Fabrication and optical studies of transparent Tm, Ho:YAG ceramics

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Abstract

The aim of this work has been to obtain transparent Tm, Ho:YAG ceramics (thulium doping range: 2–6 at.%, holmium doping range: 0.1–1.0 at.%) by reaction sintering using commercial powders. It has been proved that the particle size, purity and degree of agglomeration of the powders used are crucial from the point of view of the optical quality of ceramics. The spectroscopic measurements of Tm, Ho:YAG ceramics with different concentration of active ions (including transmission and emission spectra measurements) have been presented and discussed. As has been found, both concentration of holmium and thulium separately as well as the balance between them are of great importance. Energy transfer between Tm and Ho ions has been demonstrated.

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1. Introduction

Ceramic laser materials have arisen a profound interest recently. A great number of research works on transparent yttrium aluminum garnet ceramics doped with rare earths, including Nd3+, Yb3+ and Er3+, have been published so far [1–10]. Tm3+ and Ho3+ dopants enabling the emission of the “eye-safe” wavelength of around 2 μm prove to be particularly attractive [11–15]. Laser radiation at this range is obtained in holmium as a result of transition from the 5I8 level to the 5I7 level, which corresponds to the wavelength of 2.09 μm. Unfortunately, the arrangement of energy levels in holmium ions precludes the possibility of its pumping using traditional laser diodes emitting at 785–980 nm. This problem can be overcome by co-doping with thulium and making use of energy transfer between ions (known as the cross relaxation phenomenon). Available literature data show that attempts have been made to obtain monocrystals both doped and co-doped with holmium and thulium ions such as Tm, Ho:GdVO 4 [16] or Tm, Ho:YAlO3 [17]. In addition, works of Falconieri et al. [18,19] and French et al. [20] focusing on the spectroscopic properties of Tm, Ho:YAG crystals and, in particular, energy transfer between dopant ions, have been published. Liu et al. [21] and Urata [22,23] have proved that similar phenomena can be observed in Tm, Ho:YAG ceramics. This arrangement is possible since in the case of both ions energy transfers between the 3F4 → 3H6 levels for the Tm ion and between the 3I7 → 3I8 levels for the Ho ion are well-fitted and additionally thulium has the absorption band in the 780–790 nm range [24–26]. In the Tm, Ho:YAG arrangement, thulium plays the role of a sensitizer and is responsible for collecting energy from the excitation source, which is subsequently non-radially and resonantly transferred to the holmium ion. Next, holmium can emit the received energy through laser action from the 3I7 level. Energy transfer is possible since its duration ranges between 5 and 20 μs, i.e. considerably shorter than in the case of the lifetime of the 3F4 and 3I7 levels. When compared with materials doped only with Ho3+, materials co-doped with Tm3+ and Ho3+ ions are characterized by a long lifetime (6–15 ms) and the excitation process in their case is much more effective, which is likely to result in reaching the generation of about 2 μm. These types of lasers are particularly useful in medicine, meteorology as well as in LIDAR devices (Light Detection and Ranging) [27–29].

Polycrystalline materials intended to operate in laser systems should combine the advantages of monocrystals with those of glass. To be more precise, they ought to have good optical, thermal and spectral properties, and at the same time enable obtaining high dopant concentrations and producing big elements. Even though the manufacturing process of Tm:YAG ceramics as such seems to be less complex than this of monocrystals, the end result is dependent on a great number of factors. Reactive sintering is the simplest and the most commonly used manufacturing method of transparent ceramics. The size and shape of particles as well as the degree of agglomeration of the applied powders play a key role.
in this technique [30–34]. An incorrect choice of these parameters is likely to lower the value of transmission. As is well-known, light scattering in a polycrystalline material can take place on pores, inclusions of different phases (with different indexes of refraction) or highly defective grain boundaries. In theory, obtaining a non-porous single-phase, homogeneous material with small grains would be the most beneficial. However, just as in the case of other ceramic materials it is really tough to completely eliminate porosity, at the same time maintaining high purity which restricts the use of additives facilitating the sintering process.

2. Materials and methods

In the present work, co-doped transparent Tm, Ho:YAG ceramics have been obtained using the reactive sintering method. Both materials granulated manually using a sieve and those obtained using freeze granulation have been employed.

