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Dopant segregation in rare earth doped lutetium aluminum garnet single crystals grown by the micro-pulling down method

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ABSTRACT

Nd, Ho, Er, and Tm doped lutetium aluminum garnet (LuAG) single crystals were grown using the micro-pulling down (μ-PD) method. The crystals were produced from the melts containing 3 mol% of the dopants. The axial and radial dopant distribution were measured by electron probe micro analysis. Nd^{3+} and Ho^{3+} ions concentrated in the rim ($k^0 < 1$) and the radial concentration showed concave curvature. k^0 is the segregation coefficient of the dopant with respect to the given host phase. In the case of Er^{3+} and Tm^{3+} ions, the k^0 value is considered to be nearly 1 and the radial dopant distribution profiles were almost flat.

1. Introduction

The micro-pulling down (μ-PD) method has been used as a suitable tool for screening of single crystalline materials. It requires small amount of raw materials for one crystal growth process; typically less than 1 g. In addition, the growth speed is higher than that of conventional methods such as Czochralski (CZ), Bridgeman, and Floating Zone (FZ) methods [1]. Many novel oxide and fluoride single crystalline scintillators have been developed by the μ-PD method like Pr-doped lutetium aluminum garnet (Pr:LuAG) and Ce or Eu-doped ^{6}lithium calcium aluminum fluoride (Ce:^{6}LiCAF, Eu:^{6}LiCAF) single crystals [2–6].

In this study, we focused on the LuAG as a host lattice, which are promising candidates for scinillator applications because of the high Zeff, chemical stability, congruent composition, and rare earth site for doping of luminescence center [2,3,7]. Our group recently reported scintillation properties of Nd:LuAG single crystals grown by the μ-PD method [8]. The scintllator showed emission peaks originated from 4f–4f transitions of Nd^{3+} ions in the visible region and the light yield was 7600 photons/MeV by the irradiation of gamma-ray. However, Nd distribution in the crystal has not been clarified yet. In this work, we investigated the concentrations of the various rare earth ions (Nd, Tm, Er, and Ho) in the LuAG host lattice. All the crystals were grown by the μ-PD method. Variation of the dopant concentration along to the growth direction as well as the cross section perpendicular to the grown direction was investigated.

2. Experimental procedures

Nd:LuAG, Ho:LuAG, Er:LuAG, and Tm:LuAG single crystals were grown by the μ-PD method. The dopant concentration of nominal composition was 3 mol% for all the crystals. The corresponding starting materials were prepared from Lu_2O_3, Al_2O_3, Nd_2O_3, Ho_2O_3, Er_2O_3, and Tm_2O_3 powders (>4 N purity). The starting materials were weighed as nominal compositions and they were sufficiently mixed with an argent mortar. Mixed powders were entered into an Ir crucible with a 4×4 mm^2 die on the bottom. The Ir crucible, alumina insulators, and quartz tubes were set in the μ-PD machine. The crucible was heated up to the melting point of LuAG by the RF coil. The melt of the samples came out of the bottom of the crucible through the hole of the die and touched an undoped LuAG seed. Finally, the melt was pulled down by pulling-down of the seed at 0.05 mm/min. The seed crystal was a ⟨100⟩ oriented undoped LuAG single crystal grown by the Czochralski method. The charge in the crucible was approximately 1 g. The crystal growth was performed under 0.5 l/min flow of N_2 gas.

The radial and axial distributions of the dopant concentration in the grown crystals were measured using electron probe micro analysis (EPMA). In the EPMA measurement, the standards of LuP_5O_{14}, Al_2O_3, NdB_6, HoP_5O_{14}, ErP_5O_{14}, TmP_5O_{14} were used. Using these standards, quantitative values of elements were

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obtained. The signals were strong and EPMA measurements were performed accurately.

Transmittance and reflectivity were measured with spectrophotometer (V-550, JASCO, and UV-2550, Shimadzu, respectively). From these results, absorption coefficients were calculated.

3. Results and discussion

3.1. Crystal growth

Nd, Ho, Er, or Tm 3 mol% doped LuAG single crystals were grown by the μ-PD method. Almost all the melt of the starting materials in the crucible were pulled down. Therefore, solidification fraction of all the crystals is nearly 1. In Fig. 1, thickness of meniscus during crystal growth was about 200 μm. The interface is not flat perfectly because of the heat flow. We think that we may overcome this problem by improving the setting of the hot zone and optimization of gas flow. Therefore, further research is required in this point. As it can be seen in Fig. 2, the grown crystals were square-shaped, 4 mm in height and width, and 15 mm in length and they had a milky surface. The opaque part is considered to be Al-rich phase, which are deduced by the SEM-EDX analysis. This phase was observed in the edge of the Tm:LuAG crystal. Therefore, the cause of the opaque part is considered to be formation of the Al-rich phase. However, the phase existed only at the surface of the crystal and there is no secondary phase in the crystals except for the surface. All the crystals were polished as a mirror and they were transparent.

