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Fabrication of transparent Yb,Cr:YAG ceramics by a solid-state reaction method

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Abstract

Transparent ytterbium and chromium codoped yttrium aluminum garnet (Yb,Cr:YAG) ceramics, containing Ca as charge counter element and TEOS as sintering aid, were fabricated by a solid-state reaction method using high-purity Y_2O_3, Al_2O_3, Cr_2O_3 and Yb_2O_3 powders as raw materials. The mixed powder compacts were sintered at 1770 °C for 10 h under vacuum and annealed at 1450 °C for 20 h in air. The Yb,Cr:YAG ceramics exhibit a pore free structure with an average grain size of about 40 μm. The optical transmittance of 5 at% Yb, 0.025 at% Cr:YAG reaches 75% at 1100 nm. The strong absorptions of Yb^{3+} at 940 and 968 nm are suitable for InGaAs diode laser pumping; an absorption band at 1030 nm is suitable for passive Q-switch laser output at 1030 nm. Transparent Yb,Cr:YAG ceramics may be a potential material for compact, efficient, high-stability diode-laser-pumped passive Q-switched solid-state lasers.

Keywords: Yb,Cr:YAG; Transparent ceramics; Fabrication; Solid state reaction; Spectrum properties; Self-Q-switched lasers

1. Introduction

Recent advances in high-performance strained layer diode lasers, with a wavelength between 0.9 and 1.1 μm have stimulated interest in diode-pumped Yb^{3+} lasers [1]. InGaAs laser diodes allow the elective coupling of pumped light into the gain medium, so as to allow efficient room temperature operation of Yb:YAG. Furthermore, diode-pumped Yb^{3+}:YAG laser has several advantages relative to Nd^{3+}:YAG laser, such as low thermal load, long upper state lifetime, large absorption width around the InGaAs laser emission range, relative large emission cross section, high thermal conductivity, and strong energy-storing capacity [2].

Diode-pumped Q-switched solid-state lasers have been demonstrated to generate high efficiency, high average power and high energy per pulse. It is well known that Q-switched lasers can be applied widely in lidars, remote sensing, pollution detection, nonlinear-optical process, and material processing. In recent years, Cr^{4+}-doped crystals have attracted a great deal of attention as passive Q-switches [3], as they have many attractive characteristics such as photochemical and thermal stability, high damage threshold, large absorption cross-section and low saturation intensity at the lasing wavelength. The broad emission band centered at 1030 nm of Yb^{3+} couples well with the saturation absorption of Cr^{4+}:YAG, and passively Q-switched Yb^{3+} lasers using Cr^{4+}:YAG as saturable absorber have been demonstrated [4,5]. Cr^{4+} also can be doped into gain medium to form self-Q-switched lasers [6,7]. A self-Q-switched Yb,Cr:YAG laser, by using Yb,Cr:YAG crystal that combines the advantages of the gain medium Yb^{3+} and the saturable absorber Cr^{4+} into one, has also been achieved [8].

YAG ceramics have many advantages over YAG crystal. Therefore, Yb,Cr:YAG transparent ceramic may be a more potential self-Q-switched laser material relative to Yb,Cr:YAG crystal and can be a potential self-Q-switched laser material used for generating sub-nanosecond laser pulses [9]. It has been reported that efficient laser oscillations were performed using Nd:YAG transparent

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ceramics prepared by solid-state reaction and vacuum sintering [10]. In this work, transparent Yb,Cr:YAG ceramics with Ca as charge counter element and TEOS as sintering aid were successfully fabricated by simple solid-state reaction and vacuum sintering. The microstructural, optical and spectral properties of Yb,Cr:YAG ceramics obtained were investigated.

