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Precipitation of Tm_2O_3 nanopowders for application in reactive sintering of Tm:YAG

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Abstract

In this study thulium oxide powder has been prepared by the precipitation technique using several precipitating agents, i.e. ammonium carbonate, ammonium hydrogen carbonate and ammonia. The relation between precipitation parameters and the properties of thulium oxide nanopowders has been investigated. The morphology and physical properties of the fabricated Tm_2O_3 powders have been examined using a scanning electron microscope (SEM) and performing nitrogen sorption measurements (BET). Finally, commercially available alumina, yttria and precipitated Tm_2O_3 powders have been mixed and subsequently sintered for 6 h at 1830 °C. For comparison, ceramics with the same composition (2 at% Tm:YAG) have been prepared from commercial micrometric thulium oxide powder. The resultant ceramics have been studied in terms of their microstructure and optical transmittance. It has been found that the best homogeneity and transmittance has been obtained in the case of mixture with ammonia precipitated Tm_2O_3 powder.

Keywords: Powders; Yttrium aluminum garnet; Tm:YAG; Precipitation; Transparent ceramic

1. Introduction

Ceramic laser materials have attracted considerable interest over the last decade. Combining the advantages of single crystals and active glasses, they offer excellent optical quality, fast production time and make it possible to incorporate high dopant concentrations and fabricate large size elements. They are especially suitable for high power laser applications due to their shock resistance, which is higher than in the case of single crystals. Transparent ceramics for laser applications must fulfill many requirements, namely very high uniformity and transmittance close to theoretical maximum. The crucial factor affecting the optical properties of transparent ceramics is the potential presence of pores or other phases [1].

Rare-earth doped YAG ceramics are among the most widely produced transparent ceramics for laser applications. The typical dopants used to-date are Nd^{3+}, Yb^{3+} and Er^{3+} [2–10]. However, thulium doped yttrium aluminum garnet (Tm:YAG) ceramics have been less frequently studied [11,12]. Previous studies have shown that thulium-doped YAG lasers are important sources in the eye-safe 2 μm spectral region and have extensive applications in remote sensing and in medical and military technologies [13]. Thulium has several favorable properties with respect to laser diode pumping, such as a strong absorption band at 785 nm, which overlaps the emission from AlGaAs laser diodes, and an efficient cross-relaxation process. The upper laser level ($^3F_4$) is populated through the cross-relaxation process $^3H_4+{}^3H_6\rightarrow{}^3F_4+{}^3F_4$. Two Tm^{3+} ions will be excited to the $^3F_4$ level through this relaxation process for each photon absorbed in the $^3H_4$ level [14,15].

Reaction sintering (solid state reaction) and sintering of chemically prepared YAG nanopowders are the most important methods for synthesizing YAG ceramics [16,17]. Powders of yttrium aluminum garnet doped with rare earths are obtained in

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many different ways, including chemical methods such as co-precipitation [18], sol–gel [19] and the mechanochemical method [20]. Nevertheless, the reaction sintering still remains one of the most commonly used techniques for the fabrication of transparent yttrium aluminum garnet ceramics.

Previous studies proved that transparency in YAG based ceramics obtained by reactive sintering depends on the purity level and mean grain size of the starting powders as well as on their mutual interaction during shaping. In this method, a crucial role in high transmission of the finally sintered material is played by the particle size, shape, degree of agglomeration and sinterability of the powders used. However, there is no consensus as the size and shape of the grains influence the final transmission of YAG reaction sintered ceramics. Lee et al. [21] successfully used commercially available Al_2O_3 of submicron grain-size and Y_2O_3 and Nd_2O_3 micrometer grain-size powders without pretreatment. Also Zhang et al. [14,15] for reactive sintering of high-quality Tm^{3+}:YAG transparent ceramics, submicron Al_2O_3 powder and micrometric sized Y_2O_3 and Tm_2O_3 powders are used. Contrary to this, the work of Esposito [22] proved that YAG and Nd:YAG ceramics with transmittance value approaching the theoretical one, require highly pure, sub-micrometric, spherical and not aggregated powders. Our previous study [23] also showed that the procedure for preparation and the morphology of obtained yttria nanopowders strongly influenced final microstructure and transmission of YAG ceramics.

