Synthesis, spectroscopic characterization and laser operation of Ho^{3+} in "mixed" (Lu₁Sc)₂O₃ ceramics

Wei Jing^a, Pavel Loiko^b, Josep Maria Serres^c, Yicheng Wang^d, Esrom Kifle^c, Elena Vilejshikova^e, Magdalena Aguiló^c, Francesc Díaz^c, Uwe Griebner^d, Hui Huang^{a,f}, Valentin Petrov^d, and Xavier Mateos^{c,*}

^aInstitute of Chemical Materials, China Academy of Engineering Physics, 64 Mianshan Road, 621900 Mianyang, China ^bITMO University, 49 Kronverkskiy Pr., 197101 St. Petersburg, Russia ^cUniversitat Rovira i Virgili, Departament Química Física i Inorgànica, Física i Cristal·lografia de Materials i Nanomaterials (FiCMA-FiCNA)-EMaS, Campus Sescelades, E-43007, Tarragona, Spain. ^dMax Born Institute for Nonlinear Optics and Short Pulse Spectroscopy, Max-Born-Str. 2a, D-12489 Berlin, Germany ^eCenter for Optical Materials and Technologies (COMT), Belarusian National Technical University, 65/17 Nezavisimosti Ave., 220013 Minsk, Belarus ^fhuanghui@caep.cn *Corresponding author, e-mail: <u>xavier.mateos@urv.cat</u>

Abstract: Novel transparent Ho-doped sesquioxide ceramics are synthesized by hightemperature vacuum sintering and hot isostatic pressing. The spectroscopic properties of 1.4 at.% and 3 at.% Ho:(Lu,Sc)₂O₃ ceramics are studied within Judd-Ofelt theory, yielding the intensity parameters $\Omega_2 = 7.863$, $\Omega_4 = 1.843$ and $\Omega_6 = 0.531 [10^{-20} \text{ cm}^2]$. The radiative lifetime of the ⁵I₇ state is 10.63 ms. Absorption, stimulated-emission and gain cross-sections for the ⁵I₇ \rightarrow ⁵I₈ Ho³⁺ transition are calculated. At > 2 µm, the maximum $\sigma_{SE} = 3.41 \times 10^{-21} \text{ cm}^2$ at 2.101 µm. Under GaSb diode-pumping at 1.929 µm, the 1.4 at.% Ho:(Lu,Sc)₂O₃ ceramic laser generated 187 mW of quasi-continuous wave (CW) output at 2.114-2.135 µm with a slope efficiency η of 7.6%. When pumped at 1.946 µm with a Tm laser, η reached 25% while the CW output power was 20.5 mW. The Ho:(Lu,Sc)₂O₃ ceramics are promising for broadband tunable and ultrashort pulse laser operation at ~2.1 µm.

Keywords: transparent ceramics; sesquioxides; holmium; spectroscopy; laser operation.

1. Introduction

The trivalent Holmium ion (Ho³⁺, electronic configuration: [Xe]4f¹⁰) is attractive due to its laser emission around 2 μ m related to the 4f-4f transition ⁵I₇ \rightarrow ⁵I₈. Such an emission is eye-safe and it matches spectrally with absorption of relevant molecules such as H₂O and CO₂. Thus, it is used in remote sensing (LIDAR), range finding, wind mapping, spectroscopy and medicine. In addition, the Ho³⁺ ion shows an emission at >2 μ m which is of interest for pumping of mid-IR optical parametric oscillators (OPOs) [1]. Due to the typically large Stark splitting of both the ⁵I₇ and ⁵I₈ multiplets, a broad spectral tuning of the Ho³⁺ laser emission is feasible. The lifetime of its upper laser level (⁵I₇) is typically a few ms long, which is favorable for the generation of high-energy laser pulses in Q-switched lasers.

The Ho³⁺ ion can be excited by two commonly used pump schemes. One is the Tm³⁺,Ho³⁺ codoping system, where the Tm³⁺ ion act as donor: it can be pumped at ~0.8 µm (to the ³H₄ state of Tm³⁺) by commercial AlGaAs laser diodes [2] and transfer the excitation to Ho³⁺ according to the Tm³⁺(³F₄) \rightarrow Ho³⁺(⁵I₇) process [3]. This scheme features a high pump absorption efficiency but its capability for power scaling at room temperature (RT) is limited due to the strong heat loading arising from upconversion effects [4]. The second pump scheme is the so-called in-band (resonant) pumping to the ⁵I₇ state, e.g., by GaSb or InP laser diodes or Tm³⁺-based bulk of fiber lasers [5,6]. This scheme is characterized by a high slope efficiency [7] due to the low energy mismatch of the pump and laser photons and the possibility of power scaling. However, the absorption cross-section, σ_{abs} , of the Ho³⁺ ion for the ⁵I₈ \rightarrow ⁵I₇ transition is typically low, leading to a moderate pump absorption efficiency [8]. An increase of the Ho³⁺ doping level, to compensate this, is limited by the accompanying fast increase of upconversion effects.

