CZOCHELSKI GROWTH OF YAG:Ce IN A REDUCING PROTECTIVE ATMOSPHERE

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Ce³⁺ ions cause the destruction of colour centres in YAG crystals grown under a reducing protective atmosphere. The semitransparent Ce³⁺-doped YAG crystals have a relatively large region of undamaged to the melt and have a strongly curved interface during growth. This phenomenon brings about the possibility of the growth of perfectly pure crystals. Using molybdenum crucibles, the crystals were grown from a superheat which causes temPERATURE-quenching of Ce³⁺ due to oxygen scavenging step may be used in efficient cathode-ray excited phosphors.

1. Introduction

The structural perfection of Czochralski grown oxide crystals depends on the liquid/solid interface profile of the growing crystal [1]. Linear boundaries originating normally to the seed/crystal transition regions are oriented nearly perpendicularly to this interface. Crystals grown with a planar interface show mosaic structure similar to images of Varna mod crucible [2]. This means that perfect oxide crystals should be pulled with a conical interface and, if core-free crystals are required, this interface should be altered at some distance from the seed to a free zone [1,3]. The curve length or the volume of sub-marginal part of the crystal controls the deviation of the grain boundaries from a vertical position. The volume of the sub-marginal part depends on several factors. It is directly proportional to the transmission coefficient of the crystals.

Yttrium aluminium garnet (YAG) crystals grown under reducing conditions show no extremely serious absorption due to colour centres [4, 5] which makes the production of emission crystals possible. The suppression of colour centre formation in YAG by carbon ions and some properties of YAG:Ce crystals are described.

2. Experimental

The crystals were grown by the Czochralski method using molybdenum crucibles (dia. 9 x 9 cm), with resistance heating and a 98% Ar + 2% H₂ protective atmosphere [6], from initial material containing less than 10⁻⁵ wt% impurities. The molar ratio of (Y + Ce₂O₃):Al₂O₃ in the melt was varied from 2.05:3 to 3.05:5. The crystals were doped with Ce up to 0.8 wt% (0.4 x gomol in the melt), the Ce concentration being determined after dissolution of the specimen. The growth rate was 1.5 mm h⁻¹, the temperature at a distance of 3 cm above the melt level being 1600 ± 30°C. Interface flattening was indicated by the vanishing of the counterflow and the formation of Couette-like flow on the melt surface in the neighborhood of the crystal. The crystals were annealed in O₂ or N₂ at 1200°C for 15 h. Polished crystal plates of 3 mm or 0.8 mm in thickness were used for the absorption (Unicam SP 700) and cathodoluminescence [7].
measurements, respectively. The cathodoluminescence decay time (\(\tau\)) was measured using the technique described earlier [8] with a rectangular exciting pulse of duration of 100 ns. Optical absorption at elevated temperatures was measured using a Nd:YAG laser light transmitted through a sample of 2 cm in thickness housed in a Pt-40% Rh covered tube furnace. The intensity of the transmitted light was measured using a spectrometer. The effective extinction coefficient \(\beta\) for the growth conditions was determined with respect to the spectral dependence of the usual extinction coefficient \(\alpha\) at wavelength \(\lambda\) and spectral distribution blackbody radiation for \(T = 2900\) K using the relation [9]:

\[
[1 - \exp(-\beta \Delta l)] \cdot \eta = \int \alpha_0 \Delta l \rho(T, \lambda) \, d\lambda
\]

\[
= \sum \alpha_0 \Delta l \rho(T, \lambda) \, d\lambda,
\]

where \(\rho(T, \lambda) = \text{Planck's function}.\) The reflection of the sample surface was also taken into account.

S. Results

Crystals of approximately 2.8 cm in diameter and 10 cm in length were grown. The orientation of the interface was spontaneous, i.e., without usage of rotation rate. The crystals contained tantalum as impurity if \(x = (-10^{-2})\text{vol}\% \text{ H}_2\text{O}_2\) protective atmosphere was used, from ions if present in the initial material were never detected after 5-10 h of melting. The length of the cone of inclusion interface as well as the distance between the seed—boule and cone—seed interface remained, at a given crystal shape and dimension, indirectly proportional to its optical absorption. Ce addition improves absorption due to an increase in brown coloration of the crystals grown from a melt containing a small excess of \(\text{Y}_2\text{O}_3\) while the blue color of the crystals grown from a melt containing a large excess of \(\text{Al}_2\text{O}_3\) or a great excess of \(\text{Y}_2\text{O}_3\) \((\text{Y}_2\text{O}_3: \text{Al}_2\text{O}_3 > 3.08: 5)\) seem to be unaffected.

### Table 1

The influence of Ce\(^{3+}\) ions on the distance at the cone—seed interface transition from the seed—boule interface at the crystal was measured after 14-15 h at melting.

<table>
<thead>
<tr>
<th>Ce (wt%)</th>
<th>(T) ((^{\circ})C)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>22 rpm</td>
</tr>
<tr>
<td>(10^{-4})</td>
<td>13—15</td>
</tr>
<tr>
<td>(10^{-3})</td>
<td>20—25</td>
</tr>
<tr>
<td>(10^{-2})</td>
<td>25—26</td>
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</tbody>
</table>

### Fig. 2

(c) Newborn shape at \(t = 1.2\text{ cm} \text{ pulled} \); (d) \(38\text{ rpm} \text{ uncooled} \); (e) \(38\text{ rpm} \text{ cooled with } \text{H}_2\text{O}_2 \text{ gas} \); (f) \(22\text{ rpm} \text{ uncooled} \); (g) \(38\text{ rpm} \text{ cooled with } \text{H}_2\text{O}_2 \text{ gas}.\)
(table 1, fig. 1 and 2). The latter two types suffer from the formation of ultralight-scattering particles and they were not investigated further. The brown coloration may be irreversibly annealed under oxidizing conditions.

