements in order to suppress spiral growth, or with tetravalent dopants to decrease absorption loss. $Y_3Al_5O_{12}$:Ce has been doped with Ca^{2+} to control oxygen vacancies. Both divalent and tetravalent dopants have been used in the growth of $LuAlO_3$:Ce. LSO:Ce has been doped with 0.02% Ca^{2+} or Mg^{2+} by Zavartsev et al, who reported some improvement in light yield, though no change in decay time, relative to LSO:Ce with no co-doping.

Initial results of co-doping LSO:Ce crystals with Ca^{2+} in the range of 0.1 – 0.4% have been reported previously. These doping levels gave significant changes in scintillation properties, both in improved light yield and faster decay time. Here we present work showing the destabilizing effect of calcium co-doping on crystal growth and the use of an additional co-dopant, zinc, to restabilize growth as well as showing the impact of zinc co-doping on scintillation properties.

Crystal Growth Procedures

Cerium-doped LSO:Ce, LSO:Ce,Ca, LSO:Ce,Zn, and LSO:Ce,Ca,Zn single crystal boules, 32 mm in diameter and ~100 mm long, were grown via the Czochralski technique in a Cyberstar Oxypuller 05-03 growth station. The Lu_2O_3, SiO_2, CeO_2, ZnO and CaO starting materials were at least 99.99% pure. In all experiments the nominal Ce concentration used was 0.1 at% relative to lutetium in the melt from which the crystal was grown. Ca and Zn concentrations ranged up to 0.4 and 0.6 at%, respectively.

The 60 mm diameter x 60 mm tall iridium crucibles were inductively heated by an 8 kHz power supply. The flowing atmosphere during growth and cooldown was ~ 0.7% oxygen in bulk nitrogen, monitored continuously by a Dymaxion Dycor residual gas analyzer. Crystal growth was initiated with seed crystals, using seeds oriented along the [100] axis in all cases. The pull rate was held constant in all experiments at 1.5 mm/hour; the rotation rate was 10 rpm.

Visual observation of the solid/liquid interface during and immediately after seed-dipping clearly showed that the meniscus size diminished as the calcium concentration increased, indicating reduced surface tension. Additional experiments with ZnO showed the opposite effect. These observations were confirmed by monitoring the magnitude of the weight changes that occurred during the extraction of the boules at the end of each growth run.. The weight of each boule was recorded via the Cyberstar load cell throughout the extraction and subsequently plotted. In a manner similar to the Du Nouy ring method of measuring surface tension, the resulting curve shows a rise to a maximum measured weight, which is related to the maximum force required for separation of the boule and melt. This maximum force is proportional to surface tension.

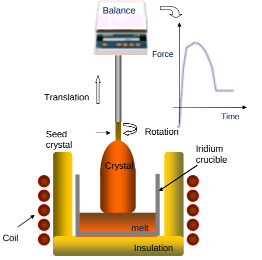

Figure 1 The method used to experimentally determine the correlation between dopant concentration and surface tension.

Crystal Growth Results

Fig. 2. LSO:Ce boule doped with 0.1 at% Ca. Note the good diameter control.

Fig. 3 LSO:Ce boule doped with 0.3 at% Ca, exhibiting stable growth.

Figure 4 LSO:Ce boule doped with 0.4 at% Ca, exhibiting unstable growth despite a convex interface.

Figure 5 LSO:Ce boule doped with 0.4 at% Ca,and 0.2 Zn. This Zn concentration is enough to delay, but not suppress, the onset of acentric growth.

Figure 6 LSO:Ce,Ca,Zn with 0.4 at% Ca, 0.6 at% Zn. Note that growth was significantly more stable.

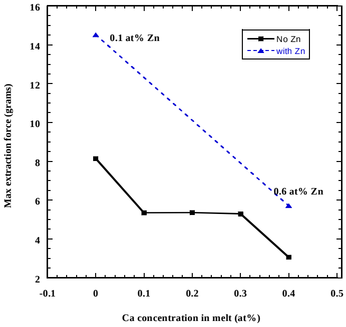

Fig. 7. The change in load cell reading during boule extraction, showing the relative force needed to separate boules of each composition from the melt. This force is proportional to surface tension.

Measurement Procedures

Absolute light output was measured with a Hamamatsu R2059 photomultiplier using a 1.0 μCi ^{22}Na source. The pulse height of a single photoelectron was measured and compared to that of the sample in order to obtain the photoelectron yield per unit gamma ray energy. The emission spectrum of the LSO crystal and the quantum efficiency curve of the photomultiplier were then used to calculate the number of photons per unit gamma ray energy.

We used the time-correlated single photon technique originated by Bollinger and Thomas to measure the scintillation decay time.

Scintillation Results

Table 1. Light output and decay time values are the average of multiple samples

Dopant concentration (atomic %)	Light output (photons/MeV)	Decay time (ns)
LSO:Ce, no co-dopant	30900	43
0.1 Ca	38800	36.7
0.2 Ca	36200	33.3
0.3 Ca	32400	31.3
0.4 Ca	34800	31
0.1 Zn	33200	40.1
0.4 Ca, 0.2 Zn	29900	28.9
0.4 Ca, 0.4 Zn	34700	30
0.4 Ca, 0.6 Zn	29000	28.5

Summary

Calcium co-doping has been found to increase the light yield and shorten the decay time of LSO:Ce. By manipulating the calcium concentration, it is possible for the first time to pre-select the decay time of the finished crystals, within the range of ~28-43 ns; the shortest decay times are achieved by the highest calcium concentrations.

However, it was found that co-doping can have an impact on crystal growth stability due to changes in the melt surface tension. Co-doping can either have a stabilizing or a destabilizing effect, depending on the nature of the surface tension change. A reduction of surface tension in LSO, as happens in calcium co-doping, was found to be potentially destabilizing, while an increase in surface tension, as happens in zinc co-doping, tends to be stabilizing.