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2.1 μm Emission Spectral Properties of Tm and Ho Doped Transparent YAG Ceramic

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ABSTRACT

Highly transparent Tm:Ho:YAG transparent ceramics were prepared using advanced ceramic technology and their spectroscopic properties were studied for infrared laser applications. Following the Judd-Ofelt procedure several spectroscopic properties such as the radiative transition probability (A_{rad}), radiative decay time (τ_{rad}) and fluorescence branching ratio (β) are quantitatively obtained from the absorption spectrum. The absorption and emission cross sections corresponding to the $5I_7 \rightarrow {}^5I_8$ transition of Ho^{3+} at 2.1 μm have been evaluated following Mc Cumber theory and found that the obtained emission spectrum very well correlates to the simulated emission spectral data. The optical gain spectrum spread from 1800 nm to 2150 nm with a spectral width of over 107 nm and maximum gain coefficient of 0.44 cm^{-1} . Thus it is expected that the $\text{Tm}^{3+}:\text{Ho}^{3+}:\text{YAG}$ ceramics would be an appropriate host material to achieve infrared laser applications at 2.1 μm .

KEYWORDS: Transparent Ceramics, Emission Spectra, YAG, Doped Transparent Ceramics.

1. INTRODUCTION

Transparent ceramics processed from micro or nanocrystallites have attracted a lot of interest by the material science community due to their several interesting properties such as low cost production and scalability to large size. These materials find wide variety of industrial applications such as lasers, armors, lenses, etc. With novel nanomaterial synthesis methodology it is now possible to make fully dens scattering free transparent ceramics that shows mechanical, thermal and optical properties equivalent to their single crystal counterpart.

Garnet structure oxide crystals doped with a rare-earth ion possess a unique combination of spectral and laser properties, as well as high mechanical strength, thermal conductivity, and optical transparency over a wide spectral region. After the first successful demonstration of lasing oscillation in Nd:YAG ceramics^{1,2} transparent ceramics of YAG have also been prepared with several other rare earth ions including Cr^{3+} ³ and Ce^{3+} ,⁴ Tm^{3+} ,⁵ Er^{3+} ,^{6,7} Yb^{3+} ⁸ and Ho^{3+} .⁹ The synthesis and composition flexibility makes this technology also enables to incorporate several dopant ions into the YAG material, which is not easy with the single crystal technology. In this study, efforts were made to prepare Tm: Ho: YAG transparent

ceramic using advanced ceramic technology^{10,11} and study the spectroscopic properties of the host with the interest of using in infrared laser applications at 2.1 μm .

2. EXPERIMENTAL DETAILS

Transparent ceramics of Tm: Ho: YAG (Tm = 6%, Ho = 1% All atomic %) have been prepared by nanocrystalline assisted advanced ceramic laser technology.^{10,11} Highly mirror polished 1 mm thick samples were used for all the optical studies. Absorption studies were carried out using (Cary, Model 14R) spectrophotometer. Emission spectrum of Ho^{3+} was obtained by exciting the Tm^{3+} at 808 nm of a Ti:S laser (Spectra Physics, Mountain View, CA). For emission lifetime studies, the 800 nm output of a pulsed (5 ns) Nd: YAG pumped MOPO SL optical parametric oscillator (Spectra-Physics, Mountain View, CA) was employed as the pumped source. The decay transients were averaged and recorded using a TDS 220 digital oscilloscope (Tektronix, Beaverton, OR). All measurements were carried out at room temperature.

3. RESULTS AND DISCUSSION

3.1. Phase and Morphology

Figure 1 shows the X-ray powder diffraction patterns of transparent ceramic in comparison with standard JCPDS data of YAG (01-073-3184). Since the peak locations are

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Fig. 1. X-Ray diffraction pattern of the Er:Cr:YAG ceramic.

exactly matching with the standard it is clear that the obtained phase is pure YAG. XRD results reveal that the polycrystalline transparent YAG ceramic sample has a cubic phase structure with unit cell parameters $a = b = c = 11.99 \text{ \AA}$.

