

Thermal and optical properties of Yb-doped Lu_2O_3 single crystal grown by the micro-pulling-down method

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Undoped and (0, 0.5, 5 mol%) Lu_2O_3 single crystals were grown by the micro-pulling-down method. Crystals were transparent with yellowish color with 4.2 mm in diameter and 6–9 mm in length. Yb-doped Lu_2O_3 single crystals have a good compositional homogeneity along the growth axis. Both, thermal diffusivity and heat capacity decrease when the Yb concentration increase. As a result, the calculated thermal conductivity for 5 mol% Yb^{3+} -doped Lu_2O_3 decreases from 14.32 to 12.42 $\text{Wm}^{-1}\text{K}^{-1}$. We have also investigated the absorption, fluorescence spectra and measured fluorescence lifetimes as a function of the Yb content.

Key words: Yb^{3+} activator, Thermal conductivity, Micro-pulling-down method, Crystal growth from the melt, Rare-earth sesquioxides.

Introduction

The sesquioxide like Lu_2O_3 , Y_2O_3 and Sc_2O_3 are a subject of interest. They crystallize in the bixbyite structure and belong to the cubic system with space group $\text{Ia}\bar{3}$ [1]. Lattice constants are 10.39 and 10.6 Å, respectively. The unit cell contains 16 formula units with 32 cations distributed between 24 sites with C_2 point symmetry and 8 sites with C_{3i} point symmetry.

The thermal conductivities of undoped scandia (16.5 W/mK), yttria (13.6 W/mK), and lutetia (12.5 W/mK) is higher than that of undoped YAG (11 W/mK) [2, 3]. If the crystals are doped with 3% ytterbium ions the thermal conductivity drops considerably; in case of scandia 6.6 and YAG 6.8 W/mK were measured. Among them, thermal conductivity of Lu_2O_3 is changed only slightly to 11.0 W/mK. These properties favor this material as a host crystal for high-power solid state lasers.

The effective phonon energy of Y_2O_3 and Lu_2O_3 is quite low compared to other oxides. Weber [4] reported value of only 430 cm^{-1} which is much lower than - for example - 700 cm^{-1} for YAG. A low phonon energy means low non-radiative transition rates of metastable electronic levels and therefore a high quantum efficiency.

Ytterbium doped materials are attractive for compact high-power laser sources around 1- μm spectral range. A particular attraction of Yb-doped materials is their

small quantum defect, given the small Stokes shift ($\sim 600 \text{ cm}^{-1}$) between absorption and emission, which reduces the thermal load and increases the laser efficiency. Additionally, excited state absorption, upconversion processes and cross-relaxation are practically absent in Yb-doped materials. Moreover, the broad absorption bands of these laser materials are covered by high-power InGaAs laser diodes, which permits efficient pumping. The emission and absorption cross sections, the upper state lifetime, the splitting of the two electronic states of Yb^{3+} and the phonon energies depend strongly on the host and its anisotropy. The host also determines the thermo-mechanical properties and the allowable doping level. In this regard, the isotropic sesquioxides Lu_2O_3 , Y_2O_3 and Sc_2O_3 [2] are promising for high-power applications because their thermal conductivity is higher and the ground state splitting is larger than YAG.

In this paper, we will report the optimization of the growth conditions for bulk single crystal growth of $\text{Yb}^{3+}:\text{Lu}_2\text{O}_3$ by the micro-pulling-down ($\mu\text{-PD}$) method which was recently successfully used to grow Yb^{3+} -doped Y_2O_3 [5]. In addition, we have also recorded absorption, fluorescence spectra and measured fluorescence lifetimes as a function of the Yb content.

Experimental

Undoped and Yb-doped Lu_2O_3 single crystals were grown by $\mu\text{-PD}$ method. To grow Yb-doped Lu_2O_3 , we applied rhenium crucible with 46 mm in height and 36 mm in diameter. The whole growth assembly was

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Table 1. Growth conditions of Yb^{3+} doped Lu_2O_3 crystal.

