Lutetium Yttrium Orthosilicate Single Crystal Scintillator Detector

Bruce Chai  
*University of Central Florida*

Yangyang Ji  
*Crystal Photonics, Inc*

Find similar works at: [https://stars.library.ucf.edu/patents](https://stars.library.ucf.edu/patents)

University of Central Florida Libraries [http://library.ucf.edu](http://library.ucf.edu)

This Patent is brought to you for free and open access by the Technology Transfer at STARS. It has been accepted for inclusion in UCF Patents by an authorized administrator of STARS. For more information, please contact [STARS@ucf.edu](mailto:STARS@ucf.edu).

**Recommended Citation**  
[https://stars.library.ucf.edu/patents/311](https://stars.library.ucf.edu/patents/311)
(54) LUTETIUM YTTRIUM ORTHOSILICATE SINGLE CRYSTAL SCINTILLATOR DETECTOR

(75) Inventors: Bruce H. T. Chai, Oviedo, FL (US); Yangyang Ji, Orlando, FL (US)

(73) Assignees: University of Central Florida, Orlando, FL (US); Crystal Photonics, Inc., Sanford, FL (US)

(10) Patent No.: US 6,624,420 B1
(45) Date of Patent: Sep. 23, 2003

(57) ABSTRACT

A single crystal having the general composition, Ce$_{2x}$(Lu$_{1-y}$Y$_y$)$_2$Si$_2$O$_8$ where x=approximately 0.0001 to approximately 0.05 and y=approximately 0.0001 to approximately 0.9999; preferably where x ranges from approximately 0.0001 to approximately 0.001 and y ranges from approximately 0.3 to approximately 0.8. The crystal is useful as a scintillation detector responsive to gamma ray or similar high energy radiation. The crystal as scintillation detector has wide application for the use in the fields of physics, chemistry, medicine, geology and cosmology because of its enhanced scintillation response to gamma rays, x-rays, cosmic rays and similar high energy particle radiation.

17 Claims, 5 Drawing Sheets

SCINTILLATING DETECTORS

Ce$^{3+}$: LYSO CRYSTAL

PHOTOMULTIPLIER OR OTHER PHOTO-DETECTOR
Ce$^{3+}$: Y$_2$ SiO$_5$ ABSORPTION AND EMISSION SPECTRA

(\text{\centering EMISSION CROSS SECTION} (10^{-18} \text{cm}^2))

WAVELENGTH (nm)

FIG. 1A (YSO)

(\text{\centering ABSORPTION CROSS SECTION} (10^{-18} \text{cm}^2))
SCINTILLATING DETECTORS

Ce$^{3+}$: LYSO CRYSTAL

PHOTOMULTIPLIER OR OTHER PHOTO-DETECTOR

FIG. 2
EFFECTIVE Z AS A FUNCTION OF Lu IN LYSO

FIG. 4

EFFECTIVE Z

% OF Lu IN LYSO
1

LUTETIUM YTTRIUM ORTHOSILICATE SINGLE CRYSTAL SCINTILLATOR DETECTOR

This application claims priority based on U.S. Provisional Application Serial No. 60/120,500 filed Feb. 18, 1999. This invention relates to a single crystal as scintillating detector for gamma ray or similar high energy radiation which single crystal is composed of Cerium doped Lutetium Yttrium orthosilicate (LYSO) with the general composition of Ce(Gd(1-y)Lu(y))ySiO5 which has excellent properties such as low light yield (15% that of NaI(Tl)), slow decay time (300 ns) and high refractive indices (n=2.15) which results in low light loss due to internal reflection. Still LYSO scintillator crystals are now used in high energy calorimetry in particle physics research institutes. It is also used as the detector for the 511 keV gamma-ray radiation of the positron emission tomographs (PET) in medical imaging application. Because of the low light and slow decay, the image produced from the LYSO PET machine tends to be blurred with poor resolution.