In order to check the quality of the ceramic microstructure of surface and internal grains were observed through SEM and TEM. The SEM image shown in Figure 2(a) indicates that the average grain size of the surface grain is about $2 \mu\text{m}$ in diameter. Figure 2(b) shows a transmission electron microscope (TEM) photograph of the YAG ceramic where the grain boundary between two grains was shown. Based on the TEM analysis the width of grain boundary was estimated to be less than 2 nm . Further, from observation of microstructure, there were no obvious defect, pore, and second phase. In order to check the internal grain size and microstructure, each of the sample were crushed down and fracture surfaces of each sample were observed under SEM (see Fig. 2(c)). As observed from surface image, the internal microstructure was consistent with the surface microstructure. Moreover, almost no residual pores and no grain boundary phases were confirmed under SEM observation. Such narrow grain boundary and very low pore volume ensures very low scattering in the ceramic material.

3.2. Radiative Spectral Properties

The room temperature UV-VIS-NIR absorption spectrum of the sample was shown in Figure 3 with the photograph of the fabricated ceramic in the inset. The spectrum is well resolved so that almost all Stark components corresponding to different manifold of Tm^{3+} and Ho^{3+} are observed. The absorption band positions are well matched with the spectral data of Ho^{3+} doped single crystal.⁹ In order to calculate the radiative spectral properties of Ho^{3+} , absorption

Fig. 2. (a) SEM image of the Surface grain. (b) TEM image of the grain boundary. (c) SEM image of the Internal grains.

dipole strength (S_{meas}) were evaluated from the absorption spectral data following standard expression¹²

$$S_{\text{mean}}(J \rightarrow J') = \frac{3hc(2J+1)}{8\pi^3 \lambda e^2 N_0} \left[\frac{9n}{(n^2+2)^2} \right] \int \alpha(\lambda) d\lambda \quad (1)$$

Here, J and J' denote the total angular momentum quantum number of the initial and final states, respectively, e is the charge of the electron, c is the velocity of the light in

Fig. 3. Optical absorption spectrum of the mirror polished Tm (6%) Ho (1%): YAG transparent ceramic. Inset shows the photograph of the fabricated ceramic.

the vacuum, h is Planck's constant, λ is the mean wavelength of the absorption band and N_0 is the Ho^{3+} ion concentration per unit volume, $\alpha(\lambda) = 2.303 A(\lambda)/d$ is the measured absorption coefficient at a given wavelength λ , $A(\lambda)$ the absorbance, d the thickness of the sample and n is the measured refractive index. The factor in bracket represents the local field correction for Ho^{3+} ion in the initial J manifold. The values of S_{meas} obtained by the numerical integration of the absorption line shapes were used to obtain the phenomenological Judd–Ofelt parameters Ω_t ($t = 2, 4, 6$) by fitting the experimental value with the theoretical expression derived by Judd¹³ and Ofelt¹⁴ as

$$S_{\text{calc}}(J \rightarrow J') = e^2 \sum_{t=2,4,6} \Omega_t |\langle (S, L)J \| U^t \| (S', L')J' \rangle|^2 \quad (2)$$

Here, $\|U^t\|$ are the doubly reduced matrix elements of the unit tensor operator of rank $t = 2, 4$ and 6 which are calculated from the intermediate coupling approximation. The reduced matrix elements are virtually independent of the ligand species surrounding the rare earth ions and thus approximately unchanged from host to host. The values of these matrix elements are obtained from the published reports.¹² The three Judd–Ofelt parameters were obtained by fitting the measured dipole strength Eq. (1) to the theoretical dipole strength Eq. (2) using the least square fitting procedure. The experimental and calculated electric dipole line strengths of the different absorption bands observed are collected in Table I along with the RMS deviation of the fit. The calculated values of the phenomenological Judd–Ofelt parameters obtained for the Ho^{3+} in the present system are $\Omega_2 = 1.22 \times 10^{-20} \text{ cm}^2$, $\Omega_4 = 2.794 \times 10^{-20} \text{ cm}^2$, $\Omega_6 = 0.97 \times 10^{-20} \text{ cm}^2$. It should be noted that these values are not in good agreement with the values reported for single crystal¹⁵ viz. $\Omega_2 = 0.10 \times 10^{-20} \text{ cm}^2$, $\Omega_4 = 2.08 \times 10^{-20} \text{ cm}^2$, $\Omega_6 = 1.72 \times 10^{-20} \text{ cm}^2$. This is

Table I. Measured and calculated line strengths of the absorption transitions of Ho^{3+} in TmHo:YAG.

