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CZOCHRALSKI GROWTH OF YAG:Ce IN A REDUCING PROTECTIVE ATMOSPHERE

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Ce^{3+} ions cause the destruction of colour centres in YAG crystals grown under a reducing protective atmosphere. The more transparent Ce^{3+}-doped YAG crystals have a relatively large region submerged in the melt and form a strongly conical interface during growth. This phenomenon brings about the possibility of the growth of relatively perfect crystals. Using molybdenum crucibles, the crystals are free from impurities which cause luminescence quenching of Ce^{3+} and, after oxygen annealing, they may be used as 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]. Grain boundaries originating usually in the seed/crystal transition region are oriented nearly perpendicularly to the interface. Crystals grown with a planar interface show mosaic structure similar to lineage of Verneuil corundum [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 flat one [1, 3]. The cone length or the volume of submerged part of the crystal controls the deviation of the grain boundaries from a vertical position. The volume of the submerged 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 an extremely strong absorption due to colour centres [4, 5] which makes the production of mosaic-free crystals difficult. The suppression of colour centre formation in YAG by cerium ions and some properties of YAG:Ce crystals are described.

2. Experimental

The crystals were grown by the Czochralski method using molybdenum crucibles (dia. 8 × 8 cm), with resistance heating and a 98% Ar + 2% H_2 protective atmosphere [6], from initial material containing less than 10^{-4} wt% impurities. The molar ratio of $(Y + Ce)_2O_3 : Al_2O_3$ in the melt was varied from 2.95:5 to 3.05:5. The crystals were doped with Ce up to 0.6 wt% (8.4 × greater in the melt), the Ce concentration being determined after dissolution of the samples. The growth rate was 1.5 mm h^{-1}, the temperature at a distance of 5 cm above the melt level being 1690 ± 30°C. Interface flattening was indicated by the vanishing of the centripetal flow and the formation of Couette-like flow on the melt surface in the neighbourhood of the crystal. The crystals were annealed in O_2 or H_2 at 1700°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 lifetime decay time (τ) 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 He–Ne laser light transmitted through a sample of 2 cm in thickness heated in a Pt–40% Rh wound tube furnace. The intensity of the transmitted light was measured using a wattmeter. The effective exctinction coefficient β for the growth conditions was determined with respect to the spectral dependence of the usual extinction coefficient α_λ at wavelength λ and spectral distribution blackbody radiation for $T = 2300$ K using the relation [9]:

$$[1-\exp(-\beta\,\Delta l)]\,\sigma T^4 = \int_0^\infty \alpha_\lambda\,\Delta l f(T,\lambda)\,\mathrm{d}\lambda \simeq \sum \alpha_\lambda\,\Delta l f(T,\lambda_i)\,\Delta\lambda, \quad (1)$$

where $f(T,\lambda)$ is Planck's function. The reflection at the sample surface was also taken into account.

3. Results

Crystals of approximately 2.8 cm in diameter and 10 cm in length were grown. The flattening of the interface was spontaneous, i.e. without change of rotation rate. The crystals contained molybdenum ions if a wet ($\sim 10^{-2}$ vol% $H_2O_{(g)}$) protective atmosphere was used. Iron ions if present in the initial material were never detected after 8–10 h of melting. The length of the conical (convex) interface as well as the distance between the seed–boule and conical–flat interface transitions are, at a given crystal shape and dimension, indirectly proportional to its optical absorption. Ce addition suppresses absorption due to an anomalous brown coloration of the crystals grown from a melt containing a small excess of Y_2O_3, while the blue colour of the crystals grown from a melt containing either excess of Al_2O_3 or a great excess of Y_2O_3 ($Y_2O_3:Al_2O_3 > 3.08:5$ [5] seem to be unaffected

Table 1
The influence of Ce^{3+} ions on the distance of the conical–flat interface transition from the seed; full diameter of the crystal was reached after 14–15 mm of pulling

Ce (wt%)	l (mm)		
	22 rpm	30 rpm	38 rpm
0	17–20	15–17	12–15
10^{-4}	23–25	21–22	15–17
10^{-3}	32–35	26–28	22–25
10^{-2}	32–35	26–28	22–25