The cubic rare-earth sesquioxides crystals, A_2O_3 (where A = Y, Lu or Sc) are attractive hosts for laser-active trivalent lanthanide ions (Ln^{3+}) [9] and, in particular, Ho^{3+} [8,10]. The A_2O_3 host crystals feature superior thermal properties, namely high thermal conductivity with a relatively weak dependence on the Ln^{3+} doping [11], low thermal expansion and positive dn/dT coefficients [12]. When doped with Ln^{3+} ions such as Tm^{3+} or Ho^{3+} , a strong crystal field in the sesquioxide matrix results in a large Stark splitting of the multiplets and consequently, broad emission bands extending well above 2 µm are observed [9]. The low phonon energies of the cubic A_2O_3 crystals ensure relatively weak non-radiative (NR) relaxations from the upper laser level.

Efficient lasers based on Ho:A₂O₃ crystals have been already demonstrated. Both GaSb laser diodes and Tm-fiber lasers were used for in-band pumping [8,10]. In [8], a Tm-fiber laser pumped a 0.3 at.% Ho:Lu₂O₃ rod laser generating an output power of ~22 W at 2.124 μ m with a slope efficiency η of 76% (with respect to the absorbed pump power). Using a GaSb diode, a 0.17 at.% Ho:Sc₂O₃ rod laser generated multi-watt output at even longer wavelengths of 2.145 and 2.158 μ m [8,13].

To resolve the growth problems for cubic A_2O_3 crystals, a significant effort has focused on the development of such ceramics. Transparent oxide ceramics as emerging laser materials offer similar spectroscopic properties of the Ln^{3+} ions but benefit from easy and size-scalable synthesis methods. Their main drawbacks - the reduced thermal conductivity and higher losses (as compared to the corresponding single crystals) - can be greatly improved by optimizing the fabrication conditions.

To date, the main efforts are devoted to the study of Lu₂O₃ ceramics doped with Yb³⁺ [14] and Tm³⁺ [15,16] ions. Less attention has been paid to the Ho³⁺-doped A₂O₃ laser ceramics. The synthesis and spectroscopic properties of Ho³⁺-doped Lu₂O₃ [17,18], Y₂O₃ [19-21], (Y,La)₂O₃ [22] and Sc₂O₃ [23] ceramics and the stoichiometric Ho₂O₃ one [24] are reported. RT laser operation was demonstrated with Ho:Lu₂O₃ [17], Ho:Y₂O₃ [21] and Ho,Yb:(Y,La)₂O₃ [22] ceramics. In the former case, a maximum peak output power of 182 mW at 2.124 µm was achieved with $\eta \approx 1\%$ (under quasi-CW Tm-fiber laser pumping) [17]. Recently, A RT CW Ho:Y₂O₃ ceramic laser was reported delivering 1.3 W at 2116.8 nm with $\eta = 31.2\%$ [21]. At cryogenic temperatures (77 K), much better output performance was demonstrated with Ho:Y₂O₃ ceramics, namely 2.5 W output power in CW mode at 2.119 µm with $\eta = 35\%$ (under InP diode pumping) [19].

In the present paper, our aim was to study a novel laser material, Ho^{3+} -doped mixed $(Lu,Sc)_2O_3$ laser ceramics. It is known, that due to the increasing strength of the crystal field in the A₂O₃ crystals in the sequence A = Y – Lu – Sc, it is possible to engineer the spectroscopic properties of the Ln³⁺ ions in compositionally "mixed" A₂O₃ matrices. This leads to broad and smooth emission bands being of interest, e.g., for mode-locked lasers [25]. A similar ceramic $(Lu,Sc)_2O_3$ doped with Tm³⁺ ions was studied recently in [26,27] and its high suitability for sub-100 fs mode-locked lasers has been demonstrated [28].

2. Fabrication of the Ho:(Lu,Sc)₂O₃ ceramics

We used high-temperature vacuum sintering and Hot Isostatic Pressing (HIP) to fabricate the $Ho:(Lu,Sc)_2O_3$ ceramics. Powders of Sc_2O_3 , Lu_2O_3 (99.99% purity, Alfa Aesar), Ho_2O_3 (99.99% purity, Jiangyin Jiahua Co. Ltd.), and ZrO_2 (99.99% purity, Alladin) were used as raw materials. The raw materials were taken according to the stoichiometry shown in Table 1 resulting in a Lu/Sc atomic ratio of ~1.4.

ZrO₂ was used as sintering agent. The addition of ZrO₂ inhibited the excessive growth of ceramic grains and improved the optical quality of the material. For this purpose, other agents such as HfO₂ can be used as well. We mixed uniformly the raw materials by ball milling for 24 h. After that, we dried (70 °C for 6 h), sieved, dry-pressed (10 MPa), and cold isostatically pressed the mixture at 200 MPa. These bodies of Ho:(Lu,Sc)₂O₃ ceramics were pre-sintered at 1750 °C for 10 h under vacuum (pressure $P < 10^{-3}$ Pa) in order to densify the preforms. Further densification was achieved after post-sintering by HIP at 1800 °C (2 h in Ar atmosphere at P = 195 MPa) in order to eliminate the closed pores around possible grain boundaries. As a last step, we annealed the ceramics (1500 °C for 10 h in an O₂ atmosphere) in order to eliminate the oxygen vacancies and remove internal stresses. Ho:(Lu,Sc)₂O₃ ceramic samples with a diameter of 28 mm and a thickness of 5 mm were fabricated. An example of polished sample (1.4 at.% Ho:(Lu,Sc)₂O₃ ceramic) is shown in Fig. 1(a). Further spectroscopic characterization and laser experiments were carried out with $3\times3\times3$ mm³ cubic elements. Depending on the illumination, the ceramics was rose (in natural light) or yellow (under fluorescent lamp).

