Growth and characteristics of LYSO \((\text{Lu}_{2(1-x-y)}\text{Y}_{2x}\text{SiO}_5:\text{Ce}_y)\) scintillation crystals

Laishun Qin*, Huanying Li, Sheng Lu, Dongzhou Ding, Guohao Ren

Shanghai Institute of Ceramics (SIC), Chinese Academy of Sciences, Shanghai 201800, PR China

Received 30 December 2004; accepted 18 April 2005
Available online 13 June 2005
Communicated by M. Schieber

Abstract

In this experiment, properties of LYSO crystals with different yttrium concentrations were investigated by Czochralski method. The concentrations of yttrium and cerium were analyzed by ICP-AES and the distribution coefficients of yttrium and cerium in LYSO crystal were calculated. It was found that the light output and the decay time of LYSO crystals are almost the same as that of cerium-doped lutetium oxyorthosilicate crystal (LSO). The energy resolutions of LYSO crystals, however, fluctuated in a large range.

© 2005 Elsevier B.V. All rights reserved.

PACS: 81.10; 29.40.M

Keywords: A2. Czochralski method; B2. LYSO crystal; B3. Scintillators

1. Introduction

Cerium-doped oxyorthosilicates of gadolinium, yttrium and lutetium, i.e. \(\text{Gd}_2\text{SiO}_5:\text{Ce}\) (GSO), \(\text{Y}_2\text{SiO}_5:\text{Ce}\) (YSO) and \(\text{Lu}_2\text{SiO}_5:\text{Ce}\) (LSO), respectively, have been grown by the Czochralski method and demonstrated as efficient scintillators \([1–3]\). The advent of above scintillators brought more and more interests in physics and crystal growth. A summary of the relevant properties of these materials along with conventional scintillation crystals such as thallium-doped sodium iodide (NaI(Tl)) and bismuth germanate (BGO) is given in Table 1.

Although LSO exhibits better scintillation properties, its melting point of 2150 °C is very close to the breakdown temperature of iridium crucible and insulating material of ZrO₂. Moreover, the Lutetium oxide is relatively expensive. Compared with LSO, both GSO and YSO have lower melting points and cheaper raw materials. As preferable
choices, the mixed scintillators such as cerium doped Lu$_{2-x}$Gd$_x$SiO$_5$ (LGSO) and cerium doped Lu$_{2-x}$Y$_x$SiO$_5$ (LYSO) were grown by researchers [5–9]. LGSO performs worse scintillation properties. However, LYSO presents similar scintillation properties and may be a good alternative to LSO. In addition, the adding of yttrium may have an improved effect on the distribution of cerium and it is necessary to know the distribution coefficient of yttrium in LYSO crystal.

In this paper, LYSO crystals with different yttrium concentrations were grown by Czochralski method and the distribution coefficient of yttrium in LYSO crystal as well as its scintillation properties was investigated.

2. Experiment

2.1. Growth of LYSO crystals

The starting powder materials are Lu$_2$O$_3$, Y$_2$O$_3$, SiO$_2$ and CeO$_2$ of 99.99% purity. All oxides were heated at 200 °C for 10 h to ensure powders free of moisture and CO$_2$. The powders were weighed in stoichiometry ratio of Lu$_{2(1-x-y)}$Y$_x$SiO$_5$:Ce$_y$, mixed and iso-statically pressed into tablets. In the experiments, the content of cerium was always at 0.5% (relative to RE). The doped concentrations of yttrium were selected as at 3.91%, 4.47%, and 10.09%. Then the tablets were sintered at 1500 °C for 6 h in order to obtain compact charge of LYSO.

Crystal growth was performed in the iridium crucible with the diameter of 80 mm. Flowing nitrogen (N$_2$) was used as protective atmosphere and LSO crystals were used as seed. The typical growth rate was 2 mm/h. The whole growth process was automatically controlled by computer. Fig. 1 shows the photo of the as-grown LYSO crystal boule with the diameter of 30 mm.

2.2. Measurements of distribution coefficient and scintillation properties

Samples were cut from the top, middle and bottom of the above crystal boule for measurement of distribution coefficient. The corresponding position is shown in Fig. 2. Then they were ground into powders. After the powders were dissolved in high temperature alkali solution, the concentrations of yttrium and cerium in LYSO crystals were analyzed by inductively coupled plasma atomic emission spectroscopy (ICP-AES).

