2-inch size crystal growth of Ce:Gd$_3$Al$_2$Ga$_3$O$_{12}$ with various Ce concentration and their scintillation properties.

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Abstract—2 inch size Ce0.2, 1%, 2.5% and 3% doped Gd$_3$(Ga,Al)$_3$O$_{12}$ (GAGG) single crystals were grown by the Cz method. Luminescence and scintillation properties were measured. Light yield change along the growth direction and effects of Ce concentration on scintillation properties in Ce:GAGG were studied. Ce$^{3+}$ 5d-4f emission within 520-530nm was observed in the Ce:GAGG crystals. The Ce1%:GAGG sample with 5x5x5mm size showed the highest light yield of 62000 photon/MeV. The energy resolution was 4.7%@662keV. With increasing solidification fraction, the LY was decreased. It is proposed that the increase of Ga concentration along the growth direction is the main cause of the decrease of LY. The scintillation decay times were accelerated with increasing Ce concentration in the Ce:GAGG crystals. The scintillation decay times were 92.0ns, 79.1ns and 68.3ns in the Ce1, 2 and 3% GAGG, respectively. Ce0.2% sample showed scintillation decay time of 61.9ns (49%) with slower decay component of 595ns(51%).

I. INTRODUCTION

Scintillator materials combined with photodetectors are used to detect high energy photons and accelerated particles in medical imaging techniques, high energy and nuclear physics detectors, high-tech industrial applications and most recently also in the advanced homeland security related techniques.[1] In the last two decades, great R&D effort brought several new material systems, namely the Ce-doped orthosilicates as Gd$_2$SiO$_5$ (GSO), Lu$_2$SiO$_5$ (LSO), (Lu$_{1-x}$Y$_x$)$_2$SiO$_5$ (LYSO), pyrosilicates based on RE$_2$Si$_2$O$_7$ (RE=Lu, Y, Gd) and most recently La$_x$(X=Cl,Br) single crystal grown by 1 inch size Czochralski (Cz) method showed high light yield of 46000 photon/MeV and fast decay dominated by 92ns decay time [18-20].

In this report, 2-inch size Ce:Gd$_3$Al$_2$Ga$_3$O$_{12}$ single crystals were grown by the Cz method with various Ce concentrations. Luminescence and scintillation properties were measured. Relationship between Ce concentration and scintillation properties was investigated.

II. MATERIALS AND METHODS

1) Crystal Growth

Stoichiometric mixtures of 4N CeO$_2$, Gd$_2$O$_3$, $\beta$-Ga$_2$O$_3$ and $\alpha$-Al$_2$O$_3$ powders (High Purity Chemicals Co.) were used as starting material. Nominally, Gd$^{3+}$ site was substituted by Ce$^{3+}$ according to the formula of (Ce$_x$Gd$_{1-x}$)$_3$Al$_2$Ga$_3$O$_{12}$ Ce:GAGG single crystals were grown by means of the Cz method using an RF heating system. The rotation rate was 4–12 rpm and the growth rate was 1.0 mm/h. An automatic diameter control system using crystal weighing was applied to control the growth parameters. Crystals were grown from a 50mm diameter Ir crucible under Ar with adding 30% of CO$_2$ atmosphere to prevent evaporation of gallium oxide. The seed crystal was a [100] oriented Ce:GAGG crystal. After the
completion of the crystal growth, the crystal was removed from the melt and was gradually cooled down to room temperature.

2) gamma-ray response measurement procedure

Light yield measurements were performed by using an avalanche photodiode (APD) (Hamamatsu, S8664-55). Sample pieces with dimensions of 5x5x5 mm were cut from the grown single crystal, all surfaces were mechanically polished. The samples were optically coupled to the APD (Hamamatsu, S8664-55). Timing resolution was measured by using 3x3x5 mm size GAGG and SiPMs from FBK (4 x 4 mm² active area, 50 μm pixel, peak spectral sensitivity at around 530 nm that coincides almost exactly with GAGG). For the decay time measurement the same setup with a photomultiplier tube (PMT Hamamatsu H6521) and digital oscilloscope TD5032B were used.

III. RESULTS

1) Crystal growth

Growth conditions such as the rotation rate, atmosphere and heat insulation design in the furnace were optimized for obtaining 2 inch size CeO.2, 1, 2 and 3% doped Gd3Al2Ga3O12 single crystals. The Ce1%, 2% and 3% doped GAGG single crystals with a diameter of 50mm and length of 80-120 mm were grown (Fig. 1). The grown crystals looked slightly cloudy because of the rough surface caused by gallium oxide evaporation or thermal etching. Metallic stripes on the crystal surfaces were identified as Ir deposit comes from oxidation of the crucible. However, the inner parts of all the crystals were perfectly transparent.

![Photographs of Ce crystals grown by the Cz method.](image)

2) Gamma-ray response

The typical energy spectra of Ce1%:GAGG excited by $^{137}$Cs at 16 °C and measured using the APD with gain=10 are shown in Fig. 2. The light yield (LY) of the sample was calibrated from the $^{55}$Fe direct irradiation peak to APD. Such direct irradiation generates 5.9 keV/3.6 eV = 1640 electron-hole pairs [1]. Based on this value, LY of Ce:GAGG is ~ 47,000 photon/MeV without correcting quantum efficiency (QE) of the APD. After correcting the QE, which is at 80% at 520 nm, the total LY becomes ~ 59,000 photon/MeV, which is around 180% of LY of a reference Ce:LYSO scintillator (32,000 photon/MeV, ~70% QE corrected) measured at the same experiment arrangement. Energy resolution of the Ce1%:GAGG sample was 4.7%@662keV.