The phase purity and the structure of the ceramics were analyzed at RT (293 K) by X-ray diffraction (XRD) with a D2 PHASER equipment (Bruker Co. Ltd), using Cu Ka radiation. The XRD patterns were measured in the range of $2\theta = 10-80^{\circ}$ with a step of 0.02° and a scan speed of 0.1°/min, Fig. 1(b) for the 1.4 at.% Ho-doped ceramics. The measured XRD pattern shows an clear agreement with the JCPDS card No. 04-002-0541 of the cubic LuScO₃ crystal (C-type bixbyite structure, space group $I_{a\bar{3}}$ - T^{7}_{h} , No. 206). Studying the position of the peaks, we deduced a lattice constant of the Ho:(Lu,Sc)₂O₃ ceramics as a = 10.1901 Å (Z = 16). This corresponds to the calculated density ρ_{calc} of 7.22 g/cm³. In the (Lu,Sc)₂O₃ structure, the Lu³⁺ and Sc^{3+} ions are located in two types of sites having C₂ and C_{3i} symmetries (24*d* and 8*b* Wyckoff positions, respectively). For both sites, these cations are VI-fold O²⁻ coordinated, so that the corresponding ionic radii are $R_{Lu} = 0.861$ Å and $R_{Sc} = 0.745$ Å. An excess of Lu over Sc will lead to an increase of the lattice constant. Indeed, a is 10.105 Å for the LuScO₃ crystal (Lu/Sc = 1). The doping ions, Ho³⁺ ($R_{\text{Ho}} = 0.901$ Å), will replace both the Lu³⁺ and Sc³⁺ ones in the two possible sites, while the spectroscopic properties of the Ho:(Lu,Sc)₂O₃ ceramics are determined by one of them, the one with C_2 symmetry [9]. For the site with C_{3i} symmetry, the electric-dipole (ED) transitions are forbidden due to the presence of an inversion center.

The Raman spectrum of the 1.4 at.% Ho: $(Lu,Sc)_2O_3$ ceramics is shown in Fig. 1(c). It was measured with a Renishaw inVia confocal Raman microscope. The excitation wavelength λ_{exc} was 0.514 µm (Ar⁺ ion laser). A total of 12 very broad Raman bands are resolved in the spectrum. The strongest one is observed at 405 cm⁻¹ and typically ascribed to A_g + F_g vibrations. Its position is intermediate between that for the Lu₂O₃ (393 cm⁻¹) and Sc₂O₃ (419 cm⁻¹) crystals [29].

The morphology of the polished and fractured surfaces of the 1.4 at.% Ho: $(Lu,Sc)_2O_3$ ceramics was studied using a scanning electron microscope (SEM, VEGA 3 SBH, Tescan), see Fig. 2. The ceramic sample is pore-free with clean grain boundaries. In addition, no secondary phase at the grain boundaries was found. We used the linear intercept method to determine the average grain size as $3...5 \mu m$.

3. Optical spectroscopy

3.1 Optical absorption

The absorption spectra were measured using a Varian CARY 5000 spectrophotometer (Agilent) with a resolution of 0.2 nm. From the measured absorption coefficient α_{abs} , we calculated the absorption cross-section, $\sigma_{abs} = \alpha_{abs}/N_{Ho}$. In terms of σ_{abs} , the spectra were almost identical for 1.4 at.% and 3 at.% Ho doping which agrees with the close composition of the host matrix, Table 1.

The Ho:(Lu,Sc)₂O₃ ceramics were highly transparent. For the 1.4 at.% Ho³⁺-doped sample, the transmission *T* out of the Ho³⁺ absorption bands was measured to be 79.5% (light wavelength: 1.0 μ m, sample thickness: 3.0 mm). This value is very close to the limit set by Fresnel losses, *T*_{Fr} = 80.6% (for a refractive index *n* of 1.94).

Due to the weak absorption bands of Ho³⁺ in sesquioxides, the 3 at.% Ho doped sample was selected for further analysis, see Fig. 3. The band at 1.8-2.15 μ m is due to the ⁵I₈ \rightarrow ⁵I₇ transition of the Ho³⁺ ion, Fig. 3(a). The maximum σ_{abs} for this transition amounts to 8.44×10⁻²¹ cm² at

1.932 µm and the full width at half maximum (FWHM) of the absorption peak is 14 nm. The peak absorption cross-section for the considered transition in the Ho:(Lu,Sc)₂O₃ ceramics is lower than in Ho:Lu₂O₃ ($\sigma_{abs} = 12.4 \times 10^{-21}$ cm² at 1.927 µm) and Ho:Sc₂O₃ ($\sigma_{abs} = 18.6 \times 10^{-21}$ cm² at 1.919 µm) crystals [13] while the absorption band is less structured for the ceramics. Indeed, the FWHM of the strongest absorption peak for the Ho:Lu₂O₃ and Ho:Sc₂O₃ crystals is <2 nm.

At shorter wavelengths, in the transparency range of the ceramics (UV absorption edge: $\lambda_g = 0.290 \ \mu$ m), the transitions from the 5I_8 ground-state to the excited states from 5I_6 to 3K_6 are observed, see Fig. 3(b-f). The assignment of the absorption bands is according to [30]. The wave functions for a scheme based on intermediate coupling corresponding to the states (energy levels) of the Ln³⁺ ions are wave functions linearly combined in the Russell–Saunders approximation (the L–S coupling scheme). The energy levels are labelled by one or more L–S wave functions contributing mainly to such a linear combination. For the Ho³⁺ ion, we used this system to designate the higher-lying excited states (${}^5G, {}^3G)_5$, (${}^5F, {}^3F, {}^5G)_2$ and (${}^5G, {}^3H)_5$.