Transition from $^5\text{I}_8$ to	Wavelength (nm)	n	S_{meas} (10^{-20} cm^2)	S_{cal} (10^{-20} cm^2)	$(\Delta S)^2$ (10^{-40} cm^2)
$^5\text{I}_7$	1910	1.80	1.54	1.90	0.13
$^5\text{F}_5$	649	1.82	1.54	1.81	0.07
$^5\text{F}_4 + ^5\text{S}_2$	539	1.83	2.26	1.61	0.42
$^5\text{G}_5$	420	1.85	0.84	0.02	0.63
$^5\text{H}_6 + ^3\text{D}_2$	375	1.86	1.60	0.05	2.38

RMS = $1.3 \times 10^{-20} \text{ cm}^2$, $\Omega_2 = 1.22 \times 10^{-20} \text{ cm}^2$, $\Omega_4 = 2.94 \times 10^{-20} \text{ cm}^2$, $\Omega_6 = 0.97 \times 10^{-20} \text{ cm}^2$ (Ceramic), $\Omega_2 = 0.101 \times 10^{-20} \text{ cm}^2$, $\Omega_4 = 2.08 \times 10^{-20} \text{ cm}^2$, $\Omega_6 = 1.72 \times 10^{-20} \text{ cm}^2$ (Single Crystal).

due to the fact that, since the present ceramic contains both Tm and Ho, there are several overlapping transitions which makes it difficult to isolate the Ho transitions by deconvolution procedure and that results in poor fitting with Judd–Ofelt model.

The obtained J–O parameters can be used to calculate the radiative probability and radiative lifetime of $\text{Ho}^{3+}: ^5\text{I} \rightarrow ^5\text{I}_8$ transition using the following formula¹²

$$A_{\text{rad}} = \frac{64\pi^4}{3h(2J+1)\lambda^3} \left(\left[\frac{n(n^2+2)^2}{9} \right] S_{\text{ed}} + n^3 S_{\text{md}} \right) \quad (3)$$

where, S_{ed} and S_{md} represent the predicted fluorescence line strength for the induced electric and magnetic dipole transition, respectively. S_{ed} is calculated using Eq. (2) and presents a host dependence through the Ω_t parameters. S_{md} can be calculated with the expression,¹²

$$S_{\text{md}} = \left(\frac{e^2 h^2}{16\pi^2 m^2 c^2} \right) |\langle (S, L)J \| L + 2S \| (S', L')J' \rangle| \quad (4)$$

where the term inside the bracket represents the magnetic dipole matrix element. The values of the radiative transition probability, fluorescence branching ratios (β) and radiative decay time (τ_{rad}) for the most common emission bands are shown in Table II along with the compared values of radiative decay times in single crystal.

3.3. Cross-Sections and Gain Properties

According to the measured absorption spectra shown in Figure 3, the absorption cross-section (σ_a) can be calculated by α/N , where α is the absorption coefficient and N is the ionic concentration. Using McCumber theory¹⁶ the emission cross-section for resonant transition can be obtained from the expression

$$\sigma_e(\lambda) = \sigma_a(\lambda) \frac{Z_l}{Z_u} \exp \left[\frac{\varepsilon - E}{kT} \right] \quad (5)$$

where Z_l and Z_u are the partition functions for the lower and the upper levels, respectively, involved in the considered optical transition, T is the temperature (here is the room temperature), k is the Boltzmann constant, and ε

Table II. Calculated radiative spectral properties of major emission transition of Ho^{3+} in $\text{Tm}^{3+}:\text{Ho}^{3+}:\text{YAG}$ ceramic and comparison with single crystalline YAG.

