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Growth of Tm, Ho-codoped YLiF₄ and LuLiF₄ single crystals for eye-safe lasers

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Abstract

YLiF₄ and LuLiF₄ single crystals codoped with thulium and holmium were successfully grown by the Czochralski Technique. The segregation coefficients of the dopants in these crystals were measured and the influence of the dopants on the lattice parameters was investigated. The distribution of birefringence along the *a*-axis was in the order of 10⁻⁷ in each crystal. Laser performance of both YLiF₄ and LuLiF₄ codoped with thulium and holmium was compared. © 2001 Elsevier Science B.V. All rights reserved

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1. Introduction

During the last few years, interest in 2 μm lasers has increased because of the availability of high power laser diodes, and the introduction of a large variety of applications that require eye-safe lasers that propagate through the atmosphere. 2 μm laser sources are potentially useful for a variety of applications, including coherent Doppler velocimetry and gas detection [1] and space applications such as atmospheric wind sensors for full-scale earth observation satellites. There are also possible medical applications since liquid water is strongly absorbed in this wavelength region [2,3].

Room temperature laser emission at 2 μm based on the holmium (Ho) ⁵I₇–⁵I₈ transition is reported in several thulium (Tm), Ho-codoped garnets [4–8]. The Tm ions act as sensitizers to efficiently transfer the absorbed pumping energy into the Ho metastable-energy state [3,4]. However, Tm, Ho-codoped oxide crystals show more severe up-conversion losses compared to Tm, Ho-codoped fluorides. We, therefore, investigated Tm, Ho-codoped YLiF₄ (Tm, Ho:YLF) and Tm, Ho-codoped LuLiF₄ (Tm, Ho:LuLF) laser crystals.

YLuF₄ (YLF) and LuLiF₄ (LuLF) both crystallize in a scheelite structure (tetragonal system and I₄/a space group). They have a congruent melting behavior and present good optical qualities. Growth and characterization of Tm, Ho:YLF have previously been reported [9–12]. In contrast, only one study on Tm, Ho:LuLF has been done, mainly because good quality LuLF crystals are

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difficult to grow [13]. As indicated before, the growth of optically clear fluoride single crystals depends not only on the growth process itself, but also on the purity of the starting materials and the presence of oxygen-containing complexes in the environment [14–16].

In this work, high optical-quality Tm, Ho:YLF and Tm, Ho:LuLF crystals were grown by the Czochralski method under CF_4 atmosphere. The Tm and Ho segregation coefficients and the lattice parameters for both Tm, Ho:YLF and Tm, Ho:LuLF were measured. Optical properties such as absorption, birefringence were also investigated. In addition, laser testing for these crystals, pumped at 790 nm (Tm $^3\text{H}_4$ -manifold) by laser diodes, is reported.

2. Experimental procedure

Crystal growth was performed in a vacuum-tight Czochralski system equipped with an automatic diameter control system. The resistive heater and thermal insulators were made of high-purity graphite. The starting materials were prepared from high-purity commercial fluoride powders of LiF, YF_3 , LuF_3 , (>99.99%). As dopants, TmF_3 and HoF_3 powders of high purity (>99.99%) were used. The concentrations of Tm and Ho in the starting material were 8 and 0.5 mol%, respectively. After mixing in an appropriate composition (52% LiF:48% YF_3) in the case of YLF and (52% LiF:48% LuF_3) in the case of LuLF, the basic compounds and the dopants were melted in a platinum crucible 60 mm in diameter. The pulling rate was 1 mm/h and the rotation rate was 15 rpm. Growth orientations were controlled using the a -axis oriented Ce-doped YLF and Ce-doped LuLF seed crystals. Prior to filling with gas and melting the charge, the growth chamber was evacuated to 10^{-2} Pa and heated to 700°C for a period of 12 h. Such treatment was carried out to eliminate water and/or oxygen from the chamber and the starting materials [17]. High-purity CF_4 gas (99.9999%) was slowly introduced into the furnace. The mixtures were melted under this atmosphere. After growth, the crystals were cooled down to room temperature at a rate of 30°C/h.

