Effect of the addition CeO$_2$ on the growth of YIG single crystal fibers using laser heated pedestal growth method

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ABSTRACT

Cerium-substituted yttrium iron garnet (Ce:YIG) exhibits the greatly large Faraday Effect, thus it has been widely studied. With a LHPG method, however, it is hard to grow pure yttrium iron garnet (YIG) single crystal fibers due to oscillatory instability of the melt and constitutional supercooling effect. From the experimental observation, the addition of CeO$_2$ into YIG fiber would increase the periodic oscillation of the melt ascribed to Ce-doping, the experimental segregation coefficient less than the unit, would decrease the melting point and the molten zone became wider, which resulted in a decrease of the temperature gradient. An increase of the laser power input could be used to introduce a steeper temperature gradient, and then the Ce-substitution YIG single crystal fibers could be grown at the faster pulling rate. But it was well considered that constitutional supercooling effect and flow oscillation in the melt would also influence the quality of the grown fibers. Moreover, the solubility limit of cerium ions in Ce-substituted Ce:YIG single crystal fiber, which was grew in an ordinary atmosphere, was found to be approximately 0.3. When the amount of CeO$_2$ added was over $x = 0.3$, the inclusion of the CeO$_2$ phase was residual in the core region of the grown Ce:YIG crystal fibers.

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1. Introduction

Yttrium iron garnet (Y\(_3\)Fe\(_5\)O\(_{12}\), YIG) single crystal has been widely used in magneto-optical applications of fiber-optical communication systems because it has both large Faraday rotation and high transparency in the near-infrared region [1-3]. However, the amount of Faraday rotation of YIG in a unit of length is not large enough to satisfy miniaturized design for the device, with the development of the technology. Therefore, how to increase the Faraday rotation of YIG has attracted much attention. Recently, much research on the substitution of YIG materials with respect to the magneto-optical properties has been carried out [4-6]. Cerium-substitution YIG (Y\(_{3-x}\)Ce\(_x\)Fe\(_5\)O\(_{12}\), Ce:YIG) single crystals have already been extensively studied because the addition of cerium oxide can significantly enhance the Faraday rotation and reduced optical propagation loss [5,7,8]. Consequently, Ce:YIG material is of more promising material for magneto-optical devices. In this study, the laser heated pedestal growth (LHPG) technique was applied to grow single crystal fibers of Ce:YIG. This system is a tiny floating zone and crucible-free method, so it can avoid contamination and the growing process is easier to observer.

Growing YIG single-crystals is difficult because of flow instability in the melt. In our previous study [9], to obtain good-quality YIG single-crystal fibers by the LHPG method, it was necessary for the melt to have proper composition and for the flow in the molten zone to be quasi-stable. For the growing Ce-substituted YIG single crystal, however, it might be harder than the growing pure YIG single crystal due to the fact that the dopant effect would induce constitutional supercooling [10]. In addition, Ce\(^{3+}\) ion is hard to substitute for the Y\(^{3+}\) ion in YIG because the radius of Ce\(^{3+}\) (0.118nm) is significantly larger than that of Y\(^{3+}\) (0.106nm). Cerium oxide is difficult to dissociate at a low temperature [11, 12] and the experimental segregation
coefficient \( k_e \) of Ce in YIG was less than the unit \([13, 14]\) which meant that the melting temperature of Ce:YIG would be lower than that of pure YIG. Therefore, the Ce:YIG single-crystal growth conditions have to be suitably modified from those of YIG single-crystal.

Up to the present, much research has been devoted to the importance of Ce-dopants on the magneto-optical properties and application \([15, 16]\). However, the growth parameters of Ce:YIG crystal such as the pulling rates and the heating input power have rarely been investigated. Perhaps it is because the use of a slower pulling rate could grow the YIG single-crystal for avoiding constitutional supercooling and holding the quasi-stable melt \([17]\). Therefore, the method of a slower pulling rate was also adopted to grow Ce:YIG single crystal. In this work, we study the influence of pulling rate and laser heating power input on the growth of YIG single crystal fibers at the various additions of cerium oxide. Moreover, the optimal relation between these parameters for growing the better quality of Ce:YIG single-crystal fibers was investigated.

2. Experimental procedure

A series of Ce:YIG ceramic rods was prepared by the solid state sintering method. Powders of \( \text{Y}_2\text{O}_3 \), \( \text{Fe}_2\text{O}_3 \) and \( \text{CeO}_2 \) (99.99% purity), \( \text{Y}_{3-x}\text{Ce}_x\text{Fe}_5\text{O}_{12} \) with atomic weight ratios of \( (x = 0, 0.1, 0.2, 0.3, 0.4) \), were milled, mixed, calcined pulverized, screened, pressed and sintered at 1300 ~ 1450\(^\circ\)C for 10 hours in air. Details of the procedure of fabricated ceramic were described in our previous report \([18]\). The density of a series of the Ce:YIG ceramics was measured, being up to 96% of the theoretical density, using the Archimedes principle. The obtained ceramic was cut into square rods approximately 0.8 mm \( \times \) 0.8 mm in cross section.
and 40 mm long.