Transition	λ (nm)	n	S_{cal} (10^{-20} cm^2)	A_{rad} (s^{-1})	β (100%)	τ_{rad} (ms)	
						Ceramic	Single crystal
$^5\text{I}_7 \rightarrow ^5\text{I}_8$	1980	1.80	1.99	94.54	100	10.58	7.82
$^5\text{I}_6 \rightarrow ^5\text{I}_7$	2941	1.78	1.35	32.61	9.2	5.30	3.48
$^5\text{I}_8$	1170	1.81	0.79	155.89	90.8		
$^5\text{I}_5 \rightarrow ^5\text{I}_6$	3922	1.75	1.14	13.13	4.4	6.66	4.27
$^5\text{I}_7$	1653	1.80	0.93	75.74	52.6		
$^5\text{I}_8$	897	1.81	0.11	61.93	43.0		
$^5\text{I}_4 \rightarrow ^5\text{I}_5$	4878	1.72	1.30	7.78	5.3	11.35	7.10
$^5\text{I}_6$	2174	1.79	0.72	31.12	38.1		
$^5\text{I}_7$	1235	1.81	0.16	38.58	47.2		
$^5\text{I}_8$	760	1.82	0.007	7.78	9.5		
$^5\text{F}_5 \rightarrow ^5\text{F}_4$	4444	1.74	0.02	0.07	0	0.294	0.307
$^5\text{I}_5$	2326	1.79	0.25	7.20	0.2		
$^5\text{I}_6$	1460	1.80	0.86	101.80	3.0		
$^5\text{I}_7$	966	1.81	1.43	754.84	22.2		
$^5\text{I}_8$	649	1.82	1.82	2542.9	74.6		
$^5\text{S}_2 \rightarrow ^5\text{F}_5$	3333	1.77	0.04	0.74	0	0.456	0.270
$^5\text{F}_4$	1905	1.80	0.35	40.34	1.8		
$^5\text{I}_5$	1370	1.81	0.11	36.23	1.7		
$^5\text{I}_6$	1015	1.81	0.21	164.19	7.5		
$^5\text{I}_7$	749	1.82	0.39	779.70	35.6		
$^5\text{F}_4 \rightarrow ^5\text{S}_2$	0	0	0.05	0.0	0		
$^5\text{F}_5$	3333	1.77	0.65	0.0	0.2	0.330	0.163
$^5\text{F}_4$	1905	1.80	0.32	20.46	0.7		
$^5\text{I}_5$	1370	1.81	0.84	102.24	3.4		
$^5\text{I}_6$	1015	1.81	0.93	281.92	9.3		
$^5\text{I}_7$	749	1.82	0.62	412.13	13.6		
$^5\text{I}_8$	542	1.837	1.39	2204.8	72.8		

is the energy for the transition between the lower Stark sublevels of the emitting multiplets and the lower Stark sublevels of the receiving multiplets (zero-phonon line). E is the energy corresponding to the peak wavelength of the absorption. Figure 4 shows the absorption and emission cross section spectral overlap. The peak emission cross section obtained at 2100 nm is $4.76 \times 10^{-21} \text{ cm}^2$ which is comparable to the result in other Ho doped materials.¹⁷

The fluorescence spectrum of the sample obtained by pumping the Tm absorption at 808 nm is shown in Figure 5. Major emission peaks observed are at 1918 and 2100 nm with several associated Stark levels. The observed transitions are assigned to be $^3\text{F}_4 \rightarrow ^3\text{H}_5$ of Tm^{3+} and $^5\text{I}_7 \rightarrow ^5\text{I}_8$ of Ho^{3+} . The emission spectrum obtained is almost identical to the reported spectra in similar ceramic.¹⁸ The intensity of the emission at 2100 nm is larger than that of the Tm emission because of the efficient energy transfer from Tm $^3\text{F}_4$ state to the Ho $^5\text{I}_7$ state. The energy level diagram shown in Figure 6 represents the excitation and energy transfer mechanisms in the Tm, Ho system. Upon excitation at 808 nm Tm^{3+} gets excited to $^3\text{H}_4$. Most of the Tm ions in the $^3\text{H}_4$ level were transferred to $^3\text{F}_4$ level by the cross relaxation between Tm ions via. $^3\text{H}_4 + ^3\text{H}_6 \rightarrow ^3\text{F}_4 + ^3\text{F}_4$. Part of the Tm ions