The crystals were sectioned longitudinally to measure the composition over the length of the boule. The Tm and Ho doping levels in the grown crystals were measured by the inductively coupled plasma technique. Powder X-ray diffraction (XRD) measurements for lattice parameter determinations were carried out on a Rigaku diffractometer (Rint model), operated at 40 kV and 40 mA in the 2θ range of 10–80°. The dependence of the lattice parameter on the temperature was measured using a high temperature XRD method under high-purity nitrogen (99.999%) gas flow atmosphere. Samples for spectroscopic measurements were cut perpendicular to the growth direction and polished manually. Absorption spectra in the Tm 690 and 790 nm wavelength regions were recorded using a Jasco V-530 UV/VIS spectrophotometer. Distribution of birefringence among Tm, Ho:YLF and Tm, Ho:LuLF-wafers was measured by the rotating analyzer

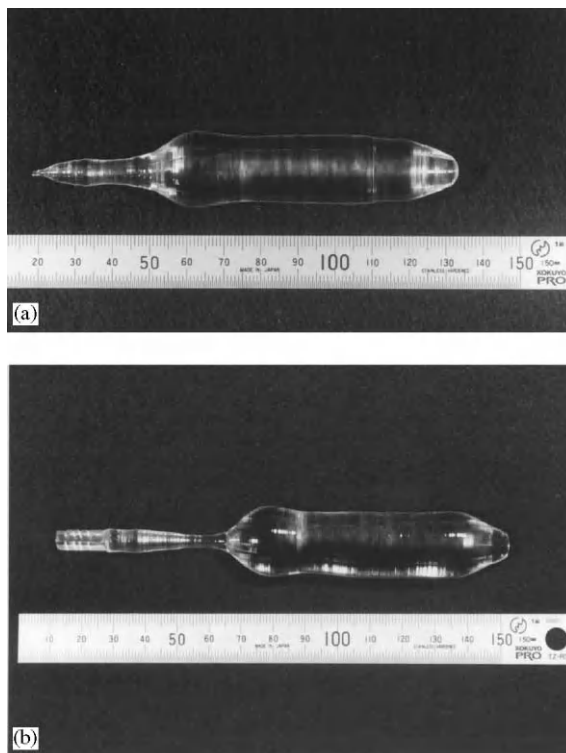


Fig. 1. (a) As grown Tm, Ho-codoped YLiF_4 single crystal. (b) As grown Tm, Ho-codoped LuLiF_4 single crystal.

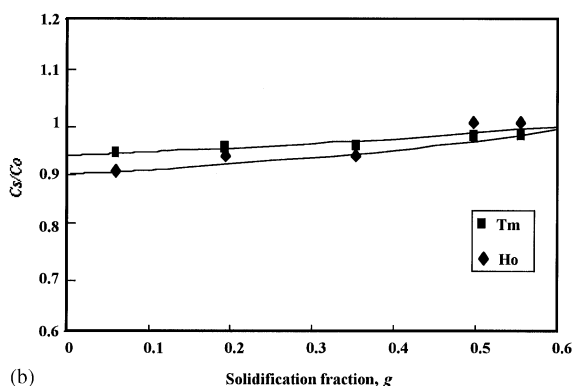
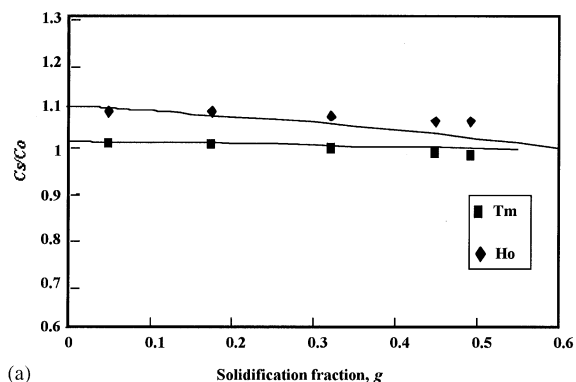


Fig. 2. Distribution of Tm and Ho along the growth axis in (a) Tm, Ho-codoped YLiF₄ and (b) Tm, Ho-codoped LuLiF₄.

method using ELP-UV apparatus, under 266 nm illumination.

3. Results and discussion

When powder raw materials were melted, a black scum was observed floating on the melt surface. This film is due to the oxygen and carbon contamination of the raw materials [15]. However, a clean and transparent melt was obtained after removing the scum by scraping the solidified surface and subsequently re-melting the compound. Fig. 1, shows the as-grown Tm, Ho: YLF and Tm, Ho: LuLF single crystals with dimensions of 18 mm in diameter and 70 mm in length. Cracks, bubbles and inclusions were not observed.

