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Growth of homogeneous Nd:LGGG single crystal plates by edge-defined film-fed growth method

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ABSTRACT

Device-size Nd^{3+}:$(Lu_xGd_{1-x})_3Ga_5O_{12}$ (Nd:LGGG) single crystal plates have been grown by edge-defined film-fed growth (EFG) method for the first time. The problems encountered during the crystal growth have been discussed and solved, resulting in a single crystal plate with a length of 180 mm. In particular, the evaporation loss of Ga_2O_3 composition during the crystal growing has been depressed efficiently by using an Ir lid. The crystal perfection was confirmed by X-ray rocking curve with a FWHM of the 32 arc-sec, meaning a high crystalline quality. It was very interesting to find that the distribution of Nd^{3+} in the crystal grown by EFG method was more homogeneous than that in Cz method, benefitting from the larger segregation coefficient of Nd^{3+} in EFG method. The thermal conductivity was measured to be 8.1 W m^{-1} K^{-1} at room temperature. All the properties showed that the Nd:LGGG crystal plates grown by EFG method were promising for high power laser application.

1. Introduction

As compact and powerful tools, the solid-state lasers have attracted great attention for numerous applications in processing, medical uses, communication, optical storage, etc. [1,2]. Therefore, many attentions have been paid to the laser crystal as a key element for laser operation. As a representative crystal, neodymium (Nd) doped $Gd_3Ga_5O_{12}$ (GGG) [3] and its modified crystals including Nd:$Gd_3(Ga_{1-x}Sc_x)_5O_{12}$ (Nd:GSGG) [4], Nd:$Gd_3(Ga_{1-x}Al_x)_5O_{12}$ (Nd:GAGG) [5,6], Nd:$(Lu_xGd_{1-x})_3Ga_5O_{12}$ (Nd:LGGG) [7–9] have been studied in detail due to the advantages of easy fabrication of large size crystal, high doping concentration of rare earth ions, good thermal conductivity and good physical and chemical stability. Among them, the disordered Nd:LGGG crystals have been proved to be suitable for mode-locking and Q-switching laser operations, especially for the selective and particular wavelength laser generation around 1.3 μm, which benefits from the broad emission spectrum [10–12]. In consideration of high power laser generation, homogeneous and big size crystal rods or slabs were necessary. However, big size Nd:LGGG crystals with high optical quality are not easy and economical to get due to the interface instability and the segregation coefficient of Nd^{3+} in Nd:LGGG is much smaller than 1 [3].

Edge-defined film-fed growth (EFG) method is a high efficient melt growth method, and has been widely used in the crystal growth of Si, sapphire, Nd:YVO_4 and so on [13–18]. The cross-section shape of the crystal is limited by the size of the die upper surface in EFG process. Therefore, a device-size crystal could be grown through using suitable die. At the same time, compared with traditional Cz method, EFG method offers a way to cut production costs of crystal. In EFG process, the momentum and mass transfer are depend on the capillary channel [19]. Therefore, the growth interface is stable and the problem of center core in Czochralski method could be avoided effectively. Moreover, the segregation coefficients of dopants are usually close to one [20]. Considering the above advantages of EFG technique, it should be a good choice for the growth of large scale RE (rare earth) doped GGG series crystals for high power laser application.

In this work, high quality and big size Nd:LGGG crystal plate has been grown successfully after optimizing of the crystal growth parameters. The distributions of the doped Nd^{3+} and Lu^{3+} were homogeneous and the segregation coefficients of Nd^{3+} and Lu^{3+} were calculated to be 0.84 and 1.12, respectively. Furthermore, the thermal and optical properties of the as-grown crystal have been investigated.

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2. Experimental section

2.1. Crystal growth

The Nd:LGGG crystals have been grown by the EFG furnace with a radio frequency heating system. Raw materials of 4N purity Nd_2O_3, Lu_2O_3, Gd_2O_3 and Ga_2O_3 powers were accurately weighed stoichiometrically according the molecular formula. In order to compensate the evaporation loss during the crystal growth, an excess of 2 wt% Ga_2O_3 was added into the oxide mixture. The concentrations of Nd and Lu ions in the starting materials were fixed to be 2.5 at.% and 10 at.%, respectively. After mixing adequately, the mixture was pressed into tablets and then sintered at 1300 °C for 30 h in air. The obtained polycrystalline materials were melted in an Ir crucible with the dimension of Φ 60 × 60 mm^3, under an atmosphere of 50% CO_2, plus 50% Ar. The CO_2 in the atmosphere would decompose into CO and O_2 at high temperature and the O_2 could minimize Ga oxide evaporation. To further decrease the evaporation of Ga oxide at melting point, an Ir lid with a diameter of 64 mm has been put atop the crucible. An Ir die, with an end face of 3.5 × 25 mm^2 and 7 capillaries with the diameter of 0.5 mm, was dipped into the crucible. The crystals were pulled at a rate of 6–15 mm/h with a ⟨1 1 1⟩ direction Nd:GGG crystal seed. After the growth, the crystals were cooled down to the room temperature at a rate of 30 °C/h. In order to release the thermal stress, the crystals were annealed at 1400 °C for 60 h in air.