Samples with dimension of 10 × 10 × 2 mm$^3$ were cut from the as-grown crystals, and six sides were all optically polished. Test on the scintillation properties of LYSO were performed in Institute of High Energy Physics, Chinese Academy of Sciences. Fig. 3 shows the schematic diagram of the equipment for measurement of light yield and decay time. In this equipment, a calibrated XP2020 photomultiplier (PMT) was used to detect the scintillation light. A conically optical wave guide was put between PMT and LYSO crystal. To achieve good light collection, the wave guide was optically coupled with PMT and crystal by the silicone, and Teflon was used as a light reflector. The radioactive source was the standard $^{22}$Na.
3. Results and discussion

3.1. Distributions of cerium and yttrium in LYSO crystals

In the study on distribution coefficient, the emphasis was paid on the boule doped by 3.91% yttrium. According to the cutting position and geometrical relationship, the crystallization fractions \( g \) can be first calculated. The concentrations of cerium and yttrium, the crystallization fractions and the corresponding positions of samples are listed in Table 2. Since the contents of cerium and yttrium in the boule are both increasing with solidifying of the melt, the distribution coefficients \( K_0 \) of cerium and yttrium in LYSO crystals must be less than 1. The equilibrium coefficient \( K_0 \) can be directly calculated on the basis of the formula, 
\[
K_0 = \frac{C_s}{C_l}.
\]
The content of the seed conjunction part is \( C_s \); the original content is equal to \( C_l \). That is to say, for distribution of cerium in LYSO, \( C_s = 100\% \) and \( C_l = 5\% \), so \( K_0 \) is equal to 0.20. While for yttrium in LYSO, \( C_s = 3.24\% \), \( C_l = 3.91\% \), so \( K_0 \) is calculated 0.83.

Based on Table 2, \( K_0 \) can be more accurately deduced from the equation \( \log(C_s/C_0) = \log K_0 - (K_0 - 1)\log(1 - g) \), which is the transformation of the general distribution equation \( C_s = K_0 C_0 (1 - g)^{g(K_0 - 1)} \). The experimental dependence of \( \log(C_s/C_0) \) versus \( \log(1 - g) \) for yttrium is shown in Fig. 4. The line is the linear fit of experimental data, whose expression equation is, 
\[
\log(C_s/C_0) = -0.0805 - 0.246\log(1 - g).
\]
According to \( K_0 - 1 = -0.246, K_0 = 0.75 \), for yttrium in LYSO is calculated 0.75, and according to \( \log K_0 = -0.0805K_0 = 0.83 \). Fig. 5 shows the experiment dependence for cerium. The fitting line can be expressed in \( \log(C_s/C_0) = -0.696 - 0.813\log(1 - g) \) and \( K_0 \) for cerium in LYSO boule is 0.20 and 0.19 by above two expressions, respectively.

The distribution coefficient of yttrium in LYSO crystal can also be calculated by the equation put forward by Brandle [10], 
\[
K_i = -5.45(R_i - R_b) + 0.99,
\]
where \( K_i \) is the distribution coefficient for \( i \)th...
dopant, \( R_i \) is the ionic radius of the \( i \)th dopant and \( R_h \) is the ionic radius of the host ion. Based on the equation, the distribution coefficient \( (K_0) \) of yttrium in LYSO is 0.77. Unfortunately the data by different methods are not consistent well with one another. This may be because the crystallization process is not strictly quasi-equilibrium. On the other side, Brandle’s equation is only a tentative expression. Anyway the distribution coefficient of yttrium in LYSO crystal is within 0.75–0.83. For the distribution coefficient of cerium in LYSO, it is 0.19–0.20, like the one in LSO, 0.22 [2], whereas it is up to 0.28 in Ref. [8]. The little difference may result from the measurement error due to the little concentration of cerium or the crystal growth parameter.

### 3.2. Photoelectron yield and energy resolution

Photoelectron yield was measured by comparing the position of the 511 keV \( \gamma \)-ray peak from a \( ^{22}\text{Na} \) source detected by the crystal with that of a single photoelectron peak. The photoelectron yield for LYSO crystals is shown in Table 3. These samples were cut in representative positions from crystal boules with different yttrium concentration. For comparison the photoelectron yield for LSO crystals is summarized in Table 4. The LSO crystals numbered 1–4 were grown under similar conditions by Czochralski method in SIC and LSO numbered 5 grown in England was provided by Institute of High Energy Physics, Chinese Academy of Sciences. The energy resolution for the 511 keV peak is also shown in both tables.

As can be seen from the Table 3, the photoelectron yield of LYSO crystals with different yttrium contents varies in the range 5022–5827 Ph.e/MeV. However, we note that there is no significantly substantial difference between the photoelectron yield of the LYSO crystals and those of LSO crystals. The data difference can be believed to be within experimental error. The result is similar to the result of radioluminescence in Ref. [8]. The energy resolution of LYSO at 511 keV fluctuated in a large range, from 27.2% to 11.0%. Even sometimes double peaks appeared in the energy spectrum of LYSO. Fig. 6 shows the good energy spectrum of LYSO-2-middle responded to \( ^{22}\text{Na} \). The energy spectrum with double peaks of LYSO-1-bottom is revealed in Fig. 7.