In early 80’s, the Ce doped GSO crystal was disclosed as a scintillator material. It has adequate density (6.71 g/cm³) and is also non-hydroscopic. The light yield is 20% of that obtained with NaI(Tl) with a much faster decay time (60 ns). Even though GSO crystals over 50 mm diameter have been produced, the crystal has not yet made in the PET marker because of a strong cleavage plane. It is very difficult to cut and polishing the crystal into any specific shape without the risk of fracturing of the entire crystal. Another unexpected problem is the high thermal neutron capture cross-section (49,000 barns) of the gadolinium. It will interfere with the gamma rays generated by neutron irradiation source. However, since there is no neutron involved in the PET process, gadolinium containing GSO is not a problem.

In the late 80’s, the Ce doped LSO crystal was disclosed as a good scintillator material. Similar to GSO, it has high density (7.4 g/cm³) and is non-hydroscopic. The light yield is significantly better and close to 75% of NaI(Tl)) and the decay time is even faster (42 ns). The index of refraction is also very low (n=1.82). Moreover, since LSO has a totally different crystal structure from GSO, it is fortuitous that in LSO structure, there is not any distinct cleavage plane making the material more suitable for detector block fabrication without the serious risk of fracturing. The thermal neutron capture cross-section is very low (84 barns) as compared to GSO. Lastly, it is now possible to commercially produce high quality, large size single crystals of LSO. Compared with all the other existing known scintillator crystals, Ce doped LSO seems to have the best combination of all the needed properties for PET or other high energy gamma-ray detector application.

Unfortunately, the lutetium element of the crystal contains a trace amount of a natural long decay radioactive isotope, Lu³⁷⁸, which will provide some background count rate that can be harmful for certain highly sensitive detector applications and the crystal has very deep trap centers. This is evidenced by the very long phosphorescence after exposure to any UV light source. The light output measurement of a large number of LSO crystals shows an anti-correlation between trap-related integrated thermoluminescence output and scintillation light output over a range of several orders of magnitude. At present time, the crystal defect is the most serious issue. One can have two crystals with identical appearance with one having 100% light yield and the other failing to scintillate. Thus far, there is no understanding how these deep traps are formed in the first place and there is also no remedy how to reduce or eliminate them.

At present, the scintillation process has been well accepted and used in many applications. The basic mechanism is also reasonably well understood. It is generally accepted that the basic scintillation process involves three steps: (1) the absorption of the incident high energy radiation and the conversion into a large number of low energy (a few multiples of the band gap energy) electrons and hole pairs,
(2) transfer the electron-hole recombination energy to the luminescence centers before its loss to multi-phonon relaxation processes, and (3) the radiative emission of the transferred energy. In other word, the scintillation efficiency (E) can be expressed as:

\[ E = \beta \cdot \eta \cdot S \]

where \( \beta \) is the conversion efficiency, \( S \) is the transfer efficiency and \( \eta \) is quantum efficiency of the radiation centers. Despite the understanding of scintillating mechanism based on the known materials, there is still lack of any good model which has the capability to predict the scintillating behavior of a specific compound. The quantum efficiency of an emission center can be predicted and tested optically; however, neither the total number of electron-hole pairs generated by an incident gamma ray radiation nor the transfer efficiency can be predicted or independently tested. In the end, the only way to confirm the scintillating behavior of a compound is to make and then test it.

SUMMARY OF THE INVENTION

The first objective of the present invention is to provide a scintillation detector for use as a high-energy radiation detector.

The second objective of this invention is to provide an improved scintillation crystal for use as a gamma ray or other high energy radiation detector.

The third objective of this invention is to provide a monocrystalline scintillation crystal of improved performance for use as a gamma ray or other similar high energy radiation detector.

In the subject invention, an improved scintillation detector assembly has been realized comprising: a cerium doped lutetium yttrium orthosilicate crystal; and, a photodetector coupled to said crystal whereby an electrical signal is generated in response to a light pulse from said crystal when exposed to a high energy gamma ray. The crystal is preferably monocrystalline and of a general composition of \( \text{Ce}_{x} \cdot (\text{Lu}_{1-x})_{0.7} \cdot \text{Y}_{0.3} \cdot 1.998 \cdot \text{Si}_{2} \cdot 0.5 \cdot 0.9999 \cdot \text{O}_{2} \cdot 5 \cdot 0.0001 \) to 0.05 and \( x=0.0001 \) to 0.99999 whereby the detector utilizing said crystal as the scintillator responsive to gamma and other similar high energy radiation is particularly useful in the fields of physics, chemistry, geology and cosmology.