The absorption bands of Ho³⁺ in the (Lu,Sc)₂O₃ ceramics related to the transitions from the ${}^{5}I_{8}$ ground-state to the excited states from ${}^{5}I_{7}$ to ${}^{3}K_{6}$ were studied using the standard Judd-Ofelt (J-O) theory [31,32]. The absorption oscillator strengths were determined from the measured absorption spectra using:

$$f_{\Sigma}^{\exp}(JJ') = \frac{m_e c^2}{\pi e^2 N_{\rm Tm} \langle \lambda \rangle^2} \Gamma(JJ'), \tag{1}$$

where m_e and e are the electron mass and charge, respectively, c is the speed of light, $\Gamma(JJ')$ is the integrated absorption coefficient within the absorption band and $\langle \lambda \rangle$ is the "center of gravity" of the absorption band. The results are shown in Table 2.

The values of f_{Σ}^{exp} were used to determine the J-O (intensity) parameters, Ω_k , k = 2, 4, 6: $\Omega_2 = 7.863$, $\Omega_4 = 1.843$ and $\Omega_6 = 0.531 [10^{-20} \text{ cm}^2]$. Such values are close to those reported in [23] for a Ho:Sc₂O₃ ceramic, $\Omega_2 = 6.01$, $\Omega_4 = 1.99$ and $\Omega_6 = 0.49 [10^{-20} \text{ cm}^2]$. The transition to the ⁵I₄ state was excluded from the analysis due to the very low f_{Σ}^{exp} , Fig. 3(c). The envelope of the hyper-sensitive transitions to the ⁵F₂ + ³K₈, ⁵G₆ and ⁵F₁ states [33] was also excluded as it typically gives rise to errors in the standard J-O analysis. Thus, a total of 10 absorption bands were analyzed. Using the Ω_k parameters, we calculated the absorption oscillator strengths showing a good agreement with the experiment (low root-mean-square (rms) deviation, 0.093):

$$f_{\Sigma}^{\text{calc}}(JJ') = \frac{8}{3h(2J+1)\langle\lambda\rangle} \frac{(n^2+2)^2}{9n} S_{\text{ED}}^{\text{calc}}(JJ') + f_{\text{MD}}^{\text{calc}}(JJ'),$$
(2a)

$$S_{\text{ED}}^{\text{calc}}(JJ') = \sum_{k=2,4,6} U^{(k)} \Omega_k, \text{ where } U^{(k)} = \langle (4f^n) SLJ \| U^k \| (4f^n) S'L'J' \rangle^2.$$
(2b)

Here, $S_{\text{ED}}^{\text{calc}}$ are the line strengths, *h* is the Planck constant, *n* is the refractive index of the crystal and $U^{(k)}$ are the squared reduced matrix elements [34]. The J-O theory describes the electricdipole (ED) transitions. The contribution of magnetic-dipole (MD) transitions with $J-J' = 0, \pm 1$ (for the ${}^{3}\text{H}_{6} \rightarrow {}^{3}\text{H}_{5}$ transition) is $f_{\text{MD}}{}^{\text{calc}} = n \cdot f_{\text{MD}}{}^{\text{vac}}$ (where the $f_{\text{MD}}{}^{\text{vac}}$ – vacuum MD oscillator strength values are taken from [35]). The calculated $f_{\Sigma}{}^{\text{calc}}$ values are also listed in Table 2.

3.2 Optical emission

We calculated the probabilities for spontaneous radiative transitions from the line strengths which, in turn, were determined from the J-O parameters Ω_k and squared reduced matrix elements $U^{(k)}$ for the emission [34], see Eq.(2b):

$$A_{\Sigma}^{\text{calc}}(JJ') = \frac{64\pi^4 e^2}{3h(2J+1)\langle\lambda\rangle^3} n \left(\frac{n^2+2}{3}\right)^2 S_{\text{ED}}^{\text{calc}}(JJ') + A_{\text{MD}}^{\text{calc}}(JJ') \cdot$$
(3)

The MD contributions were determined as $A_{\text{MD}}^{\text{calc}} = n^3 \cdot A_{\text{MD}}^{\text{vac}} (A_{\text{MD}}^{\text{vac}} - \text{vacuum MD oscillator})$ strength taken from [35]). Using the A_{Σ}^{calc} values for the separate emission channels $J \rightarrow J'$, we have determined the total probability, A_{tot} , the radiative lifetime of the excited state, τ_{rad} , and the luminescence branching ratios for the particular emission channels, B(JJ'):

$$\tau_{\rm rad} = \frac{1}{A_{\rm tot}} \text{ and } B(JJ') = \frac{A_{\Sigma}^{\rm calc}(JJ')}{A_{\rm tot}}, \text{ where } A_{\rm tot} = \sum_{J'} A_{\Sigma}^{\rm calc}(JJ').$$
(4)

The results are shown in Table 3. The radiative lifetime of the lowest excited state, $\tau_{rad}({}^{5}I_{7})$ is 10.63 ms. This value is in agreement with the luminescence lifetimes reported previously for 0.3 at.% Ho:Lu₂O₃ (~10 ms [13]), 0.12 at.% and 0.42 at.% Ho:Sc₂O₃ crystals (~8 ms [13] and 8.65 ms [36], respectively). The radiative lifetime $\tau_{rad}({}^{5}I_{7})$ for the Ho:Sc₂O₃ ceramics calculated in [23] was shorter than in the present work and amounted to 8.72 ms.