Starting materials	$\text{Lu}_2\text{O}_3(3\text{N}), \text{Yb}_2\text{O}_3(4\text{N})$
Crucible	Re
Pulling-down rate	0.05-0.1 mm/min
Seed	$\langle 111 \rangle$
Crystal diameter	4.2 mm
Atmosphere	Ar + 3% H_2

embedded in zirconia ceramics and quartz tube. The crucible was heated inductively at a frequency of 15 KHz. The starting materials were prepared from high-purity commercial powders of Lu_2O_3 (>99.9%) and Yb_2O_3 (99.99%). The starting melt composition of $(\text{Lu}_{1-x}\text{Yb}_x)_2\text{O}_3$ was varied as $x = 0.0, 0.005$ and 0.05 .

Lu_2O_3 ceramic rod was used as a seed, at first. The growth atmosphere was mixture of Ar + 3% H_2 gas in order to avoid oxidation of the Re crucible. The growth conditions are detailed in Table 1.

In order to identify the obtained phases, powder X-ray diffraction analysis was carried out using RINT Ultima (Rigaku) diffractometer with $\text{CuK}\alpha$ X-rays. The diffraction pattern was scanned over 2θ range 10-80 with steps of 0.02° . The accelerating voltage was 40 kV and the current was 40 mA.

The chemical composition was analyzed by electron probe micro analysis (EPMA) using JEOL JXA-8621MX. The atoms distribution was measured along the growth axis using an electron probe of 10 μm in diameter.

Thermal conductivity of $\text{Yb}^{3+}:\text{Lu}_2\text{O}_3$ was calculated from the values of thermal diffusivity, specific heat capacity and density. Thermal diffusivity was measured under vacuum of <10 Pa using the laser-flash method [6]. The sample size was 4.2 mm in diameter with a thickness of 0.5 mm. Both surfaces of the sample were coated with gold by a sputtering process in order to avoid the penetration of laser light. Specific heat capacity was measured with a differential scanning calorimeter (DSC) in the temperature range from 523 to 823 K [7]. The average weight of the samples used for specific heat capacity measurements was 30 mg. The measurement was carried out under high-purity argon atmosphere with a flow rate of 20 mL/min. The specific heat capacity of $\alpha\text{-Al}_2\text{O}_3$ was used as reference value.

Absorption spectra were recorded with a spectrophotometer (Cary 2300) equipped with a cryostat allowing measurements between 12 K and room temperature. Excitation of the Yb^{3+} fluorescence was performed with a frequency doubled Nd: YAG laser (10 ns, 10 Hz) pumping a Quantel three-amplifier-stage dye laser containing a mixture of DCM and LD700 and followed by a hydrogen Raman cell shifter to generate a beam in the 950-980-nm range. The specific infrared fluorescence is selected by using a Jobin Yvon HR250 monochromator fit with a 600 grooves/mm grating

blazed at 1 μm and detected by a fast North Coast germanium cell cooled by liquid nitrogen. The signal can be analyzed with the use of a Lecroy 9410 digital oscilloscope coupled to a PC.

The determination of the decay time and then of the intrinsic radiative lifetime of Yb^{3+} in crystals requires a lot of precaution. Depending of the concentration of active ion and of the size of the sample, the self-trapping process is much or less involved [8]. The lifetimes have been directly measured on one side of the sample which is directly excited by the laser beam of about 500 μm size. Because the size of sample has been chosen small, excited crystal part is small, and radiative trapping due to geometrical effect can be supposed weak due to the small size of the excited sample. Experimental lifetime values have been fitted to an unique exponential profile with an excellent agreement.

Results and Discussion

Transparent and crack-free undoped and $\text{Yb}^{3+}:\text{Lu}_2\text{O}_3$ (0, 0.5 and 5 mol%) single crystal rods with 4.2 mm in diameter and 6-9 mm in length were grown by the μ -PD method. Fig. 1 shows the as-grown $\text{Yb}^{3+}:\text{Lu}_2\text{O}_3$ single crystals. The growth was performed under Ar + 3 vol % H_2 atmosphere and a pulling rate of 0.05 to 0.1 mm/min. These crystals were slightly yellowish

