Temperature gradient technique (TGT) growth and characterizations of large-sized Ce-doped YAG scintillation crystal

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A good-quality Ce:YAG scintillation crystal with a diameter of 3 inches has been grown by temperature gradient technology (TGT) for the first time. The longitudinal distribution of cerium ions in the TGT-Ce:YAG crystal was measured by the ICP-AES method. The absorption spectrum in the range of 190–800 nm and the X-ray excited luminescence (XEL) of the as-grown Ce:YAG crystal were measured at the room temperature. The four typical absorption bands corresponding to internal 4f–5d transitions in Ce3+ ions, and the emission peak centered at 550 nm with the 2F5/2–2F7/2 ground state splitting were found in the absorption and XEL spectra.

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1 Introduction

Yttrium aluminum garnet activated by cerium (Ce:YAG) single crystal with a good thermal-mechanical property is a well-known inorganic scintillator, which is characterized by the high light yield (~20 000 photons/MeV), the short decay time constants (88 and 300 ns corresponding to the fast and slow components, respectively) and the significant difference of the light pulse response for γ-rays and α-particles [1]. All these properties suggest that the Ce:YAG scintillator can be successfully employed in various applications, mainly for detection of light charged particles and high-count-rate applications [2, 3]. Clearly, it is very important to grow the large-sized Ce:YAG scintillators with high quality for their scintillation applications.

At present, Ce:YAG scintillation crystals are mainly grown by the traditional RF-heated Czochralski method using an iridium crucible [2, 4]. However, like growing Nd-doped YAG crystals [9, 10], there may be some limitations for growing high-quality and large-size Ce:YAG crystals using Cz method. First, the large cores in the central part of the boules caused by facet growth are easily formed during Cz growth with a convex interface, which is very deleterious to the optical homogeneity of the crystals; Secondly, small variations of crystal rotation and fluid motion during Cz growth can lead to instability of the solid-melt interface, which can easily generate growth defects in crystals; Thirdly, due to the ionic radius of Ce3+ (1.18 Å) is larger than that of Y3+ (1.06 Å), it is very difficult to incorporate a large amount of cerium into the lattice using the Cz method without constitutional supercooling effects and second-phase precipitation. In addition, the great weight loss of iridium crucible frequently occurs during...
Czochralski growth, which will increase the production cost of the large-sized Ce:YAG scintillation crystals.

There are few techniques reported other than the Czochralski method for growing Ce:YAG crystals, and to our knowledge, the present size of Cz-grown Ce:YAG crystal is only 45 mm in diameter [4]. Recently, the present authors [5, 6] have established the temperature gradient technique (TGT) using an Mo crucible for growing high-quality Nd:YAG and Yb:YAG crystals with diameters of 3 inches.

In this article, a 3-inch highly transparent Ce:YAG scintillation crystal with cerium content of 0.8 at% in the melt was grown by temperature gradient technique for the first time. The segregation effect of Ce³⁺ in TGT-grown Ce:YAG crystal was investigated through measurements of cerium distributions along the growth axis. At the same time, the properties of absorption in the range of 190–800 nm and emission excited by X-rays from the TGT-Ce:YAG crystal are also discussed in the paper.

2 Experimental procedures

2.1 TGT-growth of Ce:YAG scintillation crystal

The temperature gradient technique setup for growing Ce:YAG crystals is similar to that described elsewhere [7]. The tapered molybdenum crucible with a lower seed end was used in our growth experiments. The typical dimensions of the molybdenum crucible used in our experiments are OD = 80 mm, ID = 76 mm with the cylindrical part height of 70 mm.