The light emission decay time of LYSO together with LSO grown in SIC was measured with the

---

### Table 2

The concentrations and the crystallization fractions in LYSO crystal doped by at 3.91% yttrium

<table>
<thead>
<tr>
<th>Sample position</th>
<th>( \frac{C_{c}}{C_{0}} ) (at%)</th>
<th>( \frac{C_{c}}{C_{0}} ) (at%)</th>
<th>( g ) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Top</td>
<td>0.100</td>
<td>3.24</td>
<td>0</td>
</tr>
<tr>
<td>Middle</td>
<td>0.102</td>
<td>3.28</td>
<td>0.024</td>
</tr>
<tr>
<td>Bottom</td>
<td>0.120</td>
<td>3.43</td>
<td>0.200</td>
</tr>
</tbody>
</table>
The integral method in the above equipment shown in Fig. 3. The oscillograph of TDS3052B was used to present the wave and the value of the electrical voltage. The electrical voltage at different time was read out during a coincident of scintillation. Since the electrical voltage \( V \) is proportional to the intensity of light emission \( I \), \( V/I = a \), where \( a \) is a constant, the decay time can be fitted by the formula \( V = c \exp(-t/\tau) \), where \( \tau \) is the decay time of scintillator and \( c \) is a constant. Hence, the decay times of LYSO crystal and LSO were obtained. As are expected, the decay times

\[
\begin{array}{ccc}
\text{LYSO(\%Y) boule} & \text{Sample position in crystal boule} & \text{Photoelectron yield} & \text{Energy resolution (\%)} \\
1 (3.91\%Y) & Top & Double peak & \\
 & Bottom & 5067 & 27.2 \\
2 (4.47\%Y) & Top & 5438 & 14.4 \\
 & Middle & 5827 & 11.0 \\
 & Bottom & 5260 & 20.2 \\
3 (10.09\%Y) & Top & 5316 & 13.0 \\
 & Middle & 5022 & 12.5 \\
\end{array}
\]

\[
\begin{array}{ccc}
\text{SAMPLE NUMBER} & \text{DIMENSION (\text{mm}^3)} & \text{PHOTOELECTRON YIELD} & \text{ENERGY RESOLUTION (\%)} \\
1 & 10 \times 10 \times 2 & 5507 & 9.9 \\
2 & 10 \times 10 \times 2 & 5293 & 10.8 \\
3 & 10 \times 10 \times 2 & 5498 & 10.4 \\
4 & 10 \times 10 \times 2 & 5143 & 10.4 \\
5 & 10 \times 10 \times 3 & 5200 & \\
\end{array}
\]

Fig. 6. The good pulse height spectrum of LYSO crystal excited by \(^{22}\text{Na}\).

Fig. 7. The pulse height spectrum of LYSO crystal with double peaks.
of LYSO and LSO are both 40 ns. The fit curves for LYSO and LSO are shown in Figs. 8 and 9, respectively. The vertical scale is shown in Napierian logarithm of the electrical voltage.

Although the concentration of yttrium in melts varied from 3.91% to 10.09% in this experiment, the light output and the decay time of LYSO do not show significant changes. This phenomenon can be understood from the point of their structures and radius. YSO (Y$_2$SiO$_5$:Ce) and LYSO have the same C2/c structures as LSO, and the radius of yttrium is close to that of lutetium. So the luminescent ion Ce$^{3+}$ in these crystals has the equal local environment. YSO, LSO and their mixture crystal are spontaneously expected to have the same light output and decay time. But for LGSO, gadolinium has a far larger radius than Lu. Accordingly, the adding of Gd to LSO usually has a detrimental effect on scintillation properties. It is also noticeable that the energy resolution fluctuates in a large range. Even double energy peaks appear in the energy spectrum of LYSO-1-top. The double peak phenomenon was also found in the LSO crystal in [11], which was ascribed to orthosilicate cluster and was related to crystal orientation.

4. Conclusion

LYSO crystals with different yttrium concentration were grown with Czochralski method. The distribution coefficients of yttrium and cerium in LYSO crystal are 0.83 and 0.20, respectively. Yttrium is relatively uniform in LYSO crystal.

LYSO crystal has a high light output and short decay time like LSO. However, the energy resolution seems not so good as that of LSO.

Acknowledgements

Authors thank Dr. Zhiming Zhang of Institute of High Energy Physics, Chinese Academy of Sciences, for the help of scintillation measurements of LYSO and LSO crystals. This work is sponsored by National Science Foundation of China with Grant No. 50272072 and the 863 program of Ministry of Science and Technology of China with Grant No. 2002AA324070.

References