The uniformity of the dopants (Tm and Ho) distribution along the crystal growth axis was

Table 1
Radii of the rare earth elements under coordination 8

Elements	Ionic radius under coordination 8 (Å) [18]
Y	1.019
Ho	1.015
Tm	0.940
Lu	0.9770

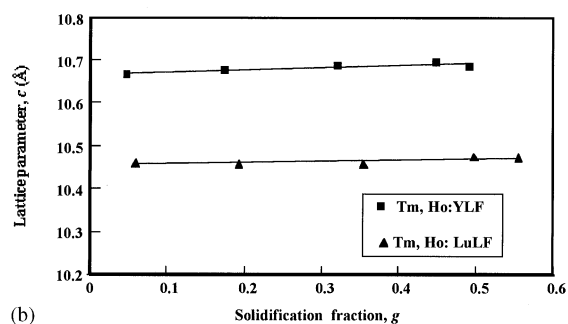
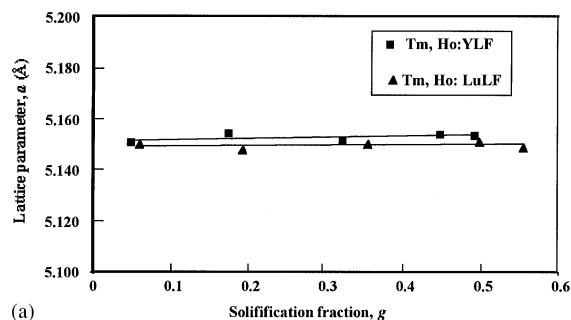


Fig. 3. Dependence of the lattice parameters on the solidification fraction for Tm, Ho-codoped YLiF₄ and Tm, Ho-codoped LuLiF₄, (a) *a*-axis and (b) *c*-axis.

inspected, with five samples taken along the crystal growth axis (Fig. 2). The distribution coefficients of Tm ($k_{\text{eff}}^{\text{Tm}}$) and Ho ($k_{\text{eff}}^{\text{Ho}}$) in YLF (LuLF) were estimated to be 1.02 (0.94) and 1.1 (0.90), respectively. These values were calculated using the normal freezing equation: $C_s = C_0 k_{\text{eff}} (1 - g)^{k_{\text{eff}}^{-1}}$ [18], where C_s is the measured concentration in the samples, C_0 is the initial concentration in the melt, g is the melt solidified fraction, and K_{eff} is the effective distribution coefficient of each dopant ion. The distribution coefficients are close to unity, as was expected, due to the comparable ionic radius of the dopants (Tm and Ho) and the host