The highly pure oxides Y₂O₃ (≥ 99.999%), CeO₂ (≥ 99.99%) and Al₂O₃ (≥ 99.95%) powders were weighed out in mole ratios according to the chemical formula (Y₀.₉₉₂Ce₀.₀₀₈)₃Al₅O₁₂, then the powders were totally mixed and pressed into blocks with dimensions of φ 75 × 40 mm at 500 kg/cm² pressure. All the blocks (total weight of 1120 g) were loaded into the Mo crucible with the cylindrical [111]-orientation YAG seed in the seed position. The furnace was then loaded for the growth process, outgassed to 10⁻³ Pa and filled with 99.99% Ar up to 1.25 atm, then heated it up to melt the materials in the crucible, and kept molten for several hours. The crystallization of Ce:YAG was started and driven by the slow cooling (at a rate of ~0.5–1 °C/h) with a high-precision temperature controller. The whole crystallization process was completed automatically. When the crystallization finished, the Ce:YAG crystal was annealed in situ and then cooled down to room temperature at the desired cooling rate (30–50°C/h). After the crystallization of Ce:YAG finished, the crystal can be removed from the Mo crucible by a little shock on the edges of the crucible. The yellow-colored Ce:YAG crystal removed from the Mo crucible and the polished highly transparent (111) Ce:YAG scintillator slice are shown in Fig. 1. The typical dimensions of the TGT-Ce:YAG crystal boule are diameter of 76 mm and height of cylindrical part of 41 mm.

2.2 Measurements of longitudinal distribution of Ce ions in crystal

The distribution of cerium ions along the [111] growth axis in the 0.8 at% doped TGT-Ce:YAG crystal was measured by inductively coupled plasma-atomic emission spectrometry (ICP-AES). The cut posi-
tions of samples (sample A-D) are shown in Fig. 2. All samples were cut perpendicular to the [111] growth axis and their thickness was 1.5 mm. The samples were powdered in an agate mortar and dissolved into hot H$_3$PO$_4$ solutions for Ce and Y ions concentration measurements.

2.3 Measurements of absorption and X-ray excited luminescence

For absorption and X-ray excited luminescence measurements, the (111)-orientation TGT-Ce:YAG crystal slices were cut and mechanically polished to a thickness of 0.3 mm. The absorption spectrum was measured on a UV/VIS spectrophotometer (Model V-570, JASCO) at room temperature. The X-ray excited luminescence (XEL) spectrum was measured on a computer-controlled X-ray excited luminescence spectrometer, FluorMain, where a F-30 movable X-ray tube (W anticathode target) was used as the X-ray source operated under the condition of 80 kV and 4 mA at room temperature. Luminescence spectra were obtained by a W-44 plate grating monochromator and Hamamatsu R928-28 photomultiplier, and a computer acquired the data automatically. In the XEL experiments, a layer of Tyvek paper was wrapped round the Ce:YAG crystals with only an exposed facet coupled to the gating of monochromator.

3 Results and discussion

3.1 The longitudinal distribution of Ce ions in TGT-Ce:YAG crystal

The concentrations of both Ce and Y atoms in the samples A-D measured by the ICP-AES method are listed in Table 1. The cerium contents in different samples are calculated by the ratios of cerium atoms contents with those of total rare-earth atoms in Ce:YAG crystal, and calculated results are also showed in Table 1. From the contents of cerium ions listed in Table 1, it can be seen that the distribution of cerium along the growth axis in the TGT-Ce:YAG crystal is increasing greatly. The small segregation coefficient (K$_0$) of cerium in Ce:YAG crystal is responsible for this distribution feature. The segregation coefficient of cerium ions (K$_0$) can be calculated from the following equation:

$$K_0 = C_A/C_m,$$

Table 1 The longitudinal distribution of cerium ions in TGT-Ce:YAG scintillation crystal.

<table>
<thead>
<tr>
<th>sample</th>
<th>Y (wt%)</th>
<th>Ce (at%)</th>
<th>crystallization fraction (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>calc. from Eq. (2)</td>
<td>calc. from Fig. 2</td>
<td></td>
</tr>
<tr>
<td>A</td>
<td>42.30</td>
<td>0.043</td>
<td>0.065</td>
</tr>
<tr>
<td>B</td>
<td>43.27</td>
<td>0.058</td>
<td>0.084</td>
</tr>
<tr>
<td>C</td>
<td>43.35</td>
<td>0.220</td>
<td>0.321</td>
</tr>
<tr>
<td>D</td>
<td>42.04</td>
<td>1.070</td>
<td>1.592</td>
</tr>
</tbody>
</table>

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where $C_A$ is the Ce concentration in the sample A near the seed crystal part, and $C_m$ is the Ce concentration in the initial melt (in this paper $C_m = 0.008$). From the results listed in Table 1, one can calculate that the segregation coefficient of Ce in the 0.8 at% doped TGT-Ce:YAG crystal is only equal to 0.082.