This LHPG system was developed by Chen and Hu [19]. The laser beam was emitted from the cavity of a CO\textsubscript{2} laser (100-watt, wavelength = 10.6 μm), then divided into two beams by a 10/90 (reflection/transmission) beam splitter. The reflection beam was used as a reference power of the heating condition measuring by a power-meter and the transmission beam was used as the heat source. During crystal growth an infrared thermal radiometer was utilized to observe the thermal-radiation intensity of the molten zone, and the observed temperature fluctuation also could reflect the flow in the melt [20, 21]. In each experiment of the crystal fiber growth both the seed ceramic rod and the feed ceramic rod were of the same type of ceramic, and the growth was processed in air. The selected pulling rates were 0.8, 0.5, 0.4, 0.3, 0.2, 0.1, 0.05 mm/min, respectively, and the downward growth was operated in order to prevent any bubbles from disturbing the crystal growth interface [22]. The size of the grown crystal fibers were around 0.7 - 0.8 mm in diameter and up to 30 – 40 mm long.

The compositions of the grown crystal fibers were examined using an X-ray powder diffractometer (XRPD). All of the diffraction intensities are read after computing and subtracting the pattern background and 0.2° of smoothness. The lattice constants of grown Ce:YIG fibers were examined by X-ray single-crystal diffraction. In order to observe the micro-structure of the interior, the fibers were mechanically polished along the pulling direction, and then an optical microscope (OM) and/or a scanning electron microscope (SEM) were used to observe the cross sections. The composition distribution along the pulling direction of the fibers was measured using an electron-probe microanalyser (EPMA).
3. Results and discussion

Lim et al. [23], Hu et al. [17], and Mao et al. [9] used the LHPG method to investigate the growth of YIG single crystal fibers, showing that a slower pulling rate would be helpful for YIG single crystal growth. Hu et al. [11] also mentioned that the flow in the molten zone was dominated by oscillatory thermocapillary convection and it oscillated periodically throughout the growth. Usually the oscillatory instability of the molten zone would cause variation in growth rate [24, 25]. Therefore, the precipitating rate would not merely include the pulling rate; it should add the oscillating rate of molten zone. The growth rate of YIG was periodical fluctuation, not a constant. Based on the constitutional supercooling criterion [10], cellular structure would occur in the grown crystal when the freezing interface rate exceeds a certain critical value. Consequently, the relationship between the quality of the grown YIG crystal fibers and the pulling rate was schematically illustrated in fig. 2. In case of precipitating rate above the threshold rate of occurring cellular structure, the grown crystal will fill with cellular structure as the status of Fig. 2a. If the precipitating rate is partial larger than the threshold rate, the periodical cellular structure may be formed in the grown crystal as the status of Fig. 2b. If the precipitating rate is below the threshold rate, it can be grown single crystal as the status of Fig. 2c. Moreover, the composition of the cellular structure in grown YIG crystal was main YFeO₃ [9, 26] so more cellular structure induced stronger diffraction intensity of the YFeO₃ appeared on the YIG XRPD diffraction pattern.

After realizing the previous mechanism of growing YIG crystal fiber, we processed the growth of Ce:YIG crystal fibers. In order to confirm whether the YFeO₃ existed in Ce:YIG fibers, we used XRPD to identify the compositions. According to the Ref. [17, 26, 27], diffraction intensity ratio (DIR) was defined as
D.I.R = \frac{I_{YIG}(420)}{I_{YIG}(420) + I_{YFeO_3}(121)} \times 100\% , \quad (1)

where $I_{YIG}(420)$ is the strongest diffraction intensity for YIG at (4 2 0) face in the XRD diffraction pattern, and $I_{YFeO_3}(121)$ is the strongest diffraction intensity for YFeO$_3$ at (1 2 1) face. The lower the DIR, the more the amount of YFeO$_3$ in the grown crystal fibers is. When a value of DIR reaches 100%, it indicates this grown crystal fiber is a pure or free foreign phase composition. Fig. 3 shows the relationship between the DIR and the pulling rates of the grown crystal fibers, for different CeO$_2$ additions to the YIG material, using 1.1 W reference power. The results indicate that, the faster the pulling rates, the poorer purity of the grown Ce:YIG ($x = 0.1 - 0.3$) crystal fibers. The grown crystal fibers at the slower pulling rates could have a pure composition. Furthermore, it could be found out the fact that more amount of Ce-doping was needed to use a lower pulling rate to grow crystal fibers with free foreign phase. It is because a higher solute concentration tends to formed cellular structure in the grown crystal according to the constitutional supercooling theory [10]. One of the best ways to avoid the occurrence of constitutional supercooling is to decrease the pulling rate or increase the temperature gradient on the freezing interface. Consequently, to grow a Ce:YIG crystal fiber with free foreign phase was basically needed to reduce the pulling rate with increasing the amount of Ce-doping.