2.2. Characterization techniques

The crystal quality was measured by using high-resolution X-ray diffraction (HRXRD) with a Bruker-AXS D5005HR diffractometer which was equipped with a Cu-Kα radiation (λ = 1.54056 Å) and four-crystal Ge (2 2 0) monochromator.

The concentrations of Nd^{3+} and Lu^{3+} in the as-grown crystal and polycrystalline materials were measured by the X-ray fluorescence analysis (Rigaku, ZSX primus II). Then the effective segregation coefficients of Nd^{3+} and Lu^{3+} were calculated based on the measured results.

The specific heat of Nd:LGGG crystal was measured by a differential scanning calorimeter (Perkin-Elmer Diamond model DSC-ZC) up to 300 °C with a heating rate of 5 °C/min. The thermal diffusivity of the crystal was measured by laser pulse method with a Netzsch Nanoflash model LFA 457 apparatus in the temperature range of 25.7–500.2 °C with the sample of 4 × 4 × 1 mm^3 in dimensions.

3. Results and discussion

3.1. Optimization of the EFG crystal growth process

Several problems have been encountered during the growth of Nd:LGGG by EFG method. The main problems have been analyzed in detail and the growth parameters have been optimized to obtain a large size and high quality crystal. The course of exploration was shown and discussed in the following text.

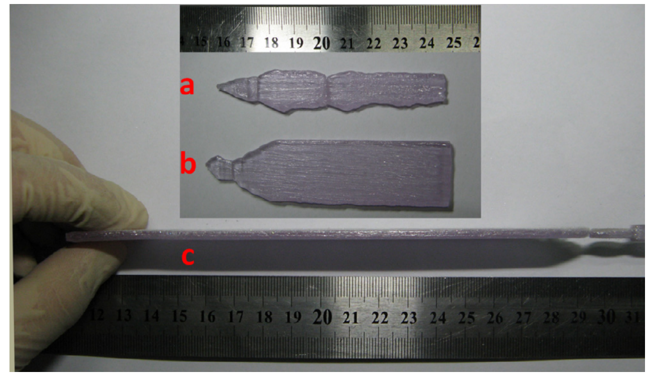

Fig. 1. Photograph of Nd:LGGG crystals grown by EFG method.

In the initial stage, the crystal could not spread out on the whole top section of the die, and shape of grown crystal was not uniform, as shown in Fig. 1a. A large lateral thermal gradient has been considered as the reason that the crystal could not expand along the width direction. This was because the both far ends of the Ir die were too hot when the temperature of the center part was suitable for the crystal growth. Therefore, the lateral thermal gradient should be decreased. After the adjustment, the crystal could spread over the whole top surface of Ir die, as shown in Fig. 1b.

However, it was still difficult to grow a big size crystal because that the crystal likely separated with the Ir die during the crystal growth. It was believed that this phenomenon was a consequence of the large thermal gradient in the pulling direction. In order to solve this problem, an Ir after-heater (Φ 60 × 100 mm^3) was added to reduce the thermal gradient in the pulling direction. After the adjustment, a high quality Nd:LGGG plate with 1 in. in width and 180 mm in length was grown successfully. The cross-section of the crystal was stable and matched the shape of the die upper surface very well, as shown in Fig. 1c.

The evaporation loss of Ga_2O_3 composition at the melting point of crystal was efficiently decreased by the Ir lid atop of the crucible. Comparing to the Cz technique with an open-like growing environment, this is a huge advantage of EFG method for improving the crystal homogeneity and growth stability.

The surfaces of the as-grown crystals were very rough which was similar to that of the crystals grown by CZ method due to the remelting during the growth process [21]. Nevertheless, the interior of the crystal was transparent, as can been seen after grinding (Fig. 2b) and polishing (Fig. 2c).

3.2. Crystal quality

The crystalline quality was evaluated by HRXRD. The peak of the rocking curve was symmetrical and a typical full width at half

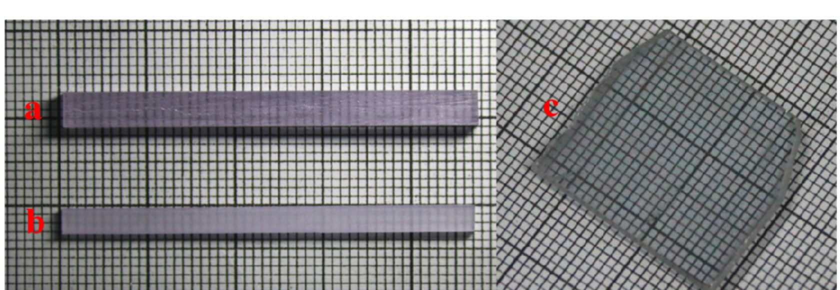

Fig. 2. Photograph of Nd:LGGG crystal rods and polished crystal plate.