The total extinction coefficient \( \beta \) of a crystal grown from a melt of composition \((Y + Ce)Al_2O_3:Al_2O_3 = (0.02 \pm 0.015) : 3 \) (fig. 1) consists of the sum of the extinction coefficients determined for:

1. An unannealed unpolished crystal: \( \beta_{\text{ppm}} = 0.002 \text{ cm}^{-1} \).
2. \( \text{Ce}^{3+} \) ions \( \beta_{\text{Ce}^{3+}} = 0.07 \text{Ce}^{3+} \text{ cm}^{-1} \) (Ce in ppm).
3. Brown color centers. This depends on the distance \( l \) (cm) from the melt level \( \beta = 0.02 \times (3 - l) \). \( \text{Ce}^{3+} \) in a concentration \( > 10^{-3} \text{ wt%} \).

Fig. 2. Absorption spectra of YAG plates made at the distance of 1.5 mm from the melt level: (1) unpolished; (2) \( 10^{-4} \text{ wt} \% \text{ Ce} \); (3) \( 10^{-3} \text{ wt} \% \text{ Ce} \). Table 1: Composition of the melt.

Fig. 3. Temperature dependence of extinction coefficient \( \beta \) of YAG grown from the melt of the composition of \((Y + Ce)_2O_3:Al_2O_3 = 3:3 0:3 \) in \( \beta \) ppm. (1) unpolished; (2) \( 10^{-4} \text{ wt} \% \text{ Ce} \).

Fig. 4. The composition of YAG plates at the distance of 1.5 mm from the melt level: (1) unpolished; (2) \( 10^{-4} \text{ wt} \% \text{ Ce} \); (3) \( 10^{-3} \text{ wt} \% \text{ Ce} \). Table 1: Composition of the melt.

leads to a decrease in \( \beta \) to about 1/2-1/3 that of room temperature and to zero at temperature near the melting point (fig. 3).

YAG:Ce grown under reducing conditions showed relatively low efficiency of cathodoluminescence and \( r = 150 \text{ mm} \). Oxidizing annealing caused the luminescence efficiency to be increased and steady state to be noticeable \( (r = 30 \text{ mm}) \). Further hydrogen annealing increased the luminescence efficiency, particularly in the presence of cathodoluminescence lines but lengthened the decay time \( (r = 180 \text{ mm}) \). The presence of Fe ions in the samples was confirmed by luminescence measurements (fig. 4).

4. Discussion

Using numerical methods and the x-ray data described earlier \([7] \) the elimination of the
coefficient $\beta$, due to presence of $\text{Co}^{3+}$ ions at high temperature may be evaluated. It causes the temperature difference between the interface and bulk of the melt to decrease from 60 to about 10 K. Supposing the same Nusselt number for a given type of melt, the interface area increases with decreasing temperature difference. Similarly, highly transmitting corundum crystals showed a substantially greater interface area if compared with that of YAG [6]. $\text{Co}^{3+}$-doped YAG crystals show themselves an enlarged interfacial area and growth may be started even a markedly smaller interface which makes the growth of perfect crystal possible. $\text{Co}^{3+}$-doped crystals may be grown in a decreased temperature gradient above the melt level, as in the case of ruby [9].

The causes of $\text{Y}^{3+}$ ions in YAG cause the substitution of some $\text{Al}^{3+}$ ions by larger $\text{Y}^{3+}$.

"Compressed" $\text{O}^-$ in the neighbourhood of $\text{Y}^{3+}$ in corundum unit may be converted to another nonbonded $\text{O}^-$ as in the case of $\text{Al}_2\text{O}_3$ [10]. Ce centre suppresses $\text{O}^-$ centre formation because of the reaction:

$$\text{Co}^{3+} + \text{O}^- \rightarrow \text{Co}^{2+} + \text{O}^2-. \quad (2)$$

Oxygen vacancy causes the formation of chlorine vacancies (e.g. ref. [11]) which may serve as more effective hole traps than compressed $\text{O}^-$ ion, whereas excess $\text{Y}^{3+}$ causes dodecahedral sites only. Both effects cause the formation centres to be dissociated and luminescence efficiency to increase. Hydrogenion dangling electrons closely links the kinetics of the formation but it does not suppress the cathodoluminescence efficiency as described earlier [6]. Good luminescence efficiency may be explained by the absence of ions of the $\text{Fe}^{3+}$, $\text{Fe}^{2+}$, $\text{Mn}^{2+}$, etc. which otherwise cause luminescence quenching.

3. Summary

YAG crystals may be grown using a reducing protective atmosphere and a small excess of $\text{Y}_2\text{O}_3$ in the melt. The crystals are free from light-scattering particles but they usually contain structural defects which may be connected with the presence of absorbing cobalt centres. Using $\approx 10^{-5}$ wt % of cobalt ions (5–9 x greater in the melt) the formation of the centres is suppressed and the crystals may be grown with a markedly smaller interface which results in mosaic-free crystals.

$\text{YAG:Co}^{3+}$ grown from the melt in thin plate and enclosed in $\text{O}_2$ seems to be an attractive flying-spot scanner or satellite material, because it contains neither Li nor Fe ions which quench $\text{Co}^{3+}$ luminescence.

References