Specifically, we see a interesting case that the maximum pulling rate for grown free foreign phase of Ce:YIG crystal fibers at $x = 0.2$ and 0.3 was equivalent, shown in fig. 3. Based on the foregoing, growing free foreign phase of crystal fiber with $x = 0.3$ should use a slower pulling rate, but the experimental results did not satisfy this trend. Besides, during the crystal growth we observed that the period of the flow oscillation in the melt increased with increasing the CeO$_2$ addition by a thermal
radiometer, and the values of the period were shown in fig. 4. It is well known that
the thermocapillary (Marangoni) flow caused by the surface tension gradient is
dominantly in the small size of the floating zone. Often, the use of the magnitude of
Marangoni number represents the strength of this flow. When the Marangoni
number is larger than a certain critical value, it was induced the instable flow such as
the periodically oscillatory motion. Consequently, the flow oscillation in the melt of
the Ce:YIG materials was a result of Marangoni flow instability. D. Schwabe et al.
[28] have pointed out that the frequency of the oscillation was proportional to the
temperature gradient. Hence, the period of flow oscillation increased with
increasing the CeO$_2$ addition was perhaps due to a decrease of the temperature
gradient in the melt. It is well know that the experimental segregation coefficient of
Ce in YIG was less than the unit, indicating that the melting point of samples
decreased with an increase of the CeO$_2$ addition. When the input power was
controlled to keep a constant, the molten zone with an addition of CeO$_2$ would
become wider. Therefore, an increasing length of the molten zone would result in a
decrease of the axial temperature gradient, and then an increase of oscillatory period
in the Ce:YIG melt was induced. Nevertheless, it may be also due to the fact that the
CeO$_2$ addition changes some physical parameters of YIG, such as viscosity and
surface tension. However these properties of the melt about YIG and Ce:YIG are
exactly unknown, it is hard to presently discuss. Therefore, the effect of the
variation of those properties on the melt flow is out of consideration in this study.

The increasing oscillatory period was ascribed to the decreasing temperature
gradient of the melt from the mention above. The temperature gradient could be
affected by adjusting power input, and it was prone to increase or decrease depending
on its properties. Fig. 5 demonstrates the relationship between the reference power
and the pulling rate of obtained good quality crystal fibers, for different CeO$_2$ additions to the YIG material. For YIG samples, the larger power input needed the slower pulling rate to grow pure crystals, which agrees well with other work [17], because the thermocapillary convection became stronger and more unsteady with the increasing power input. For the samples with CeO$_2$ addition, the use of a slight overheating could grow crystal with free foreign phase at the little faster pulling rate. However, a larger power input also needed the slower pulling rate to grow good quality crystal fibers. We suggest that the increasing power input could enhance the temperature gradient of the melt for the Ce:YIG samples, and then a induced steeper temperature gradient is helpful to grow good quality crystal fibers at the faster pulling rate. But a larger temperature gradient would also decrease the period of the flow oscillation of the melt, which would deduce the precipitating rate became faster. When the precipitating rate exceeds a certain critical value, the cellular structures would be formed in the grown crystal and degraded the quality of crystal fibers. For growing Ce:YIG crystal fibers, therefore, a suitably increasing power input, resulted in a steeper temperature gradient, was beneficial to grow good quality crystal fibers at the faster pulling rate. If the power input increased excessively, the precipitating rate would be too faster to grow good quality crystal fibers and the collapse of the molten zone could be even occurred.

For the growth of YIG and Ce:YIG at $x = 0.1$ and $0.2$, it was not enough power input to completely decompose the feed rods when reference power was 1 W. So it does not be demonstrated in fig. 5 at this growth parameter. However, in fig. 5, it could be found that the good quality crystal fiber with $x = 0.3$ was obtained at this growth parameter. Because the melting point of the Ce:YIG specimens with CeO$_2$ added at $x = 0.3$ was significantly lower than that of YIG, the good quality crystal
fibers could be grown from the complete melt in this power input. Therefore, when the reference power was adjusted to 1.1 W, it was a suitable increase of the input power to grow good quality crystal fibers with \( x = 0.3 \) for the use of a faster pulling rate. Perhaps this could interpret why the maximum pulling rate for grown free foreign phase of Ce:YIG crystal fibers at \( x = 0.2 \) and 0.3 was equivalent, as displayed in fig 3.