The lifetime of the ⁵I₇ Ho³⁺ excited-state in (Lu,Sc)₂O₃ ceramics was determined from the luminescence decay studies, Fig. 4. The quasi-CW excitation was at 1930 nm (directly to the emitting state) and the luminescence was monitored at 1970 nm. For both 1.4 at.% and 3 at.% Ho³⁺-doped samples, the decay is clearly single-exponential; the characteristic decay times τ_{lum} are 9.0 ms and 5.5 ms, respectively. Thus, a relatively high luminescence quantum yield $\eta_q = \tau_{\text{lum}}/\tau_{\text{rad}}$ of 85% is determined for 1.4 at.% Ho³⁺ doping. The shortening of τ_{lum} with Ho³⁺ doping level is due to the concentration quenching.

The stimulated emission (SE) cross-sections, σ_{SE} , for the ${}^{5}I_{7} \rightarrow {}^{5}I_{8}$ transition of Ho³⁺ in the (Lu,Sc)₂O₃ ceramics were calculated from the measured absorption spectrum, Fig. 3(a), by the modified reciprocity method [37]:

$$\sigma_{\rm SE}(\lambda) = \frac{1}{8\pi n^2 \tau_{\rm rad} c} \frac{\sigma_{\rm abs}(\lambda) e^{-hc/(kT\lambda)}}{\left[\lambda^{-4} \sigma_{\rm abs}(\lambda) e^{-hc/(kT\lambda)} \mathrm{d}\lambda\right]}.$$
(5)

Where, *k* is the Boltzmann constant, *T* is the crystal temperature (RT) and τ_{rad} is the radiative lifetime of the emitting state (⁵I₇). The SE cross-section spectrum is shown in Fig. 5(a). The maximum σ_{SE} reaches 5.07×10^{-21} cm² at 1.932μ m. At > 2 μ m where laser operation is expected for quasi-three-level Ho³⁺ lasers, σ_{SE} is 3.41×10^{-21} cm² at 2.101 μ m. Compared to the Ho:Lu₂O₃ and Ho:Sc₂O₃ crystals, the SE cross-section spectrum of the ceramics is less structured and features broader emission bands. Such a broadening results in lower peak σ_{SE} values for the ceramics as compared to the crystals for which, in the long-wavelength spectral range, the maximum σ_{SE} amounts to 3.97×10^{-21} cm² at 2.092 μ m (for Ho:Lu₂O₃) and 5.45×10^{-21} cm² at 2.110 μ m (for Ho:Sc₂O₃) [13].

The gain cross-section, $\sigma_g = \beta \sigma_{SE} - (1 - \beta) \sigma_{abs}$, where $\beta = N({}^{5}I_7)/N_{Ho}$ is the inversion ratio, for Ho^{*}(Lu,Sc)₂O₃ ceramics is shown in Fig. 5(b). The gain spectra are smooth and broad. Depending on β , local maxima at 2.133 µm ($\beta < 0.2$), 2.113 µm ($\beta < 0.25$) and 2.101 µm ($\beta > 0.25$), are observed. For $\beta = 0.35$, the gain FWHM amounts to ~80 nm.

4. Laser operation

4.1 Laser set-up

We studied the laser performance in a compact plano-plano cavity, Fig. 6(a). The active element (thickness: 3.07 mm, aperture: 3.06×2.78 mm²) was prepared from the 1.4 at.% Ho:(Lu,Sc)₂O₃ ceramics, laser-grade polished and remained uncoated. It was mounted in a Cuholder (water cooled at 12 °C) and wrapped with Indium foil to provide better thermal contact from all 4 lateral sides. The laser cavity was composed of a flat pump mirror (PM) coated for high transmission (T > 94%) at 1.9-2.0 µm and high reflection (HR) at 2.02-2.15 µm, and a flat output coupler (OC) with transmission $T_{OC} = 0.2\%$, 1.5%, 3% or 5% at 1.84-2.15 µm. Both PM and OC were placed close to the laser element. The geometrical cavity length was about 3.1 mm. The active element was pumped through the PM by a fiber-coupled GaSb laser diode (M0031-ILS, DILAS, fiber core diameter: 400 µm, N.A.: 0.22) emitting up to 16 W of unpolarized output at 1.929 µm (emission bandwidth: 6 nm). The diode laser wavelength was stabilized by watercooling. We used a lens assembly (focal length: 20 mm, 2:1 imaging ratio) to collimate and focus the pump radiation into the active element. The waist radius w_p of the pump beam in the crystal was 100 µm and the confocal parameter of the pump beam 2zR was 1.76 mm. As all OCs provided high reflection ($R \approx 1 - T_{OC}$) at the pump wavelength, the ceramics was pumped in a double-pass. The total absorption under lasing conditions was 66%. The pump was optionally modulated with a mechanical chopper (repetition rate: 5 Hz, duty cycle: from 1:2 to 1:20).