Using values of $K_0$ (0.082) and $C_m$ (0.08), the crystallization fraction ($g$) of sample A–D can be calculated from the general distribution equation:

$$C_s = C_m \cdot K_0 \cdot (1-g)K_0^{-1}.$$  

(2)

Meanwhile the crystallization fractions ($g$) of the different samples are also estimated from the geometry relationship illustrated in the Fig. 2. And all the calculated results are listed in Table 1. When comparing the crystallization fractions ($g$) calculated from Eq. (2) and from Fig. 2, with a discrepancy of only 10% between them, it can be concluded that the cerium ions distribution along the growth axis in the TGT-Ce:YAG crystal agrees well with the general distribution Eq. (2). Due to the temperature gradient technique being a simple directional solidification method with a solute mass conservation system, the distribution of doped ions in the TGT-grown crystal boules can be described well by the general distribution Eq. (2), which means the exact cerium concentration can be calculated from Eq. (2). This is very important for scintillation applications of Ce:YAG crystals, because its scintillation properties are dependent greatly upon the cerium concentration in YAG crystals.

3.2 The absorption and emission spectra of TGT-Ce:YAG crystal

The absorption spectrum of as-grown TGT-Ce:YAG crystal is shown in Fig. 3. The four typical absorption peaks centered at 223 nm, 340 nm, 372 nm, and 460 nm can be found in Fig. 3, which are related to the f–d internal transitions of the Ce$^{3+}$ ions in the Ce:YAG crystal. Generally, due to the extreme host-sensitive property of 5d levels, the excited 5d state of Ce$^{3+}$ ion is split into five levels when Ce$^{3+}$ substitutes for Y$^{3+}$ at sites of D$_2$ symmetry in YAG lattice. The unusual magnitude of this crystal field splitting places the lowest 5d state only about 22000 cm$^{-1}$ above the ground state. As can be seen in the absorption spectrum of Fig. 3, only four of the five levels are observed before the onset of YAG intrinsic absorption, which occurs at about 50000 cm$^{-1}$, which is the same as that reported elsewhere [8].

Because the X-ray excited luminescence (XEL) can exactly reflect the body luminescence emitted by the scintillator, the XEL of the as-grown TGT-Ce:YAG scintillation crystal was measured at room temperature. The measured XEL spectrum is illustrated in Fig. 4.

As can be seen in the XEL spectrum of Fig. 4, the emission peak centered at 550 nm is clearly demonstrated in the XEL spectrum. The property of the emission peak at 550 nm of TGT-Ce:YAG crystal makes it fit well with the sensitivity spectrum of silicon photodiodes [2], which is very favorable in scin-
tillation applications when the Si photodiodes serve as readout devices. At the same time, the double band can be seen in the XEL spectrum of Fig. 4, which can be ascribed to the $^2F_{5/2} - ^2F_{7/2}$ spin orbit interaction of Ce$^{3+}$ ions in Ce:YAG crystal.

**4 Conclusions**

A good optical quality [111]-oriented Ce:YAG scintillation crystal with diameter of 3 inches has been grown by the temperature gradient technique (TGT) for the first time. The segregation coefficient of cerium ions in TGT-Ce:YAG crystal is determined as 0.082 by ICP-AES method, and the longitudinal distribution of Ce ions along the growth axis in TGT-Ce:YAG crystal agrees well with the general distribution equation:

$$C_s = C_m \cdot K_0 \cdot (1 - g) K_0^{-1}.$$  

The absorption spectrum of the as-grown TGT-Ce:YAG scintillation crystal shows the four typical absorption bands related to the 4f–5d internal transitions of Ce$^{3+}$ ions in YAG lattice. The X-ray excited luminescence spectrum of the TGT-Ce:YAG scintillator shows that the emission spectrum with the double band peaks at 550 nm, which is very favorable in scintillation applications when the Si photodiodes serve as readout devices. All the results in this article suggest that large-sized and high-quality Ce:YAG scintillation crystals can be obtained by the temperature gradient technique (TGT).

**References**