The lattice constants of the grown crystal fibers were also examined by the X-Ray single-crystal diffraction. If the other phases exist in the grown crystal fiber, a value of the lattice constant cannot be successfully acquired due to the fact that it is not a single crystal. The lattice constant of all the grown crystal fibers with 100% DIR could be obtained, so this indicates that these possessed the single crystalline quality. Fig. 6 shows the lattice constant increased with an increase of \( x \). It is because the radius of Ce\(^{3+}\) is larger than that of Y\(^{3+}\) and Ce\(^{3+}\) ions were substituted for Y\(^{3+}\) ions. But the Ce:YIG samples with \( x = 0.4 \) were even grown at the slower pulling rate (0.05 mm/min is the motion limit of our facility) and in the different power input, its lattice constant cannot be acquired. Fig 7a displays the SEM image of a cross section of the grown Ce:YIG fiber with CeO\(_2\) added at \( x = 0.4 \). It can be observed that some grains were residual in the grown crystal. Fig 7b is the mapping results of Ce element from Fig. 7a. It is found that there are more Ce elements in the grains. That is a phase of CeO\(_2\), confirmed via quantifying the weight ratios of Y, Fe, Ce and O by an EPMA. Consequently, we suppose that the solubility limit of Ce\(^{3+}\) in this Ce-substituted YIG single crystal fiber, in an ordinary atmosphere, was approximately 0.3, and that an excess addition of CeO\(_2\) would result in a foreign phase. Sekijima et al. [11], who used the LHPG method, reported that the solubility limit of Ce\(^{3+}\) ions in Ce:YIG for single crystals formed in an oxygen
atmosphere was around 0.3 and in an nitrogen atmosphere was around 0.5. Furthermore, it can be observed that the inclusion of CeO₂ mainly exist in the core region of the grown fibers. Chang and Wilcox [29, 30] pointed out that this kind of convection cell would force impurities in front of the center of the freezing interface. Therefore, it could perhaps be that an excessive addition to YIG material leads to the CeO₂ phase resident inside the core of the grown fibers. Fig. 8 displays photograph of a cross section parallel to the growth direction of a Ce:YIG crystal fiber with x = 0.2 grown at a 0.15 mm/min pulling rate and in 1.1 W reference power. The periodical cellular structure was found in the grown fiber, and the evaluation of the cellular structure in the core region was finer than that in the peripheral region. This is thought to be due to the fact that constitutional supercooling will be favored in the core region of the grown fiber, where the impurity was concentrated.

4. Conclusions

To grow YIG single crystal fibers from oscillatory instability of the melt by the LHPG method, it was necessary to consider the effect of the oscillating rate. The practice growing rate need add the oscillating rate and a pulling rate. When CeO₂ added into the YIG fiber, the pulling rate of the growth should be suitably slower depending on the amount of CeO₂. Based on the experimental observation, however, the addition of CeO₂ into YIG could reduce the oscillating rate of the melt. It was suitable to slightly increase the power input, resulted in an increase of the temperature gradient of the melt, and then to grow Ce:YIG single crystal fibers could be used a faster pulling rate. Moreover, the solubility limit of cerium ions in Ce-substituted Ce:YIG single crystal fiber, which was grew in an ordinary atmosphere, was found to be approximately 0.3. When the amount of CeO₂ added was over x = 0.3, the
inclusion of the CeO$_2$ phase was residual mainly in the core region of the grown Ce:YIG crystal fibers.

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References


Fig. 2 Schematic illustration of relationship between the quality of the grown YIG crystal fibers and the pulling rate.

Fig. 3 The relationship between the DIR and the pulling rates of the grown crystal fibers with various additions CeO$_2$ in the heat of 1.1 W reference laser powers.
Fig. 4 Dependence of the estimated oscillatory period of Ce:YIG materials on the Ce-content (x value in $Y_{3-x}Ce_xFe_5O_{12}$) during the crystal growth.

Fig. 5 The relationship between the reference power and the pulling rate of obtained foreign-free crystal.
Fig. 6 Dependence of the lattice constant of grown Ce:YIG crystal fibers on the Ce-content (x value in $Y_{3-x}Ce_xFe_5O_{12}$) for samples with 100% DIR.

![Lattice constant graph](image)

Fig. 7 The Ce:YIG fiber with $x = 0.4$ grown at 0.05 mm/min pulling rate; (a) SEM image of the cross section, (b) distribution of Ce element.
Fig. 8 Photograph of a cross section parallel to the growth direction of a Ce:YIG crystal fiber with $x = 0.2$ grown at a 0.15 mm/min pulling rate and in 1.1 W reference power.