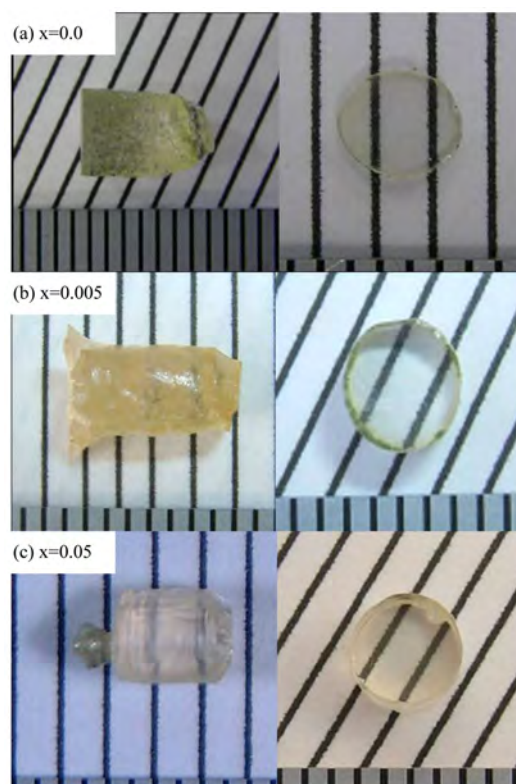


Fig. 1. As-grown $(\text{Lu}_{1-x}\text{Yb}_x)_2\text{O}_3$ single crystals and samples cross-sections after annealing in air at 1450°C for 30 hrs; (a) $x = 0.0$, (b) $x = 0.005$, (c) $x = 0.05$.

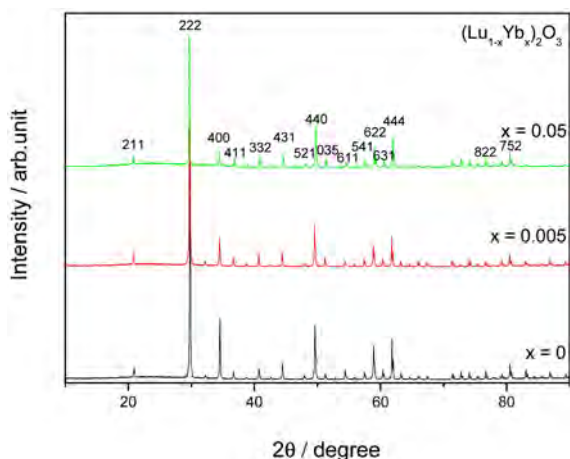


Fig. 2. Powder X-ray diffraction patterns of $(\text{Lu}_{1-x}\text{Yb}_x)_2\text{O}_3$ as a function of the Yb content.

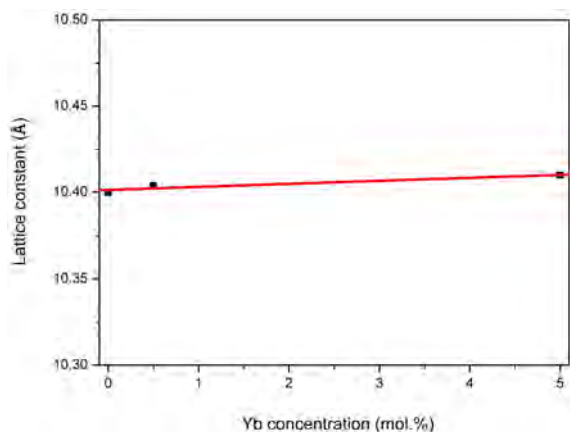


Fig. 3. Concentration dependency of lattice constants of $(\text{Lu}_{1-x}\text{Yb}_x)_2\text{O}_3$.

colored. It may suggest the existence of oxygen vacancy. As the crystals were grown in an $\text{Ar} + \text{H}_2$ mixture atmosphere. By annealing (1450°C -30 h) in air the colour could be removed as demonstrated in Fig. 1.

Evolution of the powder X-ray diffraction pattern as a function of the Yb concentration was investigated (Fig. 2). Single phase was formed in all the studied concentration range and no impurity phase was detected. As the Yb^{3+} concentration increases, the peaks were shifted left. This means the lattice constant slightly increases as Yb^{3+} increases. As the ionic radii of Yb^{3+} (0.858 Å) is larger than that of Lu^{3+} (0.848 Å), the lattice constant tends to decrease (by the substitution in Lu^{3+} site) linearly as the concentration of Yb^{3+} increases, as can be seen in Fig. 3. This result is in good agreement with Vegard's law.