The emission spectra of the laser were measured with a compact spectrometer (WaveScan, sensitivity: 1.0-2.6 μ m, APE GmbH). The intensity beam profile was measured in the far-field using a FIND-R-SCOPE near-IR camera (sensitivity: 0.4-2.2 μ m), Fig. 6(b).

4.2 Laser operation

At first, we studied the effect of the pump duty cycle on the laser performance using the OC with the lowest transmission, i.e. $T_{OC} = 0.2\%$, see Fig. 7(a). When the pump conditions were changed from true CW to quasi-CW pumping with a duty cycle varying from 1:2 (i.e., 50% pump on) to 1:20 (5% pump on), the laser output power gradually increased. For all pump conditions, a thermal roll-over was observed. In the true CW regime, the laser generated 12.3 mW for $T_{OC} = 0.2\%$ and 29.2 mW for $T_{OC} = 1.5\%$.

For further laser experiments, the 1:20 pump duty cycle was selected, see Fig. 7(b). Laser action was achieved with all studied OCs. The best output performance corresponded to $T_{OC} = 3\%$, namely a maximum peak power of 187 mW at 2.114-2.135 µm (multi-peak emission) with a slope efficiency η of 7.6% with respect to the absorbed pump power P_{abs} . The laser threshold was at $P_{abs} = 2.3$ W. The thermal roll-over occurred at $P_{abs} > 4.6$ W. The laser slope efficiency was slightly higher for $T_{OC} = 5\%$, namely 8.4% while the peak output power was limited to 140 mW due to a thermal roll-over starting at lower $P_{abs} = 4.2$ W. This is attributed to stronger upconversion effects and, thus, thermal loading for higher T_{OC} .

The emission of the Ho:(Lu,Sc)₂O₃, see Fig. 7(c), occurred between 2.111 and 2.135 μ m and the main emission peak experienced a blue-shift with T_{OC} due to the quasi-three-level nature of the Ho³⁺ laser in agreement with the gain spectra, Fig. 5(b). The CW Ho:(Lu,Sc)₂O₃ ceramic

laser generated a slightly elliptic output beam with $M^{2}_{x,y} < 1.2$ ($P_{abs} = 4.6$ W, for $T_{OC} = 1.5\%$), see Fig. 6(b).

The laser performance of the Ho:(Lu,Sc)₂O₃ ceramics was also studied under Tm-laser pumping. A Tm:KLu(WO₄)₂ microchip laser diode-pumped at 0.802 µm was used as a pump source [38]. This laser delivered up to 2.9 W of CW output at 1.946 µm (M² < 1.1). Its output was collimated and focused into the ceramics by a pair of spherical lenses with focal lengths of 150 and 60 mm, respectively. The pump spot radius in the laser element w_p was 110 µm. The double-pass pump absorption was 13% due to a mismatch of the pump wavelength and the main absorption peak of the Ho³⁺ ion, Fig. 3(a). The cavity of the Ho:(Lu,Sc)₂O₃ ceramic laser was identical to the one depicted in Fig. 6(a). More details about the pump source can be found elsewhere [7].

Under Tm-laser pumping, the Ho:(Lu,Sc)₂O₃ ceramic laser generated a maximum output power of 20.5 mW at 2.119 μ m with a slope efficiency of 25% (true CW operation, for $T_{OC} = 1.5\%$). The laser threshold was as low as 0.30 W. The power scaling was limited by the available power of the pump source.

In Table 4, the output characteristics of the Ho:A₂O₃ ceramic lasers reported so far are compared.

5. Conclusion

We report on the first investigation of a Ho³⁺-doped "mixed" transparent sesquioxide ceramics, $(Lu,Sc)_2O_3$. It is synthesized by high-temperature vacuum sintering and HIP and doped with up to 3 at.% Ho. A detailed study of the spectroscopic properties of the Ho³⁺ ion in terms of transition probabilities (within the Judd-Ofelt theory) is performed. The absorption and stimulated-emission cross-section spectra for the relevant ${}^{5}I_{8} \leftrightarrow {}^{5}I_{7}$ Ho³⁺ transition are determined. Laser operation of the Ho: $(Lu,Sc)_2O_3$ ceramics is demonstrated under GaSb diode and Tm-laser pumping.

The Ho: $(Lu,Sc)_2O_3$ ceramics are promising materials for broadly tunable and mode-locked lasers emitting above 2.1 µm. They offer broadband and strong absorption at 1.93 µm relaxing the requirements for the stabilization of the pump wavelength, and broad and smooth gain spectra (bandwidth ~80 nm). Further improvement of the laser performance of the Ho: $(Lu,Sc)_2O_3$ ceramics is feasible by optimizing the synthesis conditions, e.g., content of the ZrO₂ sintering additive and the Ho³⁺ doping concentration. Additional modification of the spectral properties is expected by varying the Lu/Sc atomic ratio. The $(Lu,Sc)_2O_3$ ceramics are also attractive for Tm³⁺,Ho³⁺ co-doping systems to further extend the broadband emission bands around 2 µm.

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Sample	Amo	ount of	cations	0	$N_{ m Ho,}$	
	Lu	Sc	Но	Zr	p meas, g/cm ³	10 ²⁰ cm ⁻ 3
1.4 at.% Ho	55	40	1.4	3.6	6.35	3.722
3 at.% Ho	54	39	3	4	6.52	8.146

Table 1. Composition of the Ho:(Lu,Sc)₂O₃ ceramics.

