Improvement of dopant distribution in radial direction of single crystals grown by micro-pulling-down method

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Abstract

Two iridium crucibles with one and five capillaries at a nozzle were developed for the growth of Ce-doped $\text{Y}_3\text{Al}_5\text{O}_{12}$ [Ce:YAG] single crystals by the micro-pulling-down [μ -PD] method. The purpose of the study was to examine the effect of the capillary number on the Ce distribution in the radial direction of the crystals. The crystals grown from 2 mol% and 5 mol% Ce-doped YAG melts were then cut perpendicular to the growth direction and polished to produce specimens suitable for the measurement of Ce distribution. The Ce:YAG crystals grown using the crucible with one capillary [Ce:YAG(1C)] had greater Ce content in the central portion of the crystal when compared to its peripheral parts. On the other hand, in the case of the Ce:YAG crystal grown using the crucible with five capillaries [Ce:YAG(5C)], the increased Ce concentration was detected in five specimen sections positioned just below the capillaries. The results indicated that increase of the number of capillaries is effective practice that results in an improvement of the radial homogeneity of the single crystals grown by the μ -PD method.

Keywords: A1. Segregation, A2. Growth from melt, A2. Single crystal growth, B1. Oxides, B3. Scintillators, B3. Solid state lasers

1. Introduction

The micro-pulling-down [μ -PD] technique is one of the methods of single crystal growth from the melt. It is widely used for materials research because it is relatively simple and exceptionally fast when compared with conventional growth methods [1-5]. Figure 1(a) presents a schematic diagram of the typical μ -PD system developed for the growth of oxide single crystals using a radio-frequency [RF] induction heating. In such μ -PD configuration, a metal crucible plays the dual role of the melt container and the heater due to its placement into the high-frequency electromagnetic field produced by the RF inductor. The bottom of the crucible is equipped with a nozzle (or die) that is produced with one or several capillary channels. These channels are responsible for the continuous delivery of the melt from the crucible container to the bottom of the nozzle as illustrated in Fig.1(b). At the beginning of the growth, when the starting materials are completely melted, the seed is displaced in the upward direction to establish its physical contact with the melt sited on the bottom of the nozzle. This event corresponds to growth initiation. Thereafter, the growth is progressed by pulling-down the melt and its solidified part (crystal) in the downward direction. A relatively high temperature gradient in the vicinity of the liquid-solid interface and the small size (cross-section) of the grown crystal allow application of growth rates that are much larger than those used in conventional methods such as Czochralski [Cz], Vertical Bridgman [VB], and Floating Zone [FZ] techniques.

Many optical and scintillating materials are composed of a host (matrix) substance that contains one or several doping ions as (an) emission center(s). Generally, the dopant concentration affects optical and scintillation properties of the material [6-8]. Therefore, inhomogeneity of the dopant distribution in the single crystals causes degradation of the optical and scintillation properties and uncertainty of the material parameters and material performance. Experimental and simulation results on the dopant distribution in the single crystals grown by the μ -PD method were discussed in the past [9-13]. The results indicated that the dopant concentration in the central parts (regarding cross-sectional cuts) was larger than that in the peripheral parts when the segregation coefficient, k , of the dopant exceeded unity ($k > 1$). Oppositely, the dopant content in the center of the crystal was lower than that around the periphery in the case of $k < 1$. Thus, the inhomogeneity of the dopant distribution in the single crystals grown by the μ -PD method is an important issue that should be examined in details. It is assumed that improvement of the uniformity of the μ -PD crystals may result in an improvement of their optical and scintillation properties.

Based on the above considerations, we simulated the dopant distribution in the radial direction of single crystals grown by the μ -PD method using the parameters of Ce-doped $\text{Y}_3\text{Al}_5\text{O}_{12}$ [Ce:YAG] together with crucibles with one and five capillaries in the nozzle to improve the homogeneity of the dopant distribution [14].

