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Full Length Article

Yb:Lu_2O_3 hydrothermally-grown single-crystal and ceramic absorption spectra obtained between 298 and 80 K

Cheryl A. Moore [a,b], David C. Brown [a,*], Liurukara D. Sanjeewa [b], Colin D. McMillen [b], Joseph W. Kolis [b]

[a] Snake Creek Lasers LLC, 26741 State Route 267, Friendsville, PA 18818, United States
[b] Department of Chemistry and Center for Optical Materials Science and Engineering Technologies, Clemson University, Clemson, SC 29634-0973, United States

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ABSTRACT

The hydrothermal growth, doping, and low temperature spectral characterization of Yb doped Lu_2O_3 was investigated. The absorption of the lutetia-based sesquioxide laser material Yb:Lu_2O_3 at temperatures of 80, 150, 200, 250, and 298 K, in the wavelength range of 850–1100 nm are reported. Data for both single crystal and ceramic Yb:Lu_2O_3 were obtained. The resulting absorption cross-section data will enable the further evaluation of Yb:Lu_2O_3 as a very promising high power cryogenic laser material.

1. Introduction

The sesquioxide laser materials Yb:Sc_2O_3, Yb:Y_2O_3, and Yb:Lu_2O_3 have undergone rapid development in the past fifteen years. Good summaries of the early work may be found in the dissertations of Mix, Fornasiero, and Peters [1–3], as well as in two other recent dissertations [4,5] and a number of recently published papers [6–9].

In order to mitigate the difficult high-temperature growth (ca. 2500 °C) of sesquioxide single crystals, sesquioxide ceramic laser materials have also been prepared, investigated, and used in laser demonstrations [10–12]. Recently, measurements of important thermal, mechanical, and thermo-optic parameters of the sesquioxides at room and cryogenic temperatures, including the specific heat, thermal conductivity, thermal expansion coefficient, and thermo-optic coefficient have begun to appear in the literature [13–16].

As described in a recent paper, our group has demonstrated the much lower temperature ($\leq$ 700 °C) hydrothermal growth of Yb:Lu_2O_3 [13,17], in a temperature regime in which defects, impurities, crystal strain, color-centers, and inhomogeneities are minimized. A comprehensive review of the hydrothermal growth process and its application to the development of new and promising laser crystals has also recently been published [18]. In earlier work [17] we presented the first room temperature absorption cross-section data for hydrothermally-grown Yb:Lu_2O_3, as well as the emission cross-sections determined by the method of reciprocity. The sesquioxide laser material Yb:Lu_2O_3 is particularly attractive as a material for high power lasers due to its moderate emission cross-section, ability to be optically-pumped at the low quantum defect ($\simeq$ 5.05%) zero-phonon line near 977 nm using powerful, efficient laser diode sources, and the close mass-match between Yb and Lu, leading to reduced impurity phonon scattering and a good thermal conductivity that is nearly independent of Yb doping level. Given the importance of reducing waste heat in extremely high-power lasers, it is essential to obtain a detailed understanding of the absorption event in pumping the laser crystals. In particular it is beneficial to minimize the quantum defect as this represents an inherent loss of efficiency and produces waste heat. In order to fully exploit the advantages of Yb^{3+} as a laser ion, cryogenic operation is most desirable. The recent development of efficient volume Bragg gratings and high power pump diodes operating at or near 976 nm makes zero-phonon line pumping technically feasible. These developments necessitate the detailed understanding of cryogenic absorption behavior of the Yb^{3+} ion doped in a Lu_2O_3 host.

* Corresponding author.
E-mail address: dbrown@snakecreeklasers.com (D.C. Brown).

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In this paper we present new absorption cross-section experimental data from room temperature to 80 K, obtained from a single crystal of Yb:Lu_2O_3, also grown by the hydrothermal method. A complementary set of emission cross-section measurements will appear in a separate future publication. This paper describes the crystal growth and preparation, the absorption cross-section data over a wide range of temperatures, calculation of the Yb density, as well as a comparison to Yb:YAG.

2. Crystal growth and polishing

Crystal growth from hydrothermal solution took place in closed, pure silver reaction tubes which contained the powdered feedstock along with a small amount of aqueous mineralizer to aid in dissolution during the growth cycle. In the case of Yb:Lu_2O_3 discussed here, rare-earth oxide powders (HEFA Rare Earth, 99.997%) of Lu_2O_3 and Yb_2O_3 were measured in the desired doping ratio such that the total powdered material was approximately 1.5 g and added directly to ¼″ O.D. × 7″ long silver tubes that had been carefully cleaned, weld-sealed, and inspected for integrity. The powdered feedstock, 3 mL of a 20 M aqueous KOH solution, was added before the tubes were welded closed.