Table 2. Experimental and calculated absorption oscillator strengths for the 3 at.%Ho:(Lu,Sc)₂O₃ ceramics

Transition	<i>«</i> λ»,	Г,	$U^{(k)}, 10^{-20} \text{ cm}^2$			$f_{\Sigma}^{exp} \times 10^6$	$f_{\Sigma}^{\text{calc}} \times 10^{6}$
	μm	cm ⁻¹	$U^{(2)}$	$U^{(4)}$	$U^{(6)}$		
${}^{5}I_{8} \rightarrow {}^{5}I_{7}$	1.9516	386.5	0.0249	0.1344	1.5216	0.722	$0.769^{\text{ED}} + 0.572^{\text{MD}}$
${}^{5}I_{8} \rightarrow {}^{5}I_{6}$	1.1567	59.7	0.0084	0.0386	0.6921	0.569	0.526^{ED}
${}^5\mathrm{I}_8 \longrightarrow {}^5\mathrm{I}_5$	0.893	6.5	0	0.0100	0.0936	0.104	0.092^{ED}
${}^{5}I_{8} \rightarrow {}^{5}I_{4}$	754.7	0.38	0	0	0.0077	0.008	754.7
${}^5\mathrm{I}_8 \longrightarrow {}^5\mathrm{F}_5$	0.6474	75.4	0	0.4250	0.5687	2.294	2.057^{ED}
${}^5\mathrm{I}_8 \longrightarrow {}^5\mathrm{F}_4 + {}^5\mathrm{S}_2$	0.5414	65.5	0	0.2392	0.9339	2.849	_
${}^{5}I_{8} \rightarrow {}^{5}F_{3}$	0.4870	10.4	0	0	0.3464	0.559	0.473^{ED}
${}^5\!I_8 \mathop{\longrightarrow} {}^5\!F_2 + {}^3\!K_8$	0.473	20.8	0.0208	0.0334	0.3576	1.059	_
${}^5\mathrm{I}_8 \to {}^5\mathrm{G}_6$	448.6	345.0	1.5201	0.8410	0.1411	21.847	_
${}^{5}I_{8} \rightarrow {}^{5}F_{1}$	-	-	0	0	0	-	_
${}^{5}I_{8} \rightarrow ({}^{5}G, {}^{3}G)_{5}$	0.4197	37.5	0	0.5338	0.0002	2.714	2.990 ^{ED}
${}^5\!I_8 \mathop{\longrightarrow} {}^3\!K_7 + {}^5\!G_4$	0.3862	6.8	0.0058	0.0361	0.0697	0.576	0.499^{ED}
${}^{5}I_{8} \rightarrow ({}^{5}F, {}^{3}F, {}^{5}G)_{2}$	0.3615	79.8	0.2155	0.1969	0.1679	7.785	7.768 ^{ED}
$+({}^{5}G,{}^{3}H)_{5}+{}^{3}H_{6}$							
${}^5\mathrm{I}_8 \longrightarrow {}^3\mathrm{L}_9 + {}^5\mathrm{G}_3$	0.345	8.5	0.0185	0.0052	0.1169	0.908	$0.832^{\rm ED} \!\!+\! 0.028^{\rm MD}$
$^5\mathrm{I}_8 \rightarrow {}^3\mathrm{K}_6 + {}^3\mathrm{F}_4$	336.5	9.6	0.0026	0.1263	0.0073	1.081	1.015 ^{ED}
rms deviation							0.093

 $\langle \lambda \rangle$ - "center of gravity" of the absorption band, Γ – integrated absorption coefficient, $U^{(k)}$, k = 2, 4, 6 – squared reduced matrix elements, f_{Σ}^{exp} and f_{Σ}^{calc} – experimental and calculated absorption oscillator strengths (ED+MD), respectively.

Exc.	Final	<i>«</i> λ»,	$U^{(k)}$, 10 ⁻²⁰ cm ²			$A_{\Sigma}^{\text{calc}}(JJ'), \text{s}^{-1}$	B(JJ'),	$A_{\rm tot}$,	$ au_{\mathrm{rad}},$
state	state	μm	$U^{(2)}$	$U^{(4)}$	$U^{(6)}$		%	s^{-1}	ms
${}^{5}I_{7}$	${}^{5}I_{8}$	1.952	0.0249	0.1344	1.5217	56.593 ^{ED} +37.474 ^{MD}	100.0	94.07	10.63
${}^{5}I_{6}$	${}^{5}I_{7}$	2.840	0.0319	0.1336	0.9308	$16.732^{ED} + 19.051^{MD}$	21.9	163.4	6.12
	${}^{5}I_{8}$	1.157	0.0083	0.0383	0.6918	127.556 ^{ED}	78.1		
⁵ I ₅	${}^{5}I_{6}$	3.917	0.0438	0.1705	0.5729	$7.309^{\text{ED}} + 9.55^{\text{MD}}$	14.4	116.7	8.57
	${}^{5}\mathrm{I}_{7}$	1.646	0.0027	0.0226	0.8887	55.070 ^{ED}	47.2		
	${}^{5}I_{8}$	0.893	0	0.0099	0.0936	44.777 ^{ED}	38.4		
${}^{5}I_{4}$	${}^{5}I_{5}$	4.911	0.0312	0.1237	0.9099	$4.501^{\text{ED}} + 4.55^{\text{MD}}$	14.1	64.31	15.55
	${}^{5}I_{6}$	2.179	0.0022	0.0281	0.6640	22.803 ^{ED}	35.5		
	${}^{5}\mathrm{I}_{7}$	1.233	0	0.0033	0.1568	26.952 ^{ED}	41.9		
	${}^{5}I_{8}$	0.756	0	0	0.0077	5.502^{ED}	8.6		
⁵ F ₅	⁵ I ₆	1.470	0.0102	0.1213	0.4995	82.431 ^{ED}	3.3	2530	0.40
	${}^{5}\mathrm{I}_{7}$	0.968	0.0177	0.3298	0.4340	502.245 ^{ED}	19.9		
	${}^{5}I_{8}$	0.647	0	0.4277	0.5686	1938 ^{ED}	76.6		
${}^{5}S_{2}+$	⁵ I ₆	1.045	0	0.0206	0.1541	94.627 ^{ED}	7.4	1741	0.57
${}^{5}F_{4}$			0.0012	0.2580	0.1697				
	${}^{5}\mathrm{I}_{7}$	0.764	0	0	0.4096	450.097 ^{ED}	29.2		
			0	0.1988	0.0324				
	${}^{5}I_{8}$	0.549	0	0	0.2270	701.411 ^{ED}	59.9		
			0	0.2402	0.7079				