The Yb distribution was investigated using EPMA. Fig. 4 illustrates that $\text{Yb}^{3+}:\text{Lu}_2\text{O}_3$ crystals grown by the μ -PD method have a good compositional homogeneity along the growth axis. Yb was homogeneously distributed in Lu_2O_3 host from the top to the end and the effective segregation coefficient of each

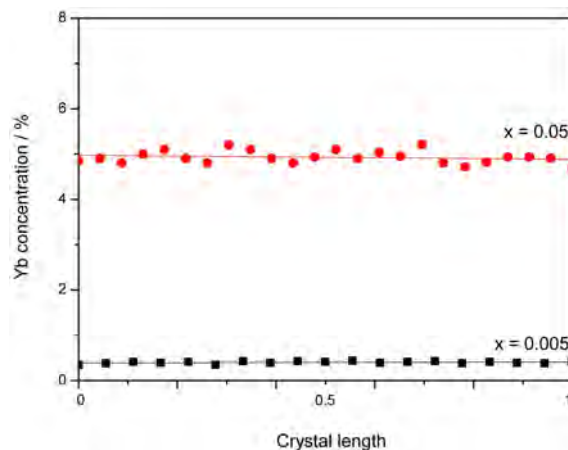


Fig. 4. Yb distribution along the growth axis for $(\text{Yb}_x\text{Lu}_{1-x})_2\text{O}_3$ crystals. ($x = 0.005$ and 0.05).

constituent of the $\text{Yb}^{3+}:\text{Lu}_2\text{O}_3$ melt became unity along the growth axis leading to the homogeneous composition throughout the crystal. EPMA measurements were also performed along a straight line across the cross-section of the $\text{Yb}:\text{Lu}_2\text{O}_3$ crystal. Within the measurement accuracy, no radial segregation was detected.

Thermal diffusivity at room temperature was measured by the laser flash method. One surface of the specimen was instantaneously irradiated by Nd^{3+} -glass laser. The temperature response at the other surface of the specimen was measured by using an InSb infrared detector. Thermal diffusivity was calculated using the following equation:

$$\alpha = \frac{1.37L^2}{\pi^2 t_{1/2}} \quad (1)$$

where L is sample thickness and $t_{1/2}$ is the time to reach a half of a maximum temperature rise. The thermal diffusivity decreases with the increase of the Yb^{3+} content. Corresponding data are summarized in Table 2. Table 3 show thermal conductivity of sesquioxides compared to the crystals investigated by other method. [9-11].

Fig. 5 shows DSC curves for specific heat capacity measurements of both sapphire and undoped Lu_2O_3 . A sapphire single crystal with precisely known heat capacity was employed as a reference. We measured the DSC signal area of sapphire, sample and holder and calculate the specific heat capacity of Lu_2O_3 using the equation:

$$C_{pS} = \frac{C_{pR}W_R S_S}{W_S S_R} \quad (2)$$

where C_{pS} is the specific heat capacity of sample, W_S is sample weight, C_{pR} is the specific heat capacity of sapphire ($1.096 \text{ Jg}^{-1}\text{K}^{-1}$ at 298 K [12]), W_R is sapphire weight, S_S is DSC signal area of sample, S_R is DSC signal area of sapphire.

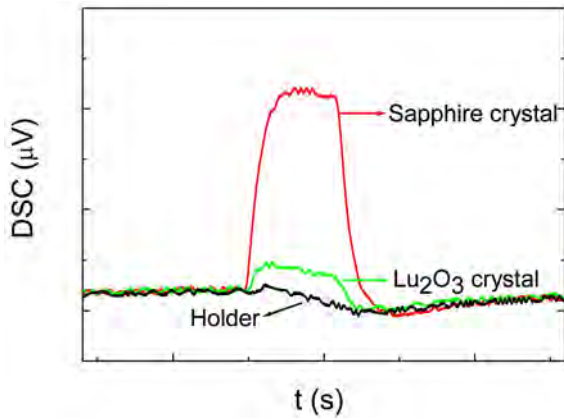
In the case of undoped- Lu_2O_3 the specific heat

Table 2. Thermal diffusivity, density, heat capacity and calculated thermal conductivity of undoped and Yb-doped Lu₂O₃ single crystals.

