Characteristics of large-sized Ce:YAG scintillation crystal grown by temperature gradient technique

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Abstract

For the first time, the highly transparent yellow Ce:YAG scintillation crystal with a diameter of 3 in has been grown by the temperature gradient technique (TGT). The segregation coefficient of Ce ions in 0.8at\% doped TGT-Ce:YAG crystal determined by the ICP-AES method was 0.082, and the Ce distribution along the [1 1 1] growth axis was also investigated. The main macroscopic defects such as striations, side cores, bubbles, inclusions and stress birefringence were observed in as-grown Ce:YAG crystal by means of cross-polarized light microscope observation. The results show that the main defects such as bubbles, inclusions and stress birefringence mainly existed near the crystal peripheral edges.

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1. Introduction

Cerium-doped inorganic scintillation single crystals are promising scintillators, newly proposed in the recent decade, which have good scintillation properties of high light output in the UV or visible range and a short decay time of 20–100 ns \cite{1,2}. Among these Ce-doped scintillators, Ce:YAG scintillators are characterized by the relatively high light yield of the order of 20 000 photons/MeV, the two decay time constants of 88 and 300 ns, respectively, the emission peak at 550 nm which can be well coupled with the silicon photodiodes, and the significant difference of the light pulse response for $\gamma$-rays and $\alpha$-particles. All these properties suggest that the Ce:YAG scintillator can be successfully employed in various applications, mainly for the detection of light charged particles and high-count-rate applications \cite{3–5}. In addition, the high melting point of Ce:YAG crystal along with its good mechanical properties and truly non-hygroscopic nature allows its long term use under high temperature and ultra vacuum conditions \cite{5}. Evidently, it is of very great importance to grow large-sized Ce:YAG...
scintillators of high quality for their scintillation applications.

At present, Ce:YAG scintillation crystals are obtained mainly from the boules grown via the traditional RF-heated Czochralski method using an iridium crucible \([4,6]\). However, like growing Nd-doped YAG crystals \([7,8]\), there may be some limitations for growing high-quality and large-sized Ce:YAG crystals using the Cz method. Firstly, the large cores at the center of the boules caused by the facets growth are easily formed during Cz growth with the convex interface, which is very deleterious to the optical homogeneity of the crystals. Secondly, slight variations in the crystal rotation and fluid motion during Cz growth can lead to the instability of the solid–melt interface (S/M), which can easily generate growth defects in crystals. Thirdly, because the ionic radius of Ce\(^{3+}\) (1.18 Å) is larger than that of Y\(^{3+}\) (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 precipitations. In addition, a great weight loss of the iridium crucible frequently occurred during the Czochralski growth process, which will increase the production cost of the large-sized Ce:YAG scintillation crystals.

In order to reduce the above limitations of the Cz method for growing large-sized pure or doped YAG crystals, the authors \([9,10]\) have well established the temperature gradient technique (TGT) for growing high-quality Nd:YAG and Yb:YAG crystals with diameters of 3 in. In this paper, we discuss how the 3 in highly transparent Ce:YAG scintillation crystal with a cerium content of 0.8at% in the melt was successfully grown by TGT for the first time. The cerium distribution along the [1 1 1] growth axis was investigated, and the main macro growth defects in TGT-grown Ce:YAG crystal were also discussed.

2. Experimental procedures

2.1. Growth of Ce:YAG crystal by TGT

The TGT is a simple directional solidification technique, where the stable thermal field with proper temperature gradient is governed by numerous factors including, primarily, the cylindrical graphite heating elements, the Mo crucible, the Mo shields in the furnace, the external cooling water system, etc. The TGT setup with the proper thermal field for growing Ce:YAG crystals is similar to that described elsewhere \([11]\). A tapered molybdenum crucible with a lower seed end was used in our growth experiments. The typical dimensions of the molybdenum crucible used in our growth experiments are OD = 82 mm, ID = 78 mm and cylindrical part height 70 mm.

The highly pure oxide powders Y\(_2\)O\(_3\) (\(\geq 99.999\%\)), CeO\(_2\) (\(\geq 99.99\%\)) and Al\(_2\)O\(_3\) (\(\geq 99.95\%\)) were weighed out in mole ratios according to the chemical formula \((\text{Y}_{0.992}\text{Ce}_{0.008})_3\text{Al}_5\text{O}_{12}\); then were totally mixed and pressed into the form of blocks with the diameter close to the inner diameter of the crucible at a 500 kg/cm\(^2\) pressure. These blocks (total weight of 1120 g) were loaded into the Mo crucible with the cylindrical [1 1 1]-orientation YAG seed in the seed position. After totally melting the materials in the Mo container and keeping the molten mixture for several hours, the crystallization of Ce:YAG was started and driven by slow cooling (\(\sim 0.5–1\)°C/h) with a high-precision temperature controller. The whole crystallization process was completed automatically in the highly pure Ar gas atmosphere in the furnace. When the crystallization was complete, the Ce:YAG crystal was annealed in situ and then cooled down to room temperature at the desired cooling rate (30–50°C/h).