2. Experimental procedure

High-purity powders of Al_2O_3 (Shanghai Wusong Chemical Co. Ltd., 99.99%, 400–600 nm), Y_2O_3 (Shanghai Yuelong New Materials Co. Ltd., 99.99%, 1–3 μm), Cr_2O_3 (Sinopharm Chemical Reagent Co. Ltd., spectral purity) and Yb_2O_3 (Shanghai Yuelong New Materials Co. Ltd., 99.99%, 400–600 nm) were used as starting materials. Y_2O_3, Al_2O_3 and Yb_2O_3 were available commercial powders. CaO (Sinopharm Chemical Reagent Co. Ltd., spectral purity) was also used, because Ca^{2+} can balance the charge when Cr^{3+} changes into Cr^{4+}. The starting powders were weighed to result in a chemical composition of 5 at% Yb, 0.025 at% Cr:YAG and mixed by ball-milling with Ø 6 mm ZrO_2 balls in anhydrous alcohol for 10 h, with an addition of 0.5 wt.% tetraethyl orthosilicate (TEOS) as sintering aid. The mixtures were dried, sieved, dry-pressed under 100 MPa into Ø 20 mm disks and finally cold-isostatically pressed under 200 MPa. The compacted disks were sintered at 1770 °C for 10 h under vacuum and then annealed at 1450 °C for 20 h in air. The phase composition of the product was identified by X-ray diffraction (Model D/MAX-2550V, Rigaku, Japan). Mirror-polished samples (1 and 0.5 mm thick) on both surfaces were used to measure optical transmittance and absorbed spectrum (Model U-2800 Spectrophotometer, Hitachi, Japan), and luminescence spectrum excited by 980 nm laser diode (Model SPEX Fluorolog-3, Jobin Yvon, France).

3. Results and discussion

Fig. 1 shows the quite transparent mirror-polished 5 at% Yb, 0.025 at% Cr:YAG sample (1 mm thick) sintered at 1770 °C for 10 h under vacuum and then annealed at 1450 °C for 20 h in air.

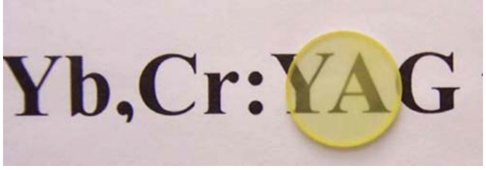

Fig. 1. Mirror-polished 5 at% Yb, 0.025 at% Cr:YAG ceramic (1 mm thick) sintered at 1770 °C for 10 h under vacuum and then annealed at 1450 °C for 20 h in air.

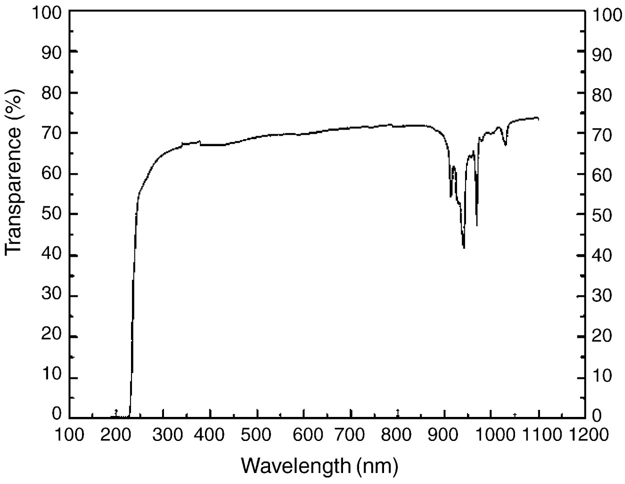

Fig. 2. Optical transmission spectrum of the transparent 5 at% Yb, 0.025 at% Cr:YAG ceramic (0.5 mm thick).

Fig. 2 shows the optical transmission spectrum of the Yb,Cr:YAG ceramic from 200 to 1100 nm. The transmittance in the visible light region reaches 70% and about 75% near 1100 nm region.

XRD pattern of the sample is shown in Fig. 3. All of the observed peaks are characteristic of YAG phase and no other phases are detected.

Fig. 4 shows the SEM microstructure of fracture surface of the specimen. The average grain size is about 40 μm and it appears relatively uniform. There are nearly no pores in or between the grains.