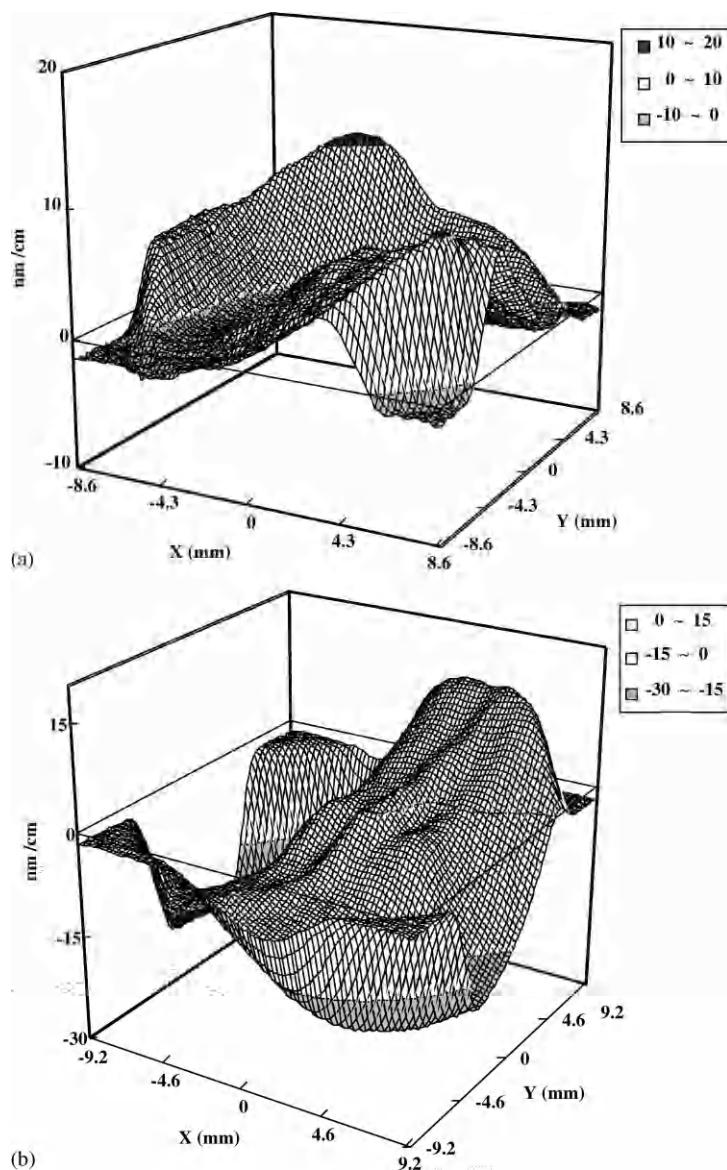


Fig. 4. Distribution of birefringence among (a) a Tm, Ho-codoped YLiF_4 -wafer and (b) a Tm, Ho-codoped LuLiF_4 -wafer.

(Y or Lu). However, it should be noted that, in the case of YLF, the distribution coefficients of Tm and Ho are slightly over unity, while in LuLF they are below. As the ionic radii of Tm and Ho are larger than Y but smaller than Lu (Table 1), the heavy rare earth dopants can substitute Y in YLF easier than Lu in LuLF.

The variation in lattice parameters of Tm, Ho:YLF and Tm, Ho:LuLF crystals as a function of the solidification fraction, were also measured as shown in Fig. 3. It can be seen from the values of a and c of Tm, Ho:YLF are larger than those of Tm, Ho:LuLF. This accords well with the size of the ionic radius. In the case of Tm,

Ho:YLF, as the ionic radii of both Tm and Ho are smaller than that of Y, the decrease of the dopants concentration results in the slight increase of the lattice constants a and c , as expected. However, for Tm, Ho:LuLF, while the a lattice parameter remains almost constant, the lattice parameter c decreases with an increase in the dopants concentration. It was expected that the lattice constants would increase because the ionic radii of both Tm and Ho are larger than that of Lu. This discrepancy may be explained by the presence of some defects such as vacancies in the host lattice.

Fig. 4 shows the distribution of the birefringence among wafers of (a) Tm, Ho:YLF and (b) of Tm, Ho:LuLF single crystals. Both wafers were cut perpendicular to the growth axis, a . As the deviation of birefringence among the wafers was of the order of 10 nm/cm, good uniformity of Tm, Ho:YLF and Tm, Ho:LuLF single crystals was confirmed.

The absorption spectra of Tm, Ho:YLF and Tm, Ho:LuLF, in the vicinity of 600–900 nm spectral region are shown in Fig. 5. It can be seen that the introduction of Tm led to the appearance of a strong absorption band at approximately 690 and 790 nm in both crystals. This means that commercially available laser diodes can be used as the pumping source for these materials. The absorption coefficient was measured for 8% and 5% Tm doped YLF (LuLF), Ho concentration was same in each case (0.5%). As expected. The absorption increases with the increase of Tm concentration in the host crystals.

As 0.5 cm long YLF (LuLF) crystals codoped with 8% Tm and 0.5% Ho crystals absorb more than 90% of the incident pump energy, compared with 68% of the incident energy in the case of 5% Tm and 0.5% Ho-codoped YLF (LuLF), we chose the latter for our laser experiment. In our set-up, the incident pump beams receive several reflections from the crystal faces and hence to have a uniform pumping intensity inside the crystal, a lower absorption coefficient is preferable. Fig. 6 shows the schematic of the laser set-up. Two 360 W quasi-cw laser diode arrays (LDA) (Hamamatsu Photonics, Japan) each are used as a pump source. The LDAS were temperature tuned such that the

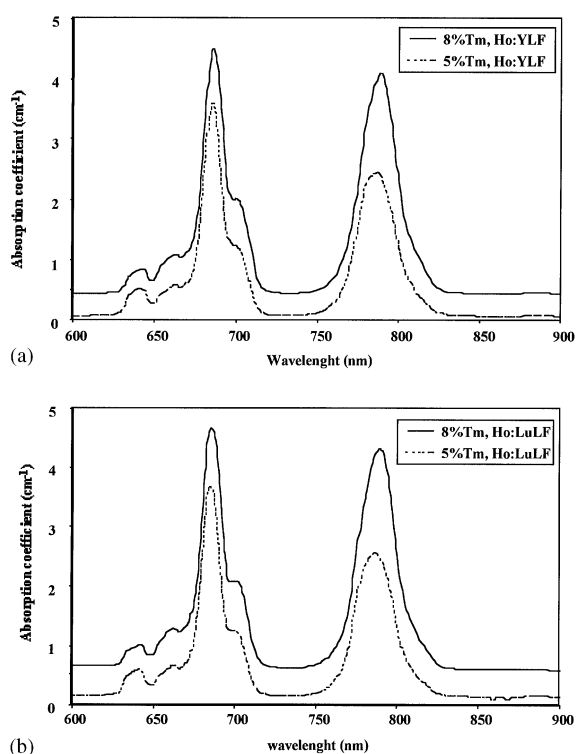


Fig. 5. Absorption spectra, in the 600–900 nm spectral region, of (a) Tm, Ho-codoped YLiF₄ and (b) Tm, Ho-codoped LuLiF₄.