The yellow-colored Ce:YAG crystal boule removed from the Mo crucible is shown in Fig. 1(a). The typical dimensions are diameter = 76 mm and height of the cylindrical part = 45 mm. The polished highly transparent (1 1 1) Ce:YAG scintillation crystal slice is also shown in Fig. 1(b).

2.2. Distribution of cerium in TGT-Ce:YAG crystal

The distribution of cerium ions along the [1 1 1] growth axis in the 0.8at% doped TGT-Ce:YAG crystal was measured by inductively coupled plasma-atomic emission spectrometry (ICP-AES). The cut positions of samples (A–D) are shown in Fig. 2. All samples were cut perpendicular to the
[1 1 1] growth axis and their thickness was 1.5 mm. The samples were powdered in an agate mortar and dissolved in hot H3PO4 solutions for Ce and Y ion concentration measurements.

2.3. Observations of macroscopic growth defects in TGT-Ce:YAG crystal

In order to investigate the macroscopic growth defects in TGT-grown Ce:YAG crystal, three typical samples were cut from the different parts of as-grown Ce:YAG crystal boule. Sample one (1) was the tapered slice parallel to the [1 1 1] growth axis cut from the shoulder part of the TGT-Ce:YAG crystal boule for observation of the defects in the early growth stage. Sample two (2) was the (1 1 1)-oriented slice with a cross section of \( \phi \) 75 mm cut from the beginning cylindrical part of as-grown crystal. And the third sample (3) containing a periphery was cut along the [1 1 1] growth axis from the outer part of the Ce:YAG cylindrical block. All three samples (1–3) were mechanically polished, which allow light to pass through the sample for observations by cross-polarized light microscopy. The observed photos were selected carefully and recorded on the PC via a CCD camera coupled with microscopy. All the photos with different magnifications are shown in Figs. 2–4, which will be discussed in the next section.
3. Discussions and results

3.1. Longitudinal distribution of Ce ions in TGT-Ce:YAG crystal

The concentrations of both Ce and Y atoms in samples A–D measured by the ICP-AES method are listed in Table 1. The cerium contents in different samples are calculated, and the results are shown in Table 1.

The segregation coefficient of cerium ions \( (K_0) \) can be calculated from

\[
K_0 = \frac{C_A}{C_m},
\]

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 0.8at% 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 fractions \( (g) \) of sample A–D can be calculated from

\[
C_s = C_m K_0 (1 - g) K_0^{-1}.
\]

Meanwhile, the crystallization fractions \( (g) \) of the different samples are also estimated from the geometrical relations illustrated in Fig. 2. All the calculated results are listed in Table 1. When comparing the crystallization fractions \( (g) \) calculated from Eq. (2) and Fig. 2, where the discrepancy between them is within 10%, 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 equation (2). Because the TGT is a simple directional solidification method with solute a mass conservation system, the distribution of doped ions in the TGT–grown crystal boules can be described well and truly by the general distribution equation (2).

3.2. Striations and side cores in TGT-Ce:YAG crystal

Fig. 3 clearly displays the growth striations observed in the tapered sample 1 of the shoulder part of the TGT-Ce:YAG crystal. At the same time, the three areas numbered 1–3 can also be distinguished from Fig. 3.

Generally, the growth striations represent the history of crystal growth, and represent the shape and change of the S/M interface during the growth process. The striations shown in Fig. 3 demonstrated that a little convex S/M interface at the shoulder part was kept during the initial stage of the TGT growth process. According to the trends of growth striations in Ce:YAG crystal shown in Fig. 3 (directions of the arrow), the nearly planar

![Fig. 4. Side cores observed in the (111) slice of TGT-grown Ce:YAG crystal (sample 2) (the cross section of observation was 50 x 50 mm²).](image)

<table>
<thead>
<tr>
<th>Samples</th>
<th>Atom content (wt%)</th>
<th>Ce contents (at%)</th>
<th>Crystallization fraction (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Y</td>
<td>Ce</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>
interface is achieved with an increase in the diameter of the crystal during TGT growth. Such an interface is advantageous for the elimination of dislocations and other imperfections, while the faceted growth in the center range of the crystal boules was still eliminated with low convexity [9].