BRIEF DESCRIPTION OF THE FIGURES

FIGS. 1a and 1b shows absorption and emission spectra of pure YSO and LSO.

FIG. 2 is a pictorial representation of a typical cerium doped LYSO scintillation detector.

FIG. 3 shows the LYSO scintillating light yield intensity as a function of lutetium concentration.

FIG. 4 shows the change of effective Z of LYSO as a function of lutetium concentration.

DESCRIPTION OF REPRESENTATIVE EMBODIMENT

For illustrative purpose, a representative embodiment of the invention is described hereinafter in the context for the detection of high energy gamma rays. It will be understood that the LYSO single crystal scintillator of the invention is not limited to the detection of gamma ray radiation but it has the general application for the detection of other types of radiation such as x-rays, cosmic and other high energy particle rays.

In the background review, it is mentioned that Ce doped LSO has the best scintillating properties among all the known materials. But it is still has a few serious problems to over come; namely, the isotopic problem and the defect (deep trap) problem. In addition to these physical issues, LSO crystals also face two tough economic issues. First is the high melting temperature for growth. The melting point of LSO is estimated around 2200° C. It is among the highest melting temperature crystals produced commercially. Special high temperature ceramics were used to build the furnace and Iridium crucibles were used to contain the melt for growth. The growth process is quite detrimental to both insulation and the crucible. High cost of frequent replacement of the hardware pushes cost too high to be bearable for practical use. Second is the high cost of raw material of lutetium oxide. It is not a common material. Moreover, the current material purity around 99.99% is not sufficient to guarantee consistent high light yield. It is highly desirable to reduce or even replace lutetium oxide as the main ingredient in new scintillator crystals.

The embodiment of this invention is to design a new crycal which can eliminate most of the problems of LSO crystal with sacrifice the scintillating properties. Our initial motivation is to reduce the growth temperature of LSO single crystals. It is a very difficult task to maintain the operation at such high temperature for long period of time (<1 week). Since YSO has lower melting temperature near 2070° C, we are seeking the possibility to find an intermediate composition (or LYSO composition) which may melt at lower temperature to ease the growth process. We also want to minimize the yttrium content to retain the LSO scintillating properties.

Since there is no known published phase diagram between YSO and LSO, the phase relationship of the intermediate composition is not available. We speculate the melting and crystallization behavior of the intermediate LYSO crystal composition based on two assumptions. First, since both YSO and LSO have the same crystallographic structure and the ionic size of yttrium 3+ ion (0.090 nm) and lutetium 3+ ion (0.088 nm) are very similar, we assume that there is a 100% miscibility between the m’o compositions. In other word, it is possible to make any intermediate composition LYSO crystals without worry about phase separation or formation of new compounds. Second, since YSO has lower melting temperature, based on the model of ideal solid solution, it is expected that all the intermediate compositions will have lower melting temperature similar to the classic example of fosterite (Mg2SiO4)-fayalite (Fe2SiO4) pseudobinary phase relations even though the exact position of the solidus and liquidus lines are not known.