Yb content (mol%)	Thermal diffusivity (10 ⁻⁶ m ² s ⁻¹)	Thermal conductivity (Wm ⁻¹ K ⁻¹)
0	6.08	14.32
0.5	6.05	13.66
5	6.00	12.42

Table 3. Thermal conductivity of sesquioxides compared to inverted crystals by other method.

Compound	Growth method	Thermal conductivity (Wm ⁻¹ K ⁻¹)
5% Yb : Y ₂ O ₃	μ-PD	8.34
5% Tm : Y ₂ O ₃	μ-PD	7.46
5% Yb : Sc ₂ O ₃	μ-PD	4.12
5% Yb : Lu ₂ O ₃	μ-PD	12.42
3% Yb : Y ₂ O ₃	HEM	7.7
3% Yb : Sc ₂ O ₃	HEM	6.6
2.7% Yb : Lu ₂ O ₃	HEM	11.0
YAG	Cz	11
5%Yb : YAG	Cz	6.8

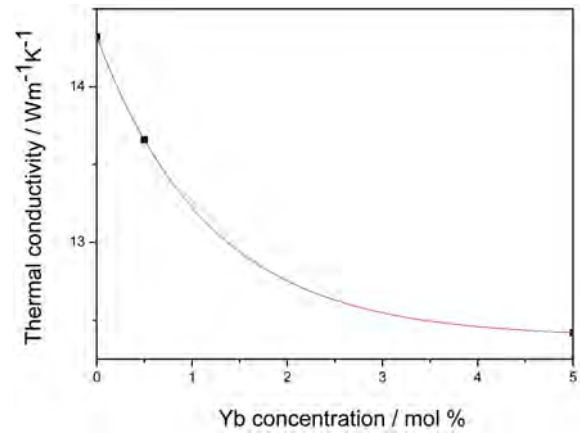
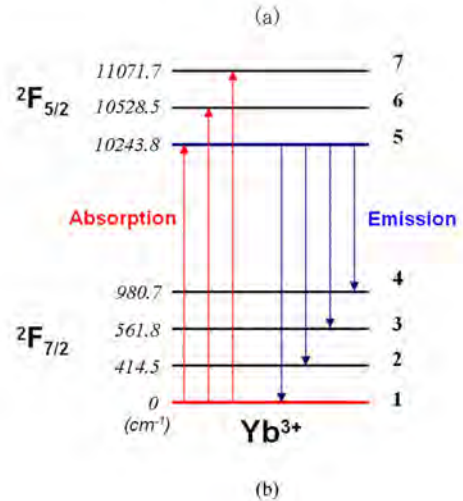
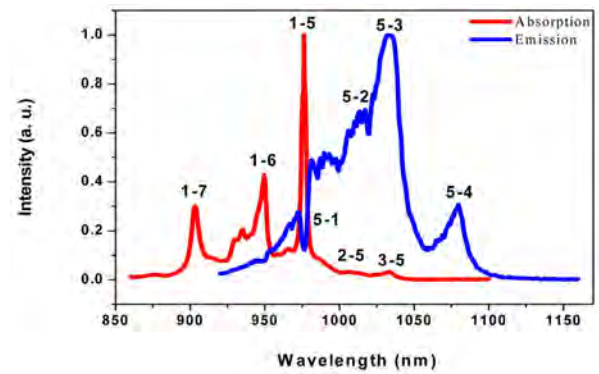
**Fig. 5.** DSC curves for specific heat capacity calculation in undoped Lu₂O₃.

capacity is 0.25 Jg⁻¹K⁻¹ at 298 K. The numerical data for Yb-doped samples are presented in Table 2. The heat capacity of Lu₂O₃ crystal increases linearly with increase of the temperature in the range from 523 to 823 K.