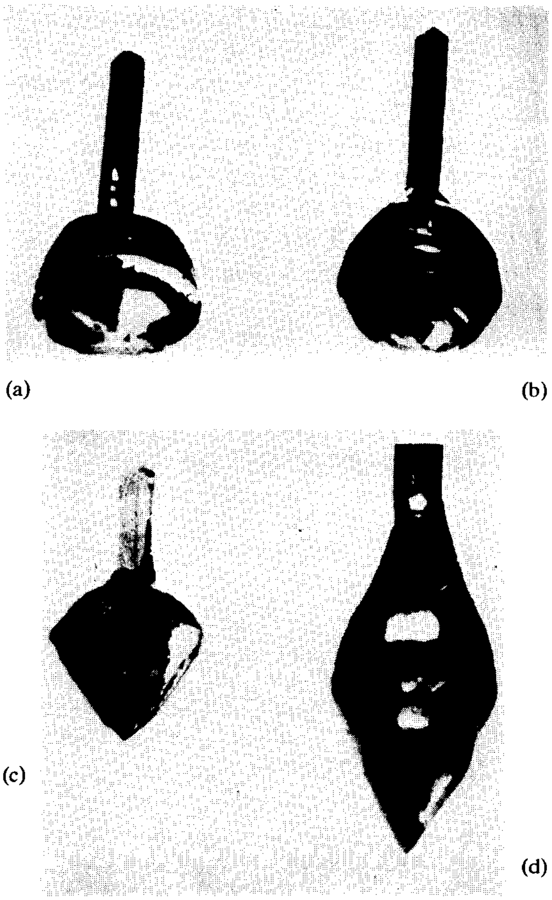

Fig. 1. Interface shape of YAG crystals of 12 mm pulled length: (a) 38 rpm undoped; (b) 38 rpm doped with 10^{-3} wt% Ce, C; (c) 22 rpm undoped; (d) 22 rpm doped with 10^{-3} wt% Ce.

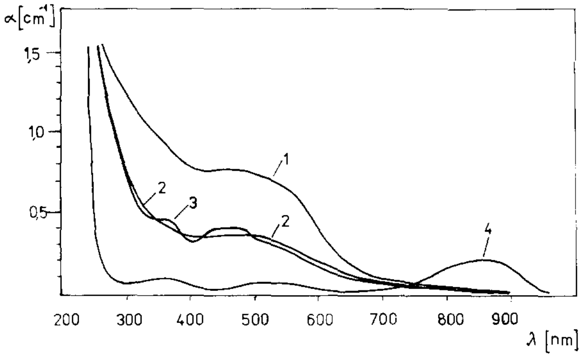

Fig. 2. Absorption spectra of YAG plates taken at the distance of 1.5 cm from the melt level: (1) undoped; (2) 10^{-3} wt% Ce; (3) 10^{-2} wt% Ce, melt composition $(Y+Ce)_2O_3:Al_2O_3 = 3.025:5$; (4) 10^{-3} wt% Ce, melt composition $(Y+Ce)_2O_3:Al_2O_3 = 2.98:5$.

(table 1, figs. 1 and 2). The latter two types suffer from the formation of ultrafine light-scattering particles and they were not investigated further. The brown coloration may be irreversibly annealed under oxidizing conditions.

The total extinction coefficient β of a crystal grown from a melt of composition $(Y+Ce)_2O_3:Al_2O_3 = (3.02 \pm 0.015):5$ (fig. 1) consists of the sum of the extinction coefficients determined for:

(1) An annealed undoped crystal: $\beta_{YAG} = 0.002\,cm^{-1}$.

(2) Ce^{3+} ions: $\beta_{Ce^{3+}} = 0.07\,C_{Ce}\,cm^{-1}$ (C_{Ce} in wt%).

(3) Brown colour centres. This depends on the distance l (cm) from the melt level $\beta_l \simeq 0.02 \times (5-l)$. Ce^{3+} in a concentration $>10^{-3}$ wt% leads to a decrease in β_l to about 1/2–1/3 that at room temperature and to zero at temperature near the melting point (fig. 3).

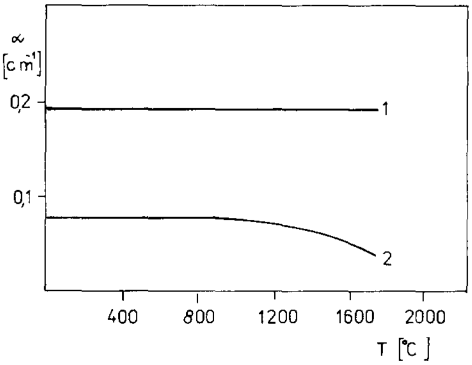

Fig. 3. Temperature dependence of extinction coefficients α of YAG grown from the melt of the composition of $(Y+Ce)_2O_3:Al_2O_3 = 3.02:5$ at 632.8 nm: (1) undoped; (2) 10^{-3} wt%, Ce.