In order to understand the melting and crystallization behavior, four intermediate LYSO charge compositions were prepared. The compositions were: \( \text{Ce}_{0.0001} \cdot (\text{Lu}_{0.7} \cdot \text{Y}_{0.3}) \cdot 1.998 \cdot \text{Si}_{2} \cdot 0.5 \cdot 0.9999 \cdot \text{O}_{2} \cdot 5 \cdot 0.0001 \) designates 70% LYSO; \( \text{Ce}_{0.0002} \cdot (\text{Lu}_{0.3} \cdot \text{Y}_{0.3}) \cdot 1.998 \cdot \text{Si}_{2} \cdot 0.5 \cdot 0.9999 \cdot \text{O}_{2} \cdot 5 \cdot 0.0001 \) designates 50% LYSO; \( \text{Ce}_{0.0002} \cdot (\text{Lu}_{0.3} \cdot \text{Y}_{0.3}) \cdot 1.998 \cdot \text{Si}_{2} \cdot 0.5 \cdot 0.9999 \cdot \text{O}_{2} \cdot 5 \cdot 0.0001 \) designates 30% LYSO; and, \( \text{Ce}_{0.0002} \cdot (\text{Lu}_{0.15} \cdot \text{Y}_{0.85}) \cdot 1.998 \cdot \text{Si}_{2} \cdot 0.5 \cdot 0.9999 \cdot \text{O}_{2} \cdot 5 \cdot 0.0001 \) designates 15% LYSO). The percentage refer the fraction of the lutetium in the crystal. A pure LSO charge was also prepared to be processed in a similar way as a reference for direct comparison. To make sure that the property comparison is meaningful, all the LYSO crystal preparation procedures are identical. The same total number of moles of chemicals in each case were used so that the finished crystals are near identical in size. To minimize the repetition, the 70% LYSO composition is hereafter set forth as the example to illustrate the preparation for all examples:
A mixture of high purity fine powders consisting of 1476 grams of Lu₂O₃, 359 grams of Y₂O₃, 317 grams of SiO₂, and 3.6 grams of CeO₂ were mechanically mixed thoroughly. The purity of Lu₂O₃ is 99.999%. The purity of both Y₂O₃ and SiO₂ is 99.9999.

(2) The mixed charge is placed in a 75 mm diameter by 75 mm deep iridium metal crucible and melted in a 50 kilowatt maximum power radio frequency (RF) heated high temperature furnace. (3) When the charge is fully molten and stabilized at near the melting temperature, a pure LSO seed crystal is lowered into the furnace and touched to the top center of the melt surface and the system is let to equilibrate. (4) Once the seed is in equilibrium with the melt, the seed is pulled up slowly with rotation. A computer controlled automatic diameter controlled program is used to finish the growth to a crystal diameter of 30 mm while using a pull rate of 1.5 mm per hour. (5) When the crystal has reached the desired length, it is separated from the melt and let cool slowly in the furnace to room temperature. The crystal is then recovered from the furnace and cut to smaller pieces for evaluation.

In order to check the melting behavior, an oversized crystal was grown in order to convert the maximum amount of melt to crystal. The resulting 30% LYSO crystal had a total length of 52 cm and a total weight of 1880.5 grams. The crystal took 8 days to complete the growth. In this case, the bottom 5 cm portion of the crystal contains a lot of visual inclusions and defects and was not usable for evaluation. It did, however, provide important information on the stability range of the melt.

Five crystals were grown consecutively in the same crucible and furnace at near identical growth conditions. There appeared to be no difference in crystal quality among all the five crystals. More interestingly, the fraction of the usable melt seems also to be quite the same regardless of the lutetium to yttrium ratio. This allows adjusting the crystal composition to best fit any specific application. In addition to the compositional flexibility, there was a significant lowering of the melting temperature which facilitates growth of these crystals.

To evaluate the scintillating properties, two 10 mm slabs were cut from each crystals, one from the top of the crystal and one from the bottom right above the defect region. It has been found that the scintillating light yield of any LSO crystal decreases systematically form the top to the bottom of the boule. The relative light yield can vary by as much as a factor of 2. It appears that this is due to the impurities in the lutetium oxide (Lu₂O₃) source material. Since the LYSO also uses the same Lu₂O₃ starting material, the LYSO will also show the same behavior.

The slab is placed under a Na²² radiation source which generates the 511 keV gamma ray as the incident light. The scintillating light from the LYSO slab is captured by a Hamamatsu R877 photomultiplier. The scale used for the light output measurement is arbitrary unit. In this case, the light output for a standard NaI(Tl) scintillator is set a 100%. In comparison, the standard BGO crystal has a light output of 12.5%. The energy resolution is expressed as the full width at half maximum of the 511 keV gamma ray peak. The result of the measurement is summarized in Table 1 and plotted in FIG. 3.