2. Simulation model and results

The dopant distribution in the radial direction of Ce:YAG single crystals grown by the μ -PD method using crucibles with one and five capillaries was simulated numerically. The computational model only includes the capillary-channel and the meniscus zone. Details of the simulation model was described in [14]. The equilibrium segregation coefficient of the Ce ion in a YAG single crystal is much less than one [12] and the Ce ion retains preferentially in the melt rather than the crystal during the crystal growth. In the simulation, the melt is taken as an incompressible Newtonian fluid with constant viscosity and density. The results of the simulations demonstrated that the application of crucibles with a multi-channel capillaries

design could improve the dopant distribution in the radial direction. In such conditions, the Ce concentration at the spots corresponding to the positions of the capillaries could be larger at several locations as compared to the unique location in the Ce:YAG crystals grown using the crucible with a single capillary channel. In this way, the overall uniformity of the crystal could be improved. For experimental examination of the above conclusions, we developed two Ir crucibles with one and five capillary channels, and Ce:YAG single crystals were grown by the μ -PD method using these crucibles to understand the effects of the capillary number on the dopant distribution.

3. Experimental

Ce:YAG single crystals were grown by the μ -PD method using two types (1C and 5C) of Ir crucibles with a square-shaped nozzle at the bottom (Fig.2). The 1C crucible had one capillary channel positioned at the center of the bottom of the nozzle as shown in Fig.2(a). Alternatively, there were five capillaries at the center and on the diagonal lines of the bottom of the nozzle of the 5C crucible as illustrated in Fig.2(b). The diameters of their capillary channels were $\phi 0.4$ mm and so the total cross section of the five capillary channels was five times larger than the cross-section of the one capillary channel. The capillaries in the 5C crucible were placed diagonally at equal distances as illustrated in Fig.2(c).

Starting materials were prepared from α - Al_2O_3 , Y_2O_3 , and CeO_2 powders ($> 4\text{N}$ purity). The powders were mixed at nominal compositions of $(\text{Y}_{1-x}\text{Ce}_x)_3\text{Al}_5\text{O}_{12}$ with $x = 0.02$ and 0.05 , and the mixed powders were sintered at 1100°C for 12 hours in air. The as-sintered substances were loaded into the crucibles and Ce:YAG single crystals were grown according to the diagram shown in Fig.1. Details of the single crystal growth by the μ -PD method are described in [3,4]. Undoped YAG single crystal was used as a seed and the Ce:YAG single crystals were produced at 0.05 mm/min (pulling-down) growth rate without rotation in N_2 gas flow to avoid oxidation of the crucible material.

The as-grown Ce:YAG single crystals were cut perpendicular to the growth direction at 2 and 20 mm distance from the position of growth initiation (first physical contact between the seed and the melt). The specimens were then polished and used for the measurements of chemical composition variations in the radial direction.

Chemical composition analysis was performed by the electron probe micro-analyzer [EPMA](JEOL JXA-8530F). The main purpose of the analysis was to examine the spatial distribution of Ce dopant because it was the only ingredient in the system that had a segregation coefficient very different from unity. The measurements of the chemical compositions were performed along two lines, A and B, as illustrated in Fig.2(c).

4. Results and Discussion

The as-grown crystals had yellow color caused by incorporation of Ce^{3+} dopant into the matrix of generally colorless YAG. The crystals had shape of rectangular columns in some degree replicating the shape of the crucible die. This was possible due to the minimization of the thickness of the meniscus established during the crystal growth (Fig.1). In this way, the experimentally observed meniscus thickness was approximately $100\sim 300$ μm . The typical liquid-solid interface and the meniscus observed during the growths are shown in Fig.3(a). The as-grown crystals are shown in Fig.3(b).

The polished specimen cut from the Ce:YAG crystal grown using the crucible with one capillary [Ce:YAG(1C)] was comparatively transparent in the center area while the peripheral fractions were opaque and had a highly saturated yellow color. Based on excessive coloration of the peripheral fractions of the crystals, it was assumed that Ce concentration in

the periphery of the polished specimens was greater than that in the center of the specimens. On the other hand, the polished specimens cut from the crystals grown using the crucible with five capillaries [Ce:YAG(5C)] presented a different color distribution as illustrated in Fig.3(c). In the Ce:YAG(5C) specimens, the yellow coloration was reduced in five spots corresponding to the five locations positioned just below the capillary channels of the crucible die. Based on this observation, it was assumed that the Ce concentration at these five spots was lower than that in the other areas.