center wavelength was 0.793 μm to match the absorption peak of the Tm ions. Two fused silica lens ducts of length 64 mm are used to focus the LDA pump light down to a 2.5×2.5 mm area to allow for side pumping of the laser crystal. The size of the laser crystal is $3 \times 4 \times 4.7$ mm ($a \times a \times c$ axes), with the c -axis being normal to the laser oscillation direction. The crystal end-faces are Brewster cut. The crystal is mounted directly on to a copper heat sink without any clamping. The hemispherical laser cavity is formed by a flat high reflector at 2 μm and a 5.0% output coupler with radius of curvature 300 mm. The pulse repetition frequency was 1 Hz, with a current pulse length of 500 μs . The laser performance of LuLF, along with the YLF, is shown in Fig. 7. The slope efficiency for LuLF is better than that for YLF (10.5% compared to 7.5%). The threshold energy for LuLF is also slightly lower compared with that of YLF: 125 mJ versus 130 mJ. Maximum output

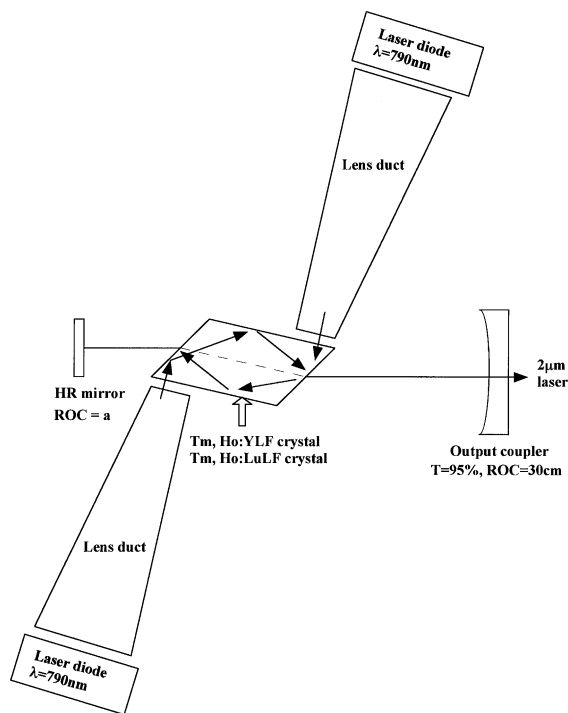


Fig. 6. Schematic of the laser set-up using the novel-side pumping technique.

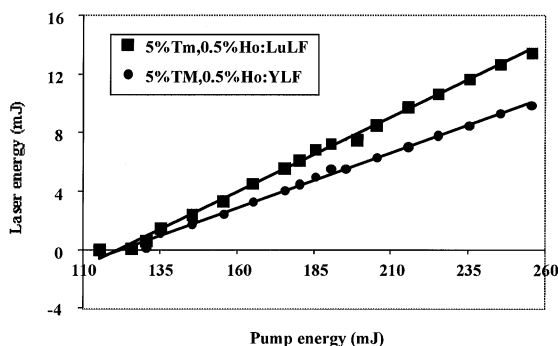


Fig. 7. Laser performance of 5% Tm, 0.5% Ho-codoped YLiF_4 and 5% Tm, 0.5% Ho-codoped LuLiF_4 .

energies of 13.5 mJ (LuLF) and 9.9 mJ (YLF) were obtained for 255 mJ of incident pump energy.

4. Conclusion

In this work, high-quality YLF and LuLF single crystals codoped with Tm and Ho were grown

under CF_4 atmosphere by the Czochralski method. The segregation coefficients of both Tm, and Ho were determined to be 1.02 (0.94) and 1.1 (0.90), respectively, in YLF (LuLF). The variation of the lattice parameters along each crystal was investigated. High uniformity of both single crystals along the a -axis was confirmed by following the birefringence variation. Laser activities of both crystals were measured. Tm, Ho:LuLF crystal presented better performance than Tm, Ho:YLF.

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