<table>
<thead>
<tr>
<th>Light yield %</th>
<th>YSO</th>
<th>LYSO</th>
<th>LYSO</th>
<th>LYSO</th>
<th>LYSO</th>
</tr>
</thead>
<tbody>
<tr>
<td>(top)</td>
<td>68</td>
<td>70</td>
<td>85</td>
<td>94</td>
<td>96</td>
</tr>
<tr>
<td>(bottom)</td>
<td>24</td>
<td>28</td>
<td>71</td>
<td>67</td>
<td>60</td>
</tr>
<tr>
<td>Energy</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Resolution %</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(top)</td>
<td>12</td>
<td>9</td>
<td>9</td>
<td>8</td>
<td>10</td>
</tr>
<tr>
<td>(bottom)</td>
<td>21</td>
<td>18</td>
<td>13</td>
<td>11</td>
<td>13</td>
</tr>
<tr>
<td>Effective Z</td>
<td>53</td>
<td>44</td>
<td>52</td>
<td>58</td>
<td>63</td>
</tr>
<tr>
<td>Density</td>
<td>4.62</td>
<td>5.04</td>
<td>5.45</td>
<td>6.01</td>
<td>6.57</td>
</tr>
<tr>
<td>Radiation</td>
<td>9.5</td>
<td>4.5</td>
<td>2.3</td>
<td>1.6</td>
<td>1.2</td>
</tr>
<tr>
<td>length (cm)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Phosphorescence</td>
<td>No</td>
<td>No</td>
<td>No</td>
<td>very weak</td>
<td>weak</td>
</tr>
</tbody>
</table>

Fist, the top portion of each crystal has the best scintillating value since the crystallization process has been found to be a purification process. The first (top) portion the result has many important implications of a crystal will have the least impurity content and thus the best performance. It is interesting to notice that the pure LSO crystal has produced light yield of 93% of that of NaI(Tl). This is significant higher than the published result of 75%. This value may approach to the ultimate scintillating power for LSO. Second, simply because of the top portion of each crystal has the highest purity, these measured values are good gauges for the comparison of the ultimate scintillating efficiency of these crystals. The light yield (or scintillating efficiency) remains constant for at least 50% percent substitution of lutetium with yttrium. Degradation of the light yield occurs after 70% replacement of lutetium. All the samples are of approximately equal thickness of 1 cm with no correction imposed for the reduction of density or effective Z. The scintillating efficiency drops rapidly with further addition of yttrium and the Compton signal rises rapidly with more than 85% substitution. The simple conclusion can be drawn that LYSO is a valuable and very efficient scintillator as long as the crystal contains more than 30% lutetium.

Third, the result also shows the rapid reduction of the light yield as the growth is progressing and the greater fraction of the melt is converted to crystal. This is consistent with all the published speculation that impurities are the primary cause to create the deep trap, which gives the long phosphorescence and reduces the scintillating light yield. In the case of pure LSO, the light yield drops by a factor of 2 when 80% of the melt is converted to crystal. This is the largest drop as compared to all the other LYSO crystals.

In FIG. 3, it is shown that there is a linear reduction of light yield for the bottom portion of the LYSO and LSO crystals with linear increasing of lutetium content. This is the most direct evidence to show that the impurity is coming from the Lu₂O₃ starting material. The phosphorescence is greatly reduced with more yttrium substitution and is nearly unnoticed beyond 50% substitution. In addition to the advantage directly observed from the light yield measurements, LYSO also resolves other problems associated with pure LSO. First the growth temperature of LYSO is lower than that of pure LSO be approximately 100° C. which is very significant in high temperature processes. Since the radiation heat loss is proportional to the 4th power of temperature (or T₈) the high temperature insulation and iridium crucible will last longer. Second, substituting yttrium will reduce proportionally the trace concentra-
tion of the naturally radioactive Lu\textsuperscript{176} isotope without sacrificing the net light yield. This will, in effect, reduce the background noise of the detector. Third, both the cost and purity of the Lu\textsubscript{2}O\textsubscript{3} starting material is a serious issue. Thus, yttrium substitution will reduce the cost and improve the uniformity of scintillating efficiency for large single crystal plates. Further, since a low index of refraction is preferred for scintillating crystals to reduce the effect of total internal reflection, the substitution of yttrium reduces the already low value of the index of refraction of LSO.