The reason for the three areas distinguished in Fig. 3 can be ascribed to the strong facet growth in Ce:YAG crystal growth, which can lead to the formation of the cores shown in Fig. 4. Unlike the faceted growth occurring in the Cz growth of pure or doped YAG crystals [7,8,12], the facet growth usually occurred at the edge of the cross section of the TGT-Ce:YAG crystal. Therefore the cores caused by the facets growth in TGT-Ce:YAG crystal are the side cores shown in Fig. 4. However, the sizes of the side cores in TGT-Ce:YAG crystal are very large in the present experiment, which greatly reduce the dimension of the non-core area existing in the center of the crystal boule (seen in Fig. 4). The large-sized side cores in TGT-Ce:YAG crystal can be eliminated by employing the planar S/M interface during TGT growth.

Therefore, the proper thermal field that allows the planar interface for growing TGT-Ce:YAG with small-sized side cores should be optimized further in the future.

3.3. Defects near the peripheral edges of TGT-Ce:YAG crystal

Figs. 5(a)–(c) clearly demonstrates the main defects such as bubbles, inclusions and stress birefringence existing near the peripheral edges of the TGT-Ce:YAG crystal boule.

The bubbles in the TGT-Ce:YAG crystal originate mainly from the gas bubbles in the melt, especially bubbles in the melt near the Mo crucible, which are frequently assumed to be associated with the numerous small-sized gas bubbles trapped during melt preparation and conserved in the saturated liquid. Due to the solubility change, segregation of gaseous impurity occurs during the liquid–solid transition [12]. In our growth case, due to only Ce$^{3+}$ ions entering into the Y$^{3+}$ sites in YAG lattice, to maintain

![Fig. 5. Bubbles, inclusions and stress birefringence observed near the peripheral edge of the Ce:YAG boule: (a) observation perpendicular to [1 1 1] growth axis; (b–d) observations along the [1 1 1] growth axis; (c) as-grown sample 3; (d) annealed sample 3 in H$_2$ at 1400°C for 20 h).](image-url)
electroneutrality, the starting material CeO$_2$ will decompose into Ce$_2$O$_3$ and O$_2$ gases, which would give rise to the small-sized gas bubbles in the melts.

From Fig. 5(a), the inclusions tails connected with the gas bubbles are observed, and the direction of inclusions tails is along the [1 1 1] growth axis. One can conclude that these inclusions are mainly caused by the upward motion of gas bubbles, which leads to the change of the solubility of the impurities along the tracks of the gas bubbles in the melts. With the crystallization of the crystal, the impurities would congregate along the tracks of bubbles and form large inclusions (0.5–1 mm), which are illustrated in Fig. 5(b).

The stress birefringence displayed in Fig. 5(c) is also observed near the peripheral edges of the TGT-Ce:YAG crystal boule (sample 3). After sample 3 is annealed in H$_2$ atmosphere at 1400°C for 20 hours, the region of the stress birefringence near the peripheral edges can be reduced a little (shown in Fig. 5(d)), which means that this stress not only belongs to the thermal stress but also to other stresses that cannot be eliminated by thermal treatment. Because of many defects such as bubbles and inclusions observed near the peripheral edges of the crystal boule, besides the thermal stress, the chemical or structural stresses caused by these defects should also be responsible for the stress birefringence near the peripheral edges of the TGT-Ce:YAG crystal. In addition, due to the thermal expansion coefficients of the rare-earth aluminum garnets being larger than those of Mo [12,13], the Mo crucible imparts little mechanical stress on the TGT-Ce:YAG crystal boule in the cooling process.

All the bubbles, inclusions and stress birefringence shown in Fig. 5 are confined within an area of 1–2 mm from the crystal peripheral edges, which means that the large-sized Ce:YAG scintillation crystals with high quality can be grown by the TGT method with carefully selected growth conditions. The proper thermal field or other measures for growing TGT-Ce:YAG scintillation crystal with small-sized side cores should be adopted in future growth experiments.

The optical and scintillation properties of TGT-Ce:YAG crystal are being studied and comparisons of optical and scintillation properties between TGT-grown Ce:YAG crystals and Cz-grown Ce:YAG crystals will be performed and reported in the future.

4. Conclusions

The highly transparent Ce:YAG scintillation crystal with a diameter of 3 in has been successfully grown by the temperature gradient technique (TGT) for the first time. The segregation coefficient of Ce ions in TGT-Ce:YAG crystal was equal to 0.082 measured by the ICP-AES method, and the Ce distribution in as-grown Ce:YAG crystal is agrees well with the general distribution equation $C_s = C_m K_0 (1 - g K_0)$. The main macroscopic defects such as striations, side cores, bubbles, inclusions and stress birefringence were observed in TGT-grown Ce:YAG crystal, and all these defects except for striations and side cores are confined within an area of 1–2 mm from the crystal peripheral edges, which means that large-sized Ce:YAG scintillation crystals with high quality can be obtained by the TGT method with carefully selected growth conditions. The proper thermal field or other measures for growing TGT-Ce:YAG scintillation crystal with small-sized side cores should be adopted in future growth experiments.

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References
