Optical Materials 33 (2011) 501–505

Contents lists available at ScienceDirect

Optical Materials

journal homepage: www.elsevier.com/locate/optmat

Intensity parameters of Tm^{3+} doped Sc_2O_3 transparent ceramic laser material

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A R T I C L E I N F O

Article history:
Received 31 August 2010
Received in revised form 18 October 2010
Accepted 20 October 2010
Available online 16 November 2010

Keywords:
Sesquioxides
Transparent ceramics
Judd Ofelt analysis
Tm^{3+}:Sc_2O_3
Laser material
Diode-pumped solid-state lasers

A B S T R A C T

This work is focused on spectral investigations of Tm^{3+} doped Sc_2O_3 transparent ceramic as potential material for diode-pumped solid-state laser emitting around 2 μm. In the context of the Judd–Ofelt (J–O) theory a series of spectroscopic parameters such as J–O intensity parameters, oscillator strengths, radiative transitions probabilities, and radiative lifetimes as well as branching ratios are evaluated. The gain cross-sections which lead to an estimation of the probable operating laser wavelength for the $^3F_4 \rightarrow {}^3H_6$ Tm^{3+} laser transition were also calculated.

1. Introduction

The high-melting sesquioxides of scandium, yttrium, and lutetium are attractive laser systems because their favorable properties, especially high thermal conductivity [1] and low phonon energies [2] and the possibility of doping with rare earth ions. Due to their very high melting point [1] >2400 °C, it is very difficult to grow crystals with high optical quality and large sizes. However, laser operation of sesquioxides crystals doped with various RE^{3+} (Ho, Tm, Er, Yb) ions has been demonstrated [3–6]. The possibilities to overcome the crystal growth problems of sesquioxides by using transparent polycrystalline materials produced by ceramic technologies were also exploited [7], but the papers refer mainly to Nd^{3+} or Yb^{3+} doped or co-doped ceramics, with very promising results on Yb^{3+} emission in high-power laser experiments [8–12].

Diode-pumped solid-state lasers operating in the eye-safe spectral region near 2 μm and based on Tm^{3+}-doped solid-state media have a number of applications, first of all medical, because of the strong water absorption in this wavelength region. Surgical tissue treatment using such systems can be performed with minimal local thermal damage, which is especially important in ophthalmologic surgery. Due to water–vapor transparency and the presence of absorption lines of a number of chemical compounds in the 1.9–2.0 μm spectral region, two-micron tunable lasers offer the possibility to be used for such applications as a coherent source for laser radar, atmospheric sensing, and also for laser photo acoustic spectrometry where free-running multimode operation can be successfully used. Tm^{3+} doped crystalline materials can generate laser emission from blue to 2 μm. The ~2 μm $^3F_4 \rightarrow {}^3H_6$ emission can be achieved by diode lasers pumping in the $^3H_4$ level (800 nm range), followed by the cross-relaxation ($^3H_4 \rightarrow {}^3F_4$)–($^3H_6 \rightarrow {}^3F_4$). The visible emission is difficult to stimulate by direct pumping; there are no suitable sources. It was, however, proved that the visible (blue) emission from the $^1G_4$ Tm^{3+} level can be obtained by up conversion of near infrared radiation (using the existing efficient diode lasers in the 800 or 940–980 nm ranges), especially in co-doped systems. Thus, blue Tm^{3+} up conversion emission was obtained in Yb, Tm systems under Yb^{3+} 980 nm excitation [13]; even higher up conversion efficiency was reported by Tm^{3+} excitation in the 800 nm range, with participation of Yb^{3+} [13,14]. Blue up conversion was also studied under excitation in the 800 nm range in (Nd, Tm) [15] or (Nd, Tm, Yb) co-doped systems [16–18].