Lastly, let us examine the issue of stopping power, radiation length and effective Z. For practicality, it is desirable to use material with highest Z and shortest radiation length. Interesting enough, we find that in the case of LYSO, the effective Z increases rapidly with small substitution of 15\textsubscript{Ti} and 60\% LYSO has the same effective Z as NaI (Tl) and 60\% LYSO has the same effective Z as GSO. In terms of the radiation length, we can save 30\% lutetium with 10\% increase of radiation length, save 50\% and 70\% lutetium with 1.5 and 2 times that of pure LSO. In other words, the reduction is not linear to the substitution. In fact, it is favor for the substitution.

FIG. 2 illustrates the structure of the scintillation device with the crystal of the invention optically connected to the photomultiplier or other photon detector, which can include a photomultiplier tube, a PIN diode, and an APD (avalanche photo detector) diode.

While the invention has been described, disclosed, illustrated and shown in various terms of certain embodiments or modifications which it has presumed in practice, the scope of the invention is not intended to be, nor should it be deemed to be, limited thereby and such other modifications or embodiments as may be suggested by the teachings herein are particularly reserved especially as they fall within the breadth and scope of the claims here appended.

We claim:

1. A scintillator detector for high energy radiation comprizing: a monocrystalline structure of cerium doped lutetium yttrium orthosilicate, Ce\textsubscript{2x},(Lu\textsubscript{1-x}Y\textsubscript{y})(Si\textsubscript{5}O\textsubscript{15}) where x=approximately 0.0001 to approximately 0.05 and y=approximately 0.0001 to approximately 0.9999.

2. The crystal of claim 1 wherein x ranges from approximately 0.0001 to approximately 0.001 and y ranges from approximately 0.3 to approximately 0.8.

3. A scintillation detector assembly comprizing: a cerium doped lutetium yttrium orthosilicate monocrystal; and,

a photon detector coupled to said crystal, wherein an electrical signal is generated from the photon detector in response to said crystal being exposed to a high energy gamma ray.

4. The detector assembly of claim 3 wherein said monocrystal has the general composition of Ce\textsubscript{2x},(Lu\textsubscript{1-x}Y\textsubscript{y})\textsubscript{2(3-x-y)}Si\textsubscript{5}O\textsubscript{15} where x=approximately 0.00001 to approximately 0.05 and y=approximately 0.0001 to approximately 0.9999.

5. The detector assembly of claim 4 wherein x ranges from approximately 0.0001 to approximately 0.001 and y ranges from approximately 0.3 to approximately 0.8.

6. The detector assembly of claim 3 wherein said coupled photon detector is selected from at least one of a photomultiplier tube, a PIN diode and an APD (avalanche photo detector) diode.

7. A method of detecting energy with a scintillation detector, comprising the steps of:

receiving radiation by a crystal comprising cerium doped lutetium yttrium orthosilicate; and

detecting photons with a photon detector coupled to the crystal.

8. The method of claim 7, wherein the step of receiving radiation includes the step of: receiving gamma rays.

9. The method of claim 7, wherein the step of receiving radiation includes the step of: receiving x-rays.

10. The method of claim 7, wherein the step of receiving radiation includes the step of: receiving cosmic rays.

11. The method of claim 7, wherein the step of receiving radiation includes the step of: detecting light with a photo detector coupled to the crystal.

12. The method of claim 7, wherein the step of detecting includes the step of: detecting light with a photo detector coupled to the crystal.

13. The method of claim 12, wherein the step of detecting includes the step of: detecting light with a photomultiplier tube coupled to the crystal.

14. The method of claim 12, wherein the step of detecting includes the step of: detecting light with a PIN diode coupled to the crystal.

15. The method of claim 12, wherein the step of detecting includes the step of: detecting light with a APD diode coupled to the crystal.

16. The method of claim 7, wherein the crystal includes a composition of Ce\textsubscript{2x},(Lu\textsubscript{1-x}Y\textsubscript{y})\textsubscript{2(3-x-y)}Si\textsubscript{5}O\textsubscript{15} where x=approximately 0.00001 to approximately 0.05 and y=approximately 0.0001 to approximately 0.9999.

17. The method of claim 16, wherein x ranges from approximately 0.0001 to approximately 0.001 and y ranges from approximately 0.3 to approximately 0.8.