The energy resolution of a 3x3x5 mm GAGG crystal excited by $^{22}$Na gamma-ray source measured with FBK Si-PM is shown in Fig. 3. GAGG, with a higher light output, produced better energy resolutions of 7.3 % at 5.7 V overvoltage (breakdown voltage is 27.8). The coincidence resolving time (CRT) was also measured using a $^{22}$Na source placed between two head-on detector modules with the 3x3x5 mm GAGG crystal and FBK Si-PM and with the PZ noise compensation [21]. Obtained time-delay histogram is shown in Fig. 4. CRT at the optimum bias voltage and threshold level was 286 ps (FWHM).

Scintillation decay curves were observed by using the PMT and an digital oscilloscope under excitation by $^{137}$Cs radioisotope. Scintillation decay curves of the Ce0.2, 1, 2 and 3% GAGG crystals are shown in figure 5. The scintillation decay times become shorter with increasing Ce concentration. The scintillation decay times were 92.0ns, 79.1ns and 68.3ns in the Ce1, 2 and 3% GAGG, respectively. Ce0.2% sample showed scintillation decay time of 61.9ns (49%) with slower decay component of 595ns(51%). Obtained scintillation properties were shown in Table 1. Decay time was accelerated with increasing Ce concentration and slower decay component was also reduced. Ce1% sample shows the highest light field.

![Energy spectra of Ce1%:GAGG and Ce:LYSO standard excited by a 662 keV gamma-ray using the APD at 16 °C (gain=10)](image)

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103

32000photon/MeV

$\Delta E/E=9.7%@662keV$

62000photon/MeV

$\Delta E/E=4.7%@662keV$

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Fig. 2 Energy spectra of Ce1%:GAGG and Ce:LYSO standard excited by a 662 keV gamma-ray using the APD at 16 °C (gain=10)
Fig. 3 The energy resolutions excited by $^{22}$Na gamma-ray source measured with the Si-PM form FBK.

Fig. 4 Time-delay histogram measured with the Si-PM detectors.

Fig. 5 Scintillation decay curves of the Ce0.1, 1, 2 and 3% GAGG crystals using the PMT and digital irradiated by $^{137}$Cs.

Table 1. Scintillation properties of Ce:GAGG

<table>
<thead>
<tr>
<th></th>
<th>Light yield (photon / MeV)</th>
<th>Energy resolution (% at 662keV)</th>
<th>Decay time (ns)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ce0.2%</td>
<td>36,000</td>
<td>7.5</td>
<td>61.9ns (49%) 595ns (51%)</td>
</tr>
<tr>
<td>Ce1%</td>
<td>62,000</td>
<td>5.8%</td>
<td>88ns (92%) 254ns (8%)</td>
</tr>
<tr>
<td>Ce2%</td>
<td>42,000</td>
<td>6.4%</td>
<td>80.6ns (95%) 800ns (5%)</td>
</tr>
<tr>
<td>Ce3%</td>
<td>38,000</td>
<td>6.6%</td>
<td>75ns (99%) 855ns (1%)</td>
</tr>
</tbody>
</table>

Fig. 6 Dependence of relative photoelectron yield on shaping time. Excitation by $^{137}$Cs.

Fig. 7 Nonproportionality of GGAG:Ce 1, 2, 3%

The dependence of relative photoelectron yield on shaping time (normalized to 0.5 us value) for variously selected sample groups are shown at fig. 6. The smallest increase of yield with shaping time is achieved for GGAG:Ce2% and 3%. It is good agreements of smaller ratio of slower decay component in these samples Ce:GAGG.

The nonproportionality of the Ce:GAGG samples are shown in fig. 7. The GGAG:Ce2% and 3% samples show better nonproportionality than that of Ce1% GAGG. The smallest non-proportionality and increase of yield with shaping time is achieved for GGAG:Ce 2% and 3%, but the absolute value of photoelectron yield is by far the highest for GGAG:Ce1% sample. According to the above results, it is clear that concentration quenching of Ce affects the acceleration of decay time and improve nonproportionality. In the higher Ce concentration samples, concentration quenching or increase of Ce$^{3+}$ 4f-5d absorption around the absorption...
edge cause the decrease of L.Y. Emission and absorption spectra will be also discussed in the presentation.

IV. CONCLUSION

The Ce0.2, 1, 2 and 3% doped GAGG single crystals were grown by the Cz method. Luminescence and scintillation properties were measured. Light yield change along the growth direction and effects of Ce concentration on scintillation properties in Ce:GAGG were studied. The Ce1%:GAGG sample shows the highest light yield of 59000 photon/MeV. The energy resolution was 4.7%@662keV using the APD and 7.3%@511keV using the Si-PM. On the other hands, Ce2% and 3% samples show better nonproportionality than that of Ce1% GAGG. The scintillation decay times were 92.0ns, 79.1ns and 68.3ns in the Ce1, 2 and 3% GAGG, respectively. Timing resolution was 286 ps (FWHM) using 3x3x5 mm size GAGG and the SiPMs.

REFERENCES