Ce distribution in the radial direction for the specimens cut at 2 mm position from the growth initiation is shown in Fig.4. In the case of the Ce 2 mol%:YAG(1C) specimen, the Ce concentration in the peripheral area was greater than that in the center portion (Figs.4(a),(b)). This observation correlated well with the low segregation coefficient ($k \sim 0.01$) of the Ce^{3+} ion in the YAG single crystals [12]. The result is also consistent with the results of our simulations. However, the Ce 2 mol%:YAG(5C) specimen showed a Ce distribution similar to that of the Ce 2 mol%:YAG(1C) specimen, and there was no clear effect of the number of capillary channels on the Ce distribution. Moreover, the Ce 2 mol%:YAG and Ce 5 mol%:YAG specimens had a very different Ce distribution as it follows from the comparison of Figs.4(a),(b) and Figs.4(c),(d), respectively. In the case of the Ce 2 mol%:YAG, Ce concentration around the periphery area was higher than that around the center area while the center point indicated slightly higher Ce concentration than the surround. Meanwhile, Ce distribution was improved in the Ce 5 mol%:YAG(5C) compared to the Ce 5 mol%:YAG(1C). However, the variations of the Ce concentration on the measurement lines were not symmetric. The reason of the asymmetric variations is considered to be due to the instability of crystal growth at the position just after the seed-touch.

Figure 5 presents the Ce distribution in the radial direction in the specimens cut at 20 mm distance from the position of growth initiation for the Ce 5 mol%:YAG(1C) and Ce 5 mol %:YAG(5C) crystals. The Ce concentration in the center area of the Ce 5 mol %:YAG(1C) crystal at this distance (20 mm) was lower than that at the peripheral area and the latter qualitatively similar to the distribution observed in the specimens cut at 2 mm distance as it follows from comparison of Figs.5 and 4(d), respectively. Moreover, there was a clear effect of the increase of the number of capillary channels on the Ce distribution in 20 mm distant samples (Fig.5). This effect was more pronounced compared to the results for the specimens cut at 2 mm position, Fig.4(d). The Ce concentration at the positions below the capillaries was larger than in other areas and the overall homogeneity of the Ce distribution in the radial direction was improved by the increase of the number of capillaries. These results are consistent with our previous report on the simulation of the μ -PD method for the crucible with multi-channel capillaries design [14].

5. Conclusions

2 mol% and 5 mol% Ce-doped YAG single crystals were grown by the μ -PD method from Ir crucibles having one and five capillaries at the nozzle. Ce distribution in the radial direction was inspected for the specimens cut at 2 and 20 mm distance from the positions of growth initiation (first physical contact between the seed and the meniscus). In some degree, the Ce distribution at 2 mm position was improved in the Ce 5 mol%:YAG(5C) crystal compared to the Ce 5 mol%:YAG(1C) one according to Fig.4(c) while the variations of the Ce concentration on the measurement lines were not symmetric. However, a clear positive effect of the increase of the number of capillaries on the Ce distribution was observed in the specimen cut at 20 mm position (Fig.5), and the Ce concentration at the positions below the capillaries was higher than that at the other areas. The results indicated that increase of the

number of capillaries is an efficient strategy of improvement of the μ -PD crystals in the radial direction.

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Figure Captions

Figure 1 (a) Schematic diagram of the μ -PD system used for the growth of oxide crystals and (b) details of the μ -PD crucible setup.

Figure 2 View of the Ir crucibles produced with (a) one and (b) five capillary channels at the nozzle. (c) The chemical composition analysis of the polished specimens cut perpendicular to the growth axes was performed along lines A and B.

Figure 3 (a) View of the liquid-solid interface observed during the crystal growth and (b) appearance of the as-grown Ce:YAG single crystals grown by the μ -PD method. (c) Non-uniform coloration of the polished Ce:YAG specimens cut at the distances of 2 and 20 mm from the position of growth initiation correlated with the number of channels in the crucible nozzle.

Figure 4 Ce distribution in the radial direction for the specimens cut at 2 mm distance from the position of growth initiation. The results correspond to (a) lines A and (b) B for the Ce2mol%:YAG crystals and (c) line A and (d) B for the Ce5mol%:YAG crystals.

Figure 5 Ce distribution in the radial direction for the specimen cut at 20 mm distance from the position of growth initiation for the Ce5mol%:YAG crystals.

Figure 1

(a)

(b)

(c)

Figure 2

Figure 3

Figure 4

Figure 5