Few spectral data have been reported on Tm^{3+} in Sc_3O_3 single crystals [3] and recently on transparent ceramics [19] and no J–O analysis has been published for these materials. In the previous study [19] of Tm:Sc_2O_3 ceramics, an extended energy level scheme of Tm^{3+} has been obtained from spectral measurements at various temperatures, and the concentration quenching mechanisms of the $^3H_4$ level were investigated. In the present study we analyze in details the spectral characteristics of Tm^{3+}:Sc_2O_3 transparent ceramics determining a series of spectroscopic parameters such as J–O intensity parameters, oscillator strengths, radiative transitions probabilities, and radiative lifetimes as well as branching ratios.

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doi:10.1016/j.optmat.2010.10.032

2. Experimental methods

Transparent Sc_2O_3 ceramic doped with Tm^{3+} ions were prepared at the World Lab. Co. Nagoya, Japan by by the solid-state synthesis followed by isostatic compression (~2 Mpa) and vacuum sintering at 1750 °C. The Sc_2O_3 – sesquioxide forms at room temperature a cubic *C*-type structure, belonging to the $IA\overline{3}$ space group [20]. The unit cell contains two types of centers: C_2 site is an eightfold cubic structure with two oxygen vacancies on a face diagonal, while C_{3i} site corresponds to a cube with two vacancies on a body diagonal. The cationic density ($3.338 \times 10^{22}/cm^3$) is rather high compared to other laser crystals. The RE^{3+} dopants are assumed to occupy randomly both sites, but the induced electric dipole transitions are allowed only for C_2 centers.

The optical spectroscopic measurements of 5 at.% $Tm:Sc_2O_3$ were performed. The sample was double-side polished to 1.0 mm thick to measure the optical transmittance spectra at room temperature using a Cary 5000 UV–VIS-NIR spectrometer. The fluorescence decay curves were measured by exciting at 800 nm with optical parameter oscillator (OPO) (pumped at 355 nm triple harmonic generation of a 10 Hz, 7 ns O-switched YAG:Nd laser was used as pump source).

3. Results and discussion

3.1. Absorption data and Judd–Ofelt analysis

The sample of 5 at.% Tm doped Sc_2O_3 transparent ceramic used in spectral measurements have good optical quality as show the photograph (Fig. 1) of a 5 mm thick sample (not polished at laser quality). Figure 2 show the transmittance of $Tm^{3+}:Sc_2O_3$ transparent ceramic, it reaches about 75% for 1 mm thick sample in the ~2 micron range.

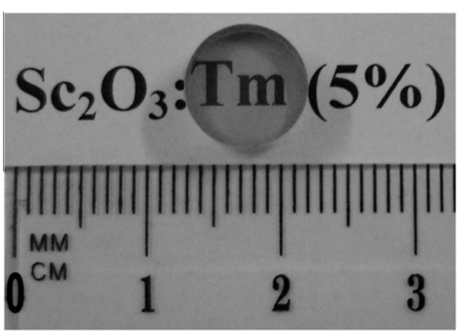

Fig. 1. Photograph of 5 at% Tm-doped Sc_2O_3 transparent ceramic sample.

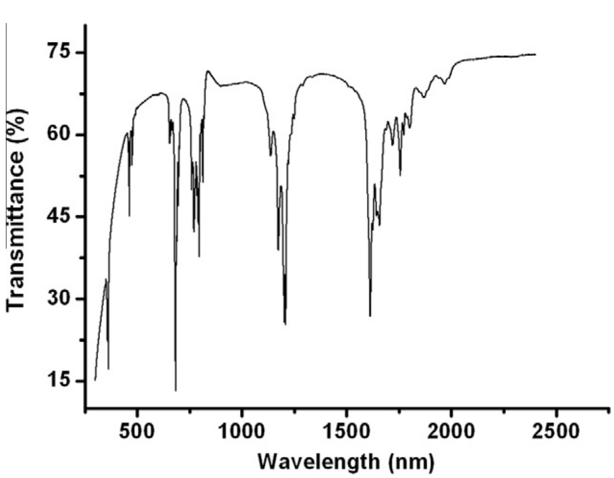

Fig. 2. The transmittance of the $Tm^{3+}:Sc_2O_3$ transparent ceramics.