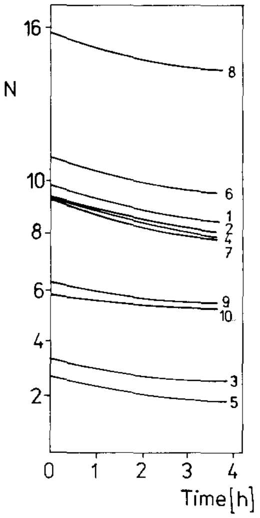

Fig. 4. The comparison of the cathodoluminescence output N (in arbitrary units) [7] for different YAG:Ce and other phosphors, all doped with 0.6 wt% Ce: (1) single crystal fired in O_2 and then powdered; (2) melted in Mo crucible, fired in O_2 and powdered; (3) melted in Ir crucible in N_2, fired in O_2 and powdered; (4) as sample 2, initial material doped with 5 ppm Fe; (5) as sample 3, initial material doped with 5 ppm Fe; (6) single crystal plate (the side exposed to the electron beam polished, the other matted) made of oxygen-treated crystal; (7) as sample 6 but thermally treated in the form of a plate; (8) plate made of the crystal containing 5×10^{-2} wt% Mo, treated in O_2 and then in H_2; (9) $Y_2Si_2O_7:Ce^{3+}$-powdered sintrate; (10) $Ca_2Al_2SiO_7:Ce^{3+}$-powdered sintrate.

YAG:Ce grown under reducing conditions showed relatively low efficiency of cathodoluminescence and $\tau \simeq 150$ ns. Oxygen annealing caused the luminescence efficiency to be increased and decay time to be shortened ($\tau \simeq 80$ ns). Further hydrogen annealing increased the luminescence efficiency, particularly in the presence of molybdenum ions but lengthened its decay time ($\tau = 180$ ns). The absence of Fe ions in the samples is confirmed by luminescence measurements (fig. 4).

4. Discussion

Using numerical methods and the material data described earlier [9] the elimination of the coefficient β_l due to presence of Ce^{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 flow, 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]. Ce^{3+}-doped YAG crystals show therefore an enlarged interface area and growth may be started using a markedly conical interface which makes the growth of perfect material possible. Ce^{3+}-doped crystals may be grown in a decreased temperature gradient above the melt level, as in the case of ruby [9].

The excess of Y^{3+} ions in YAG causes the substitution of some Al^{3+} ions by larger Y^{3+}. "Compressed" O^{2-} in the neighbourhood of Y^{3+} in octahedral sites may be converted to smaller coloured O^- as in the case of Al_2O_3 [10]. Ce admixture suppresses O^- centre formation because of the reaction:

$$Ce^{3+} + O^- \rightleftarrows Ce^{4+} + O^{2-}. \qquad (2)$$

Oxygen annealing causes the formation of aluminium vacancies (e.g. ref. [11]) which may serve as more effective hole traps than compressed O^{2-} ion, whereas excess Y^{3+} enters dodecahedral sites only*. Both effects cause the colour centres to be dissociated and luminescence efficiency to increase. Hydrogen annealing elongates decay time of the luminescence but it does not suppress cathodoluminescence efficiency as described earlier [8]. Good luminescence efficiency may be explained by the absence of ions of the 8b group (Fe, Ir) which otherwise cause luminescence quenching.

5. Summary

YAG crystals may be grown using a reducing protective atmosphere and a small excess of Y_2O_3 in the melt. The crystals are free from light-scattering particles but they usually contain structural defects which may be connected with a nearly flat interface resulting from the presence of absorbing colour centres. Using $\geqslant 10^{-3}$ wt% of cerium ions (8–9 × greater in the melt) the formation of the centre is suppressed and the crystals may be started with a markedly conical interface which results in mosaic-free crystals.

YAG:Ce^{3+} grown from the melt in Mo crucibles and annealed in O_2 seems to be an attractive flying-spot scanner or scintillator material, because it contains neither Ir nor Fe ions which quench Ce^{3+} luminescence.

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* A detailed discussion of the non-stoichiometric colour centres will be given elsewhere.