Table 3. Calculated emission probabilities for the Ho^{3+} ion in $(Lu,Sc)_2O_3$ ceramics.

 $\langle \lambda \rangle$ - calculated mean wavelength of the emission band, $U^{(k)}$, k = 2, 4, 6 – squared reduced matrix elements, A_{Σ}^{calc} – probability for radiative spontaneous transition (ED + MD), B(JJ') – luminescence branching ratio (only transitions with B(JJ') > 2% are listed), A_{tot} and τ_{rad} – total probability for radiative spontaneous transition (et al. (constrained by the spontaneous transitions) and the radiative lifetime of the excited state, respectively.

Material	Ho ³⁺ doping	Т	$\lambda_p, \mu m$	Pump	Mode	$P_{\rm out,}{ m W}$	η, %	$\lambda_L, \mu m$	Ref.
Ho: $(Lu,Sc)_2O_3$	1.4 at.%	RT	1.929	diode	qCW	0.187	7.6	2.114-2.135	*
					CW	0.029	1.6	2.134	*
			1.946	laser	CW	0.020	25	2.119	*
Ho:Lu ₂ O ₃	2 at.%	RT	1.942	laser	qCW	0.182	1	2.124	[17]
Yb,Ho:(Y,La) ₂ O ₃	1 at.%	RT	1.910	laser	CW	0.138	2.7	2.077-2.095	[21]
Ho:Y ₂ O ₃	3 at.%	77 K	1.930	diode	CW	2.5	35	2.119	[19]

Table 4. Output characteristics of Ho:A₂O₃ ceramic lasers reported so far.

*This work.



Figure 1. A 1.4 at.% Ho:(Lu,Sc)₂O₃ ceramic: (a) image of a laser-grade-polished ceramic disk and laser elements; (b) X-ray diffraction (XRD) pattern (in *blue*) compared with the standard pattern of LuScO₃ (in *black*), numbers indicate the (*hkl*) Miller's indices; (c) Raman spectrum, $\lambda_{exc} = 0.514 \,\mu\text{m}$, with positions of the Raman bands in cm⁻¹.



Figure 2. Scanning electron microscope (SEM) images of a 1.4 at.% Ho: $(Lu,Sc)_2O_3$ ceramics: (a) polished (scale bar: 20 µm) and (b) fractured (scale bar: 10 µm) surfaces.



Figure 3. (a-f) Absorption spectra of the 3 at.% Ho:(Lu,Sc)₂O₃ ceramics.



Figure 4. Luminescence decay curves for 1.4 at.% and 3 at.% Ho³⁺-doped (Lu,Sc)₂O₃ ceramics: *circles* – experimental data, *lines* – single-exponential fits for the determination of luminescence lifetime τ_{lum} .



Figure 5. Spectroscopy of Ho³⁺-doped (Lu,Sc)₂O₃ ceramics: (a) absorption, σ_{abs} , and stimulated-emission, σ_{SE} , cross-sections for the ⁵I₈ \leftrightarrow ⁵I₇ transition; (b) gain cross-sections, $\sigma_g = \beta \sigma_{SE} - (1 - \beta)\sigma_{abs}$, for the ⁵I₇ \rightarrow ⁵I₈ transition, $\beta = N({}^{5}I_{7})/N_{Ho}$ is the inversion ratio.



Figure 6. Diode-pumped Ho: $(Lu,Sc)_2O_3$ ceramic laser: (a) scheme of the laser, LD – laser diode, PM – pump mirror, OC – output coupler; (b) far-field intensity beam profile captured at $P_{abs} = 4.6$ W, corresponding to an output power of 29.2 mW ($T_{OC} = 1.5\%$).



Figure 7. Diode-pumped 1.4 at.% Ho:(Lu,Sc)₂O₃ ceramic laser: (a,b) inputoutput dependences for various (a) pump duty cycles and (b) transmissions of the OC (for a fixed pump duty cycle of 1:20), η – slope efficiency; (c) typical laser emission spectra measured at $P_{abs} = 4.9$ W in quasi-CW (qCW) operation with a duty cycle of 1:20.