Fig. 5 shows the absorption spectra of the Yb,Cr:YAG ceramic in the wavelength range from 200 to 1150 nm. The absorption bands centered at 913, 940, and 968 nm are attributed to the $^2F_{7/2} \rightarrow {}^2F_{5/2}$ transition of Yb^{3+}. As the sample also has a strong absorption band at Yb^{3+} fluorescent

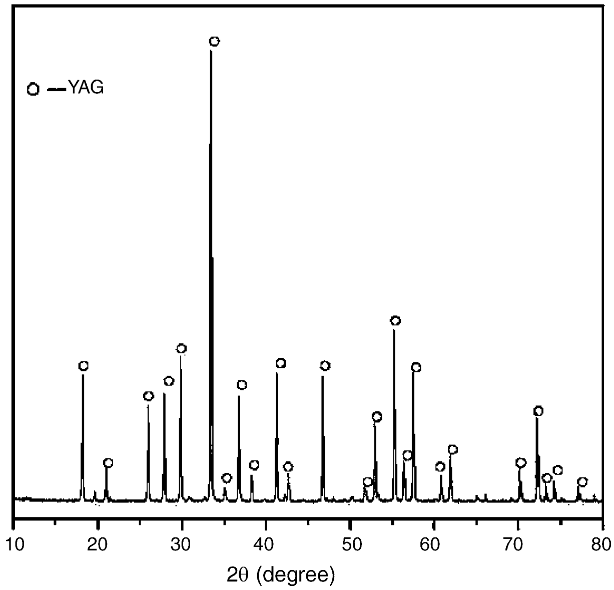

Fig. 3. XRD pattern of the transparent 5 at% Yb, 0.025 at% Cr:YAG ceramic.

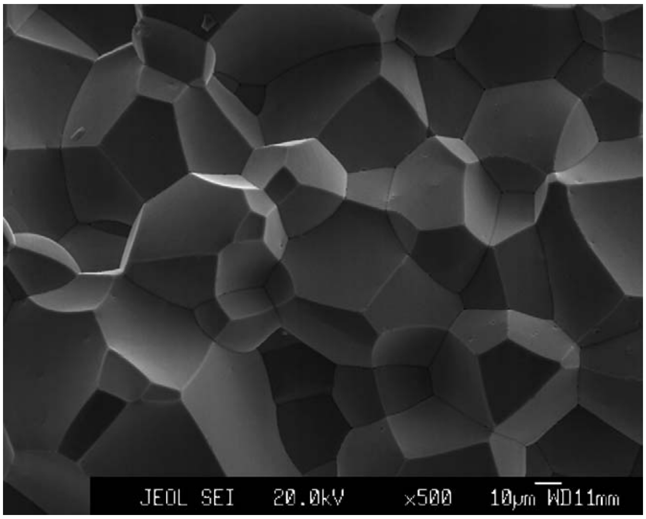

Fig. 4. SEM microstructure of fracture surface of the 5 at% Yb, 0.025 at% Cr:YAG ceramic.

wavelength 1030 nm, transparent Yb,Cr:YAG ceramics have potential for self-Q-switched monolithic laser. The absorption band of Cr^{4+} ranges from 900 to 1100 nm. But, the absorption bands of Yb^{3+} overlaps the Cr^{4+} absorption band, as the concentration of Cr^{4+} is much lower than that of Yb^{3+}. The difference of lattice constant between Yb and Y is 1.5%, thus, most of the Yb substitutes the Y site in the dodecahedron in YAG. Since we use Cr_2O_3 as starting material, chromium ions exist as trivalent Cr^{3+}. Nevertheless, Cr^{3+} may change into Cr^{2+}, when the sample was sintered under vacuum, and may become Cr^{4+}, when annealed at 1450 °C in air. So, chromium ions in YAG may have different valent state: divalent Cr^{2+}, trivalent Cr^{3+}, tetravalent Cr^{4+}, among them, Cr^{3+} is the most stable, and is substituted at the octahedral Al site. However, Cr^{4+} is a saturable absorber in Yb,Cr:YAG ceramics. So, controlling Cr ions valence states is the key step to obtain high Cr^{4+} concentration in Yb,Cr:YAG ceramics. Cr^{4+} is regarded to be substituted into tetrahedral Al site, therefore charge compensation is required, which is accomplished by the substitution of Ca^{2+} into the dodecahedral Y site. Thus CaO was added to as a charge compensator. The changes of chromium ions, in the annealing process, may be expressed as follow:

$$Cr^{3+}_{oct} + \tfrac{1}{2}(V^{2+}_{o} + 2Ca^{2+}) + \tfrac{1}{4}O_2 \rightarrow (Cr^{4+}_{oct} + Ca^{2+})$$

$$Al^{3+}_{tetra} + Cr^{4+}_{oct} \rightarrow Cr^{4+}_{tetra} + Al^{3+}_{oct}$$

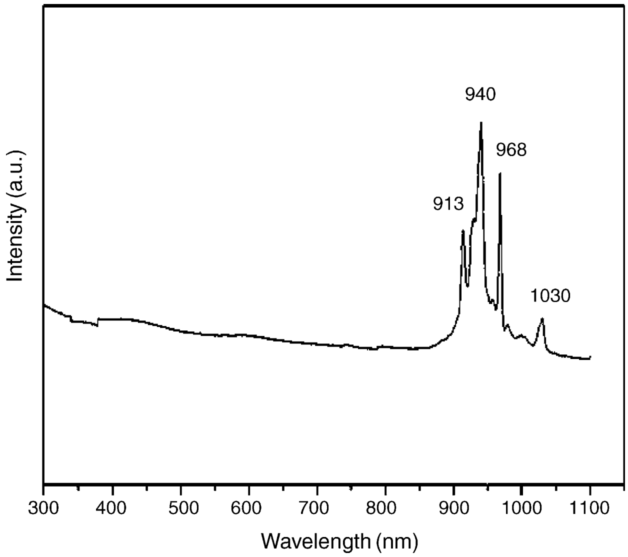

Fig. 5. Absorption spectrum of the 5 at% Yb, 0.025 at% Cr:YAG ceramic.

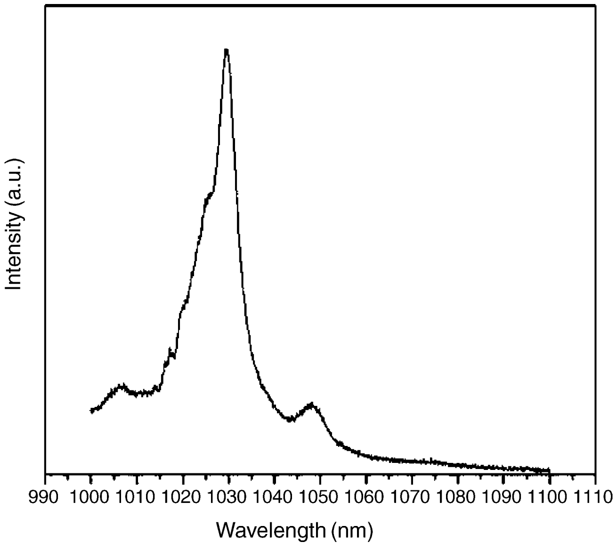

Fig. 6. Emission spectrum of the transparent 5 at% Yb, 0.025 at% Cr:YAG ceramic excited by 980 nm laser diode.

From Fig. 5, there are no absorption peaks of Cr^{3+}(440 and 605 nm) and Cr^{2+}, so we consider chromium ions most exist as Cr^{4+} in the Yb,Cr:YAG ceramics.

Fig. 6 shows the main features of the emission spectra to be the well-known Yb^{3+} emissions located at 1030 nm. Cr^{4+} has a strong absorption band centered at 1030 nm, so it can act as saturable absorber of Yb^{3+}.

4. Conclusions

Transparent 5 at% Yb, 0.025 at% Cr:YAG ceramics were fabricated successfully by a solid-state reaction method. The Yb,Cr:YAG ceramics exhibit a pore-free structure and average grain size is about 40 μm. The transmittance of the Yb,Cr:YAG ceramics reaches 75% at 1100 nm and the strong absorption at 940 and 968 nm of Yb^{3+} appears suitable for InGaAs diode laser pumping. Yb,Cr:YAG ceramics have a strong absorption band at 1030 nm, which is the fluorescent wavelength of Yb^{3+}, so they can be a saturable absorber as a passive Q-switch for Yb^{3+} in monolithic Yb,Cr:YAG laser ceramics, these possibly being good self-Q-switched laser materials.

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