In the case of the former technique, the following commercial powders have been used: \( \text{Al}_2\text{O}_3 \) (Taimei TM DAR, 99.995%), \( \text{Tm}_2\text{O}_3 \) (Alfa Aesar, 99.99%) and \( \text{Ho}_2\text{O}_3 \) (MetallRare Earth, 99.99%), three types of yttrium oxide powder: submicronic \( \text{Y}_2\text{O}_3 \) powder (InframatAdv. Mat. 39R-0801, 99.99%), micronic \( \text{Y}_2\text{O}_3 \) powder (InframatAdv. Mat. 39R-0803, 99.99%) and \( \text{Y}_2\text{O}_3 \) nanopowder obtained by precipitating yttrium nitrate using ammonium bicarbonate (AHC) calcinated in air at the temperature of 1100 °C for 2 h [24]. The powders have been mixed for 1 h in an attritor mill using \( \text{ZrO}_2 \) balls measuring 2 mm in diameter in 96% ethanol with an addition of 0.5% tetraethyl orthosilicate (TEOS) facilitating the sintering process. After drying the mixture for 24 h at 50 °C, the granulated material with an addition of polyvinyl alcohol (PVA) has been subsequently sieved through a polyethylene laboratory sieve.

Moreover, the granulates have been produced in this work by freeze granulation using the following commercially available powders: \( \text{Al}_2\text{O}_3 \) (Taimei TM DAR, 99.995%), \( \text{Y}_2\text{O}_3 \) (InframatAdv. Mat. 39R-0803, 99.99%), \( \text{Tm}_2\text{O}_3 \) (Alfa Aesar, 99.99%) and \( \text{Ho}_2\text{O}_3 \) (MetallRare Earth). The powder mixture has been mixed for 2 h with a velocity of 350 rpm in a Pulverisette 6, Fritsch high-energy planetary mill using \( \text{Si}_3\text{N}_4 \) balls in water with an addition of a Dolapix CE-60 deflocculant, Duramax B-1000 binder and silica in the form of octanion dissolved in water. The suspension prepared in this manner has been sprayed using a nozzle to intensively mix liquid nitrogen. The obtained frozen granules have been freeze-dried (Lyovac GT 2, Steris, Germany).

Next, all outcome granulates have been uniaxially pressed to form pellets having 20 mm in diameter and isostatically pressed at the pressure of 120 MPa. In order to remove the binder, at first
the samples have been annealed in air at 1000 °C for 1 h. The ceramics prepared in this manner have undergone reactive sintering in a vacuum furnace at the temperature of 1715 °C for 6 h. Both the applied starting powders and the ceramics have been analyzed in terms of their phase composition using XRD (Siemens D-500). The apparent density of the ceramics has been determined hydrostatically. The microstructure of the sintered materials has been observed using a scanning electron microscope (Carl Zeiss Crossbeam Workstation AURIGA). All obtained ceramics have been ground to the thickness of 1 mm and double side polished. The

Fig. 2. SEM pictures of the microstructures of Tm, Ho:YAG ceramics obtained by reaction sintering using different particle size of yttrium oxide powders (a) nanometric, (b) submicron and (c) micron.

Fig. 3. SEM pictures and Energy Dispersive X-ray maps of unreacted areas.
transmission spectra of ceramics have been measured by a Varian Cary500 spectrophotometer in the infrared and visible light range. The measurements of emission spectra have been performed using an Opto Power Corporation temperature-stabilized 785 nm laser diode operating in the q-cw regime as a light source. All luminescence spectra have been obtained at room temperature using in the following order: an ACTON SpectraPro 2300i grating monochromator, Hamamatsu G 6122 InGaAs detector (sensitivity range 1.1–2.1 μm) and SR830 lock-in amplifier system.

3. Results and discussion

Fig. 1 presents SEM images of all powders used to prepare transparent Tm, Ho:YAG ceramics. As can be noticed all used commercial powders, except for alumina (TM-DAR Taimei submicronic powder with the average grain size not exceeding 200 nm), are strongly agglomerated. Y₂O₃ obtained at ITME is nanometric, and it consists of spherical particles having the size of below 150 nm which are weakly clustered to form soft agglomerates.

SEM images presenting the microstructures of Tm, Ho:YAG ceramics prepared by reactive sintering at 1715 °C for 6 h using...
different yttria powders are presented in Fig. 2. Even though the X-ray phase analysis has shown that all obtained ceramics are single-phase materials, SEM observations have proven that there is a strong correlation between the microstructure of the obtained ceramics and the used powders. One can observe random, local areas having a different composition (Fig. 2 b and c) in the case of commercial Y$_2$O$_3$ powders. Fig. 3 presents Energy Dispersive X-ray maps. It suggests that the inclusions are most probably Tm:Y$_2$O$_3$. The occurrence of these unreacted areas arises from the presence of big compact agglomerates of Y$_2$O$_3$ powder which have not been eliminated during milling in the attritor mill (Fig. 4). Only in the case of Y$_2$O$_3$ nanopowder the microstructure is homogeneous, without any secondary phase inclusions (Fig. 2a). Recently, Kupp et al. [34] have reported on the effect of particle size on yttrium aluminum garnet (YAG) phase formation by a solid-state reaction. As proved appropriate particle size and optimal distribution of starting powders are required to accelerate the kinetics of phase formation allowing phase-pure YAG formation. However, when prolonging the mixing time, ZrO$_2$ impurities (originating from balls and the milling container) have been observed in the XRD analysis.