These loaded tubes were themselves inserted into Inconel autoclaves equipped with two external, individually-controlled ceramic band-heaters with temperature probes and pressure gauge assemblies in order to monitor temperatures and pressure throughout the entire growth process. Water added inside the autoclaves provides the counter pressure necessary to prevent bursting of reaction tubes when heated. The fully loaded and prepared autoclaves were then lowered into insulating pits and covered up to the pressure gauge in vermiculite. A temperature gradient was established with the band heaters of 670 °C for the top, growth zone, and 700 °C in the lower, dissolution zone, for this prograde solubility system. These temperatures typically resulted in pressures of around 207 Mpa (30,000 psi). The autoclaves were left undisturbed in these insulated pits during the entire growth run of between 12 and 14 days. After this time the heat was discontinued and autoclaves were left to cool naturally over several hours or quick-quenched by an air stream. The cooled reaction tubes were then carefully cut open to reveal various-sized single crystals of up to several mm on a side. While the temperature used in the present study represents a seemingly modest increase over our previous work [13], we observe improved faceting and a greater amount of optically clear regions in the as-grown crystals, compared to those grown at 630–650 °C. We postulate that moving the growth conditions farther away from the Lu_2O_3/LuO(OH) phase transition around 600 °C may be the source of such positive effects.

Elemental analysis by EDX (Energy Dispersive X-Ray Analysis) indicated only the presence of Lu, Yb and O. No spectroscopic abnormalities were observed to suggest the presence of other impurity ions at an appreciable level.

Crystals determined to be of sufficient optical quality for spectral analysis were further prepared, if necessary, by polishing. Progressive lapidary discs were used starting with 1200 grit and ending with 100,000 mesh diamond spray.

3. Crystal spectral characterization

3.1. Lu_2O_3 crystal properties

Lutetia is one of three recently developed isomorphic sesquioxide host crystals: Lu_2O_3, Y_2O_3, and Sc_2O_3. These crystals have been primarily developed to provide possible alternatives, with more favorable physical properties, to the well-developed classic oxide host YAG ($Y_3Al_5O_{12}$). As shown in Table 1, where for convenience we provide a summary of the crystal properties, Lu_2O_3 is an optically isotropic (anaxial) host that provides a strong, robust, easily doped host for rare-earth ions, which substitute into Lu sites of the body-centered Lu sites. Unlike YAG, however, which has one substitutable rare earth site, Lu_2O_3 has two six-coordinate lutetium sites [19], with local point group symmetries of C_2 and C_{3i}. The former is non-centrosymmetric and has no inversion center, while the latter is centrosymmetric with a center of inversion. Thus, according to the LaPorte rule, electric dipole transitions are allowed in the C_2 site, while for the C_{3i} site such transitions are forbidden. Indeed, this conclusion is found to be obeyed experimentally, where C_2 radiative sites predominate while the C_{3i} transitions are very weak. The Lu_2O_3 unit cell has been found to contain 32 cations, with 24 being found in the C_2 sites and 8 in the C_{3i} sites. Thus the ratio of C_2 to C_{3i} sites found in the unit cell is 3:1.

Table 1
Lu_2O_3 crystal properties.

Property	Value
Crystal Structure	Bixbyite
Transparency Band Gap (eV)	5.8
Chemical Formula	Lu_2O_3
Dopant	Yb^{3+}
Name	Lutetia
Crystal System	Body-Centered Cubic
Optical Class	Anaxial (Isotropic)
Space Group	$Ia\bar{3}$
Number of Unique Cation Sites	2
Local Point Group Symmetry C_2	Non-centrosymmetric
Local Point Group Symmetry C_{3i}	Centrosymmetric
Lattice Parameter (Å)	10.391
Unit Cell Volume $(Å)^3$	1125.84
Number of Formula Units Per Cell, Z	16
Total Number of Cation Sites Per Unit Cell	32
Number of C_2 Sites Per Unit Cell	24
Number of C_{3i} Sites Per Unit Cell	8
Coordination Number	6
Lu Ion Density ($ions/cm^3$)	2.85×10^{22}

3.2. Spectrophotometer and cryostat descriptions

Absorption cross-section results for the laser material Yb:Lu_2O_3, were measured at 80, 150, 200, 250 and 298 K. Data was obtained using a 1.42 mm thick hydrothermally-grown Yb:Lu_2O_3 crystal with a nominal Yb doping of 2 at%, and with polished faces. Absorption was measured using a Shimadzu SolidSpec – 3700 DUV high-resolution spectrophotometer that enables optical absorption measurements from 175 to 3300 nm. The spectrometer was modified to incorporate a custom cryogenic optical cell with liquid nitrogen boiloff gas cooling that allows operation from 77 K to room temperature, controlled by suitably adjusting the gas flow. The cell is evacuated to less than 5×10^{-4} Torr to avoid water vapor condensation on the crystal, and incorporates two uncoated SiO_2 windows for transmission measurements. The Yb:Lu_2O_3 crystal was heat sunk using indium foil and the temperature measured close to the crystal using an RTD sensor with a Lake-Shore Model 218 temperature monitor.

3.3. Calibration of Yb density

To determine the Yb doping density in our Yb:Lu_2O_3 crystal, we adopted the approach of Kuhn et al. [20], who showed that by combining the Fuchtbauer–Ladenburg equation for calculating the emission cross-section with the reciprocity method, the ion