were transferred from $^3\text{H}_4$ to $^3\text{H}_5$ and relaxed to $^3\text{F}_4$ state through multiphonon relaxation. Tm ion in the $^3\text{F}_4$ level transfer their energy to the $^5\text{I}_7$ level of Ho through the process $^3\text{F}_4 + ^5\text{I}_8 \rightarrow ^3\text{H}_6 + ^5\text{I}_7$. Since the Ho^{3+} concentration is high the probability of such energy transfer and cross

Fig. 4. Absorption and emission cross section spectra of Ho^{3+} in YAG ceramic corresponding to transition from $^5\text{I}_7$ to $^5\text{I}_8$ manifold. Emission spectrum was simulated from absorption data using McCumber theory.

Fig. 5. Emission spectrum of Ho^{3+} in YAG ceramic obtained by exciting the Tm^{3+} at 808 nm.

Fig. 7. Decay curve of the Ho^{3+} emission at 2100 nm.

relaxation are high enough to have efficient energy transfer from Ho to Tm. The population accumulated at the $^5\text{I}_7$ decay to the ground state $^5\text{I}_8$ giving the radiative emission at 2100 nm. The fluorescence decay curve of the Ho emission under 808 nm excitation of Tm is shown in Figure 7. Using the experimentally measured decay time of 7.37 ms and calculated radiative decay time of 10.58 ms the internal radiative quantum yield of the 2100 nm emission was calculated to be $\sim 70\%$.

Gain cross section is an important parameter in analyzing the optical gain and stimulated emission characteristics of an amplifier medium. By measuring the absorption and emission cross sections using standard procedure¹⁹ one can simulate the gain spectrum using the expression

$$G(\lambda) = N [P\sigma_e(\lambda) - (1 - P)\sigma_a(\lambda)] \quad (6)$$

Fig. 6. Mechanisms of energy transfer from Tm^{3+} to Ho^{3+} . CR-cross relaxation; ET-Energy transfer.

where, σ_a is the absorption cross section, σ_e is the emission cross section, P the population of the emitting level and N is the total concentration of Ho^{3+} ions. The calculated gain spectra for P ranging from 0 to 1 shown in Figure 8 for the $^5\text{I}_7 \rightarrow ^5\text{I}_8$ transition indicate that, the gain increases with the population inversion and positive gain in the system can be achieved only for a population inversion of 60% and above. At 100% population inversion a maximum gain coefficient of 0.44 cm^{-1} was obtained which is similar to the values obtained in several glassy hosts.^{20,21} Further, the obtained gain spectrum spread from 1800 nm to 2150 nm with a spectral width of over 107 nm. Thus it is expected that the present Tm: Ho: YAG ceramic because of its excellent optical quality and infrared emission properties, is an appropriate host to make 808 nm pumped solid state laser operating at 2100 nm.

Fig. 8. Simulated optical gain spectrum for the $^5\text{I}_7 \rightarrow ^5\text{I}_8$ transition of Ho^{3+} under various population inversion (P) conditions.

4. CONCLUSIONS

Transparent YAG ceramic doped with Tm and Ho fabricated by the vacuum sintering method shows excellent optical quality and emission characteristics comparable to the single crystalline material. Due to the strong energy transfer from Tm to Ho, the present YAG ceramic shows excellent emission properties at 2100 nm under 808 nm pumping with an internal quantum yield of $\sim 70\%$, optical gain coefficient of 0.44 cm^{-1} and a spectral width of 107 nm which are favorable to consider this as a potential host to make 808 nm pumped solid state laser operating at 2100 nm.

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