The transmission spectra of ceramics prepared with different yttria powders have been measured (Fig. 5). The highest transmission (70% for the wavelength of 1.5 μm) has been obtained for the sample manufactured using precipitated Y$_2$O$_3$ nanopowder. For other ceramics, the transmission values at this wavelength do not exceed 60%. It can be observed that the higher the average particle size on yttrium aluminum garnet (YAG) phase formation by a solid-state reaction, the lower the transmission value. Insufficiently low transmission values obtained for ceramics probably result from the presence of undesirable secondary phases (Figs. 2 and 3) and residual porosity in the samples, which needs to be eliminated.

Fig. 6 presents an SEM picture of the freeze granulated powders. It can be noticed that the granules are homogeneous and no agglomerates are visible, which proves the efficiency of planetary milling. The weight loss of Si$_3$N$_4$ balls during milling is around 0.03 wt.%. The earlier works proved that Si$_3$N$_4$ contamination due to milling does not affect transparency; however, it can slightly influence the luminescence spectra [35,36].

In consequence, the ceramics have had homogeneous microstructures without unreacted areas (Fig. 7). In addition, it is also noticeable that the average grain size changes depending on the doping level. The average grain size for the sample with the lowest amount of doping ions (2% Tm, 0.1% Ho) is around 6 μm (Fig. 7a). If the same thulium doping level is maintained and the holmium rate is increased, the grain size reaches more than 21 μm (Fig. 7b). An opposite trend has been observed for samples doped with 6% thulium. The average grain size for ceramics containing 6% Tm and 0.1% Ho is about 25 μm (Fig. 7c). This value is decreased to around 15 μm when the holmium content gets higher (Fig. 7d).

Fig. 8 presents the transmission spectra of Tm, Ho:YAG fabricated using freeze granulation and vacuum sintered for 6 h at 1715 °C. The transmission values measured at 1.5 μm are ranging between 75% and 80% for samples with 2% of thulium and differing holmium doping level. The best results have been achieved for the ceramics containing 2% Tm and 0.5% Ho. Among the samples with 6% thulium doping level the highest transmittance has been recorded for ceramics with 0.1% of Ho. Increasing the holmium doping level results in a slight decrease in the transmission value (75% for the wavelength of 1.5 μm).

The emission spectra of the obtained Tm, Ho:YAG ceramics have been measured by excitation with a 785 nm laser diode. With this type of a pump in the 1500–2150 nm spectral range, the emission of both thulium ions and holmium ions can be observed. A comparison of the emission spectra for ceramics doped with thulium ions only and ceramics co-doped with holmium ions has allowed the identification of emission lines characteristic of active ions separate (Fig. 9). The emission of Ho$^{3+}$ ions under Tm$^{3+}$ excitation indicates the phenomenon of energy transfer. Moreover, it has been recorded that the concentration of each active ion as well as the ratio between these ions have a strong influence on the emission
spectrum. In the case of ceramics with a constant concentration of Tm ions (2% or 6%) with increasing the concentration of Ho ions the intensity of holmium lines (Figs. 10 and 11) in the emission spectrum is enhanced.

4. Summary

In the present work co-doped transparent Tm, Ho:YAG ceramics (thulium dopant rate: 2–6 at.%; holmium dopant rate: 0.1–1.0 at.%) have been obtained by the reactive sintering method using both...
commercially available powders and the nanopowders produced at ITME. Both materials granulated manually using a sieve and those obtained using freeze granulation have been employed. The research works carried out have shown that the properties of the applied powders, including the size of particles as well as the degree of agglomeration, are of great importance to the optical quality of ceramics. In addition, it has been found that the dopant concentration exerts a significant influence on the average grain size in Tm:Ho:YAG ceramics. When using identical technological parameters its value has varied between 10 and 30 µm. The best transmission of around 80% for the wavelength of 1.5 µm has been recorded for a series of samples manufactured by freeze granulation. Nonlinear phenomena connected with the transfer of energy between dopant ions have been noted. Emission spectra depend on the concentration of active ions and the concentration of holmium and thulium alone as well as the proportion of the former to the latter are fundamentally important.

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References