Thermal conductivity was calculated from thermal diffusivity α , specific heat capacity C_p and density ρ using the following standard expression:

$$\lambda = \alpha C_p \rho \quad (3)$$

Figure 6 shows the thermal conductivity versus the Yb³⁺-dopant content in Lu₂O₃. The value of the thermal conductivity of undoped Lu₂O₃ is 14.32 Wm⁻¹K⁻¹ at room temperature and the data for Yb-doped samples are also provided in Table 1. The thermal conductivity

**Fig. 6.** The thermal conductivity versus the Yb-dopant content in Lu₂O₃.**Fig. 7.** (a) Absorption and emission spectra of 5% Yb³⁺-doped Lu₂O₃ at room temperature. (b) Energy levels diagram of Yb³⁺.

of Yb³⁺-doped Lu₂O₃ decreases with the increasing of Yb content.

We have recorded the absorption and emission spectra of Yb³⁺-doped Lu₂O₃ for all the concentration (0, 0.5 and 5 mol%). Generally, the shape of the spectra changes with the ytterbium concentration. Here, we will present only the spectroscopic properties related to the 5% Yb³⁺-doped Lu₂O₃. Absorption and broad emission bands were recorded at room temperature and

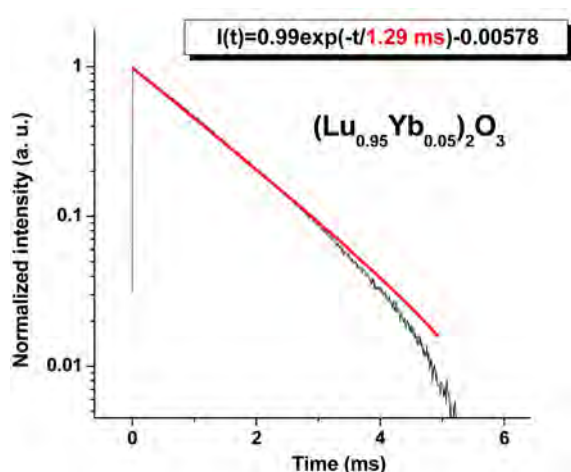


Fig. 8. $^2F_{5/2}$ lifetime of 5% Yb^{3+} -doped Lu_2O_3 under excitation at 978 nm.

the corresponding spectra are shown in Fig. 7(a). Obtained results appeared to be very similar to those obtained on $\text{Yb} : \text{Lu}_2\text{O}_3$ fibers grown by LHPG method [13] and we take advantage of their assignments of Yb^{3+} Stark levels. The absorption spectrum from the 5% Yb^{3+} -doped Lu_2O_3 sample consists of three main lines assigned to transitions from the lowest level of the ground state to the three components of the excited state: the reabsorption at 976 nm and 1-7 and 1-6 lines located around 903 and 949 nm, respectively. The emission spectrum exhibits high intensity and broad lines at around 1032 nm that most probably contains the transition of the first excited multiplet to both the second and third Stark level of the ground level because of the low energy splitting of these two levels [14]. The energy diagram of Yb^{3+} was calculated from the experimental absorption and emission data and the corresponding scheme is proposed in the Fig. 7b.

The decay time of the $^2F_{5/2}$ excited state for the 5% Yb^{3+} -doped Lu_2O_3 displayed in Fig. 8 was measured for an excitation at 978 nm and emission at 1000 nm. This experimental lifetime has been fitted with a single exponential profile and approximated to be equal to 1.29 ms at room temperature.

Conclusions

Transparent and crack-free undoped and $\text{Yb}^{3+} : \text{Lu}_2\text{O}_3$

(0, 0.5 and 5 mol.%) single crystal rods with 4.2 mm in diameter and 6–9 mm in length were grown by the μ -PD method. The best single crystals were obtained for pulling-down rate equal to 0.1 mm/min. Yb^{3+} -doped Lu_2O_3 single crystals had good compositional homogeneity along the pulling-down axis and lattice constant became systematically smaller with the increase of Yb^{3+} concentration. The thermal diffusivity of undoped Lu_2O_3 was measured as $6.08 \times 10^6 \text{ m}^2\text{s}^{-1}$. Specific heat capacity was measured for the temperature region from 523 to 823 K. Thermal conductivity of undoped Lu_2O_3 was calculated as to $14.32 \text{ Wm}^{-1}\text{K}^{-1}$ at room temperature. Broadband emission around 1.0 μm with a long decay time (1.29 ms) was obtained at room temperature.

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