3.2. Dopant segregation

The crystals polished were analyzed for dopant concentration. Fig. 3 shows the composition analysis of the central region of the crystals made in the axial direction. Dopant concentration in the Nd:LuAG single crystals was nearly constant along to the growth direction except for the final edge of the crystal and the value was about one tenth of the initial doping level. Excess Nd^{3+} ions were located in the final edge of the crystal. Except Nd:LuAG, the dopant concentrations in all the crystals were nearly constant in the entire central region of the crystals and they were almost equal to the initial doping level.

Radial dopant distributions along the radial direction of the samples are illustrated in Fig. 4. Nd^{3+} ions showed strong radial distribution and formed the concave profile. Ho^{3+} ions demonstrated the same axial segregation behavior like Nd^{3+} ions, however the radial concentration profile was flatter than that of Nd^{3+} ions. The rim region had a little higher concentration than the central region. In the case of Er^{3+} and Tm^{3+} ions, the profiles were nearly flat.

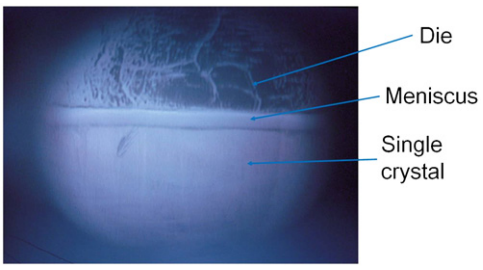

Fig. 1. Solid–liquid interface observed by CCD camera during the single crystal growth of Ho:LuAG by the μ-PD method.

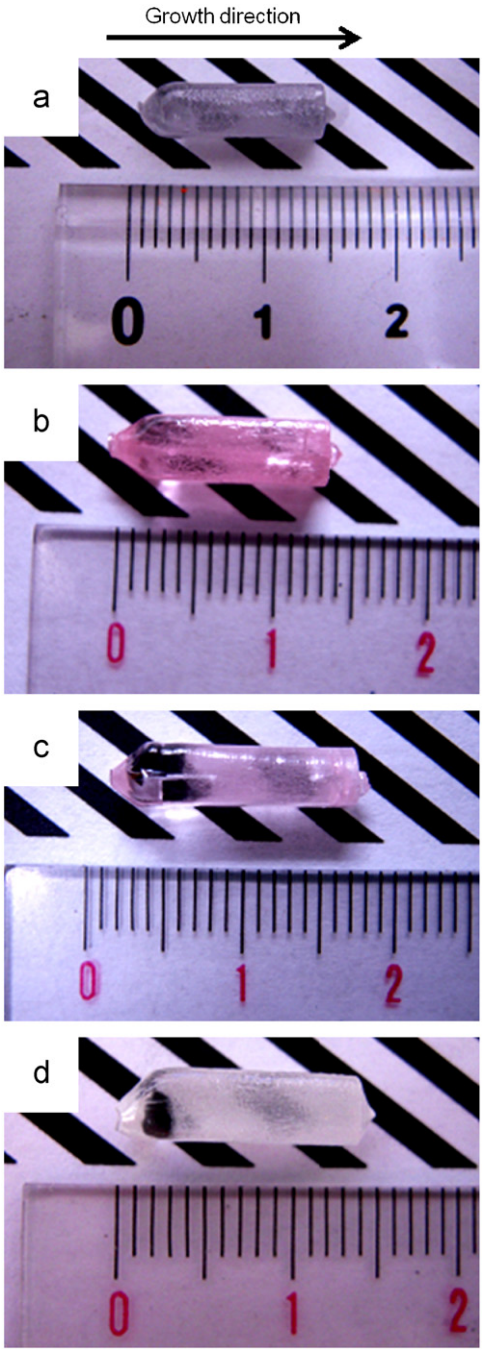

Fig. 2. View of as grown (a) Nd:LuAG, (b) Ho:LuAG, (c) Er:LuAG, and (d) Tm:LuAG single crystals.

Simura et al. calculated the radial dopant distribution in yttrium aluminum garnet (YAG) single crystals grown by the μ-PD method using the crucible with a die [9]. The dopant concentration is higher at the rim than that in the core for the segregation coefficient (k^0) < 1. If the k^0 is nearly 1, the radial concentration profile is flat. Taking into account this report, k^0 values of the dopants in the crystals are estimated as listed in Table 1. Table 1 also shows ionic radii of the dopant elements and lutetium [10]. The difference between the ionic radii of Nd^{3+} and Lu^{3+} ions is very large compared to the other dopants. Therefore, it is difficult for Nd^{3+} ions to substitute with Lu^{3+} ions in the crystal. As a result, Nd concentration in the rim of the crystal was higher than the doping level and k^0 is less than 1. When the ionic