In our preliminary study [19] on $Tm:Sc_2O_3$ transparent ceramics, Tm^{3+} energy level scheme (Fig. 3) and the main mechanisms involved in 2 μm emission have been investigated. In order to examine other spectral characteristics of this system, the absorption spectra ranging from 300 to 2400 nm for 5 at.% $Tm:Sc_2O_3$ were recorded. The 300 K absorption spectra, presented in Fig. 4, correspond essentially to electric dipole transitions, associated to Tm^{3+} in C_2 centers (3/4 from the actual Tm^{3+} content).

According to Judd–Ofelt theory [21,22], described in detail in Ref. [23], the calculated line strengths for electric dipole (ED) transitions between two manifolds can be expressed in terms of three Ω_t phenomenological parameters by

$$S_{calc}^{ed} = \sum_{t=2,4,6} \Omega_t |\langle 4f^n[S,L]J\|U^{(t)}\|4f^n[S',L']J'\rangle|^2 \quad (1)$$

where $\langle\|U^{(t)}\|\rangle$ are the reduced matrix elements corresponding to the transition from *J* to *J*' manifolds of the $U^{(t)}$ irreducible tensor forms of the electric dipole operator.

The line strengths due to the magnetic dipole (MD) contribution were determined using the following expression:

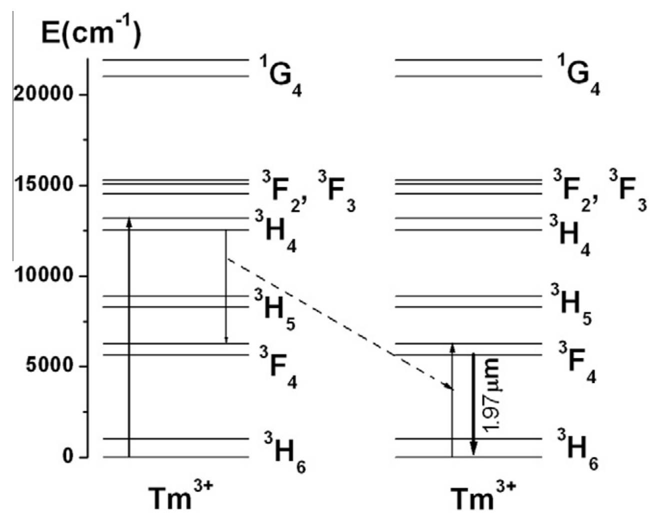

Fig. 3. Energy level diagram of Tm^{3+} doped Sc_2O_3.

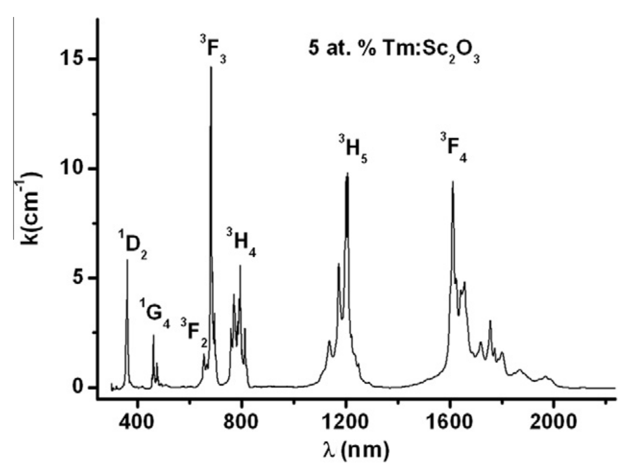

Fig. 4. Room temperature absorption spectra in 300–2400 nm range of $Tm:Sc_2O_3$ transparent ceramic.