There is very little information on the influence of the properties of rare earth oxides' powders used as a source of doping agent in YAG. Despite they are added in relatively small amounts, their impact on the sintering appears to be significant. e.g. Hostasa et al. [7] observed in the case of Yb:YAG that although the best density was observed in ceramics containing the highest ytterbium doping (20 at%) the final transmittance was significantly worse compared to lower doped compositions. Concerning the large value of the Yb^{3+} segregation coefficient (1.09 in YAG ceramic [24]) it could not be explained by segregation of ytterbium at grain boundaries.

The aim of this work has been to investigate the effect of the thulium oxide powder characteristics on the microstructure and optical properties of polycrystalline yttrium aluminum garnet (Tm:YAG). Due to very small size difference between Y^{3+} and Tm^{3+} ions, the crystal structure allows compositions from YAG to fully substituted TmAG [25], which is isostructural to YAG.

In order to minimalize the impact of factors other than the grain size and morphology all powders were prepared by one method (precipitation and calcination) and with the use of reagents of the same purity level. It is known that, precipitation can provide a very wide variety of particles size and shapes of powders depending on preparation parameters [26]. For the studies, three Tm_2O_3 powders of very different morphologies were prepared using thulium nitrate and several precipitating agents, i.e. ammonium carbonate, ammonium hydrogen carbonate and ammonia.

2. Materials and methods

Thulium oxide (Tm_2O_3) nanopowders have been obtained by precipitation using three types of precipitants, namely ammonium carbonate, ammonium hydrogen carbonate and ammonia (analytic grade, Chempur). Synthesis has been carried out at room temperature by the drop-wise addition of thulium nitrate $Tm(NO_3)_3$ (4N, Alfa Aesar) at a concentration of 0.25 M to the stirred precipitant solution. The resultant suspensions have been washed twice by decantation using water, centrifugally separated and rinsed with ethanol. This procedure has been repeated two times. Finally, the precursor powder has been dried at room temperature and calcinated in air at 1100 °C for 2 h. Commercially available Al_2O_3 (Taimei TM DAR, 99.99%), Y_2O_3 (Inframat Adv. Mat. 39R-0801, 99.99%), Tm_2O_3 (Alfa Aesar, REacton, 99.99%) and Tm_2O_3 powders obtained by precipitation have been used to prepare 2 at% Tm:YAG ceramics. The powders have been mixed and homogenized in an attritor mill with 2 mm ZrO_2 balls in ethanol with 0.5 wt% addition of tetraethyl orthosilicate (TEOS, Aldrich), dried and granulated with PVA. Then the mixture has been compacted into a 20 mm disc and has undergone cold isostatic pressing (120 MPa). This step has been followed by removing the organic components during pre-sintering (1000 °C/1 h). Finally, the specimens have been vacuum-sintered (Balzers vacuum furnace, 10^{-6} mbar vacuum) at 1830 °C for 6 h.

Both powders and sintered samples have been investigated in terms of their phase purity by XRD (Siemens D-5000). The morphology and specific surface of the fabricated Tm_2O_3 powders have been examined by SEM (Carl Zeiss Crossbeam Workstation AURIGA) and BET (Quantachrome's Quadrasorb-SI Surface Area and Pore Size Analyzer). The microstructure of the sintered ceramics has been observed by SEM on polished and thermally etched samples. The average grain size has been evaluated by CLEMEX image analysis software. The apparent density of the samples has been determined hydrostatically. The transmission of the sintered ceramics in the infrared and visible light range has been measured by a VarianCary500 spectrophotometer.

3. Results and discussion

Fig. 1 presents SEM images of the Tm_2O_3 powders used in this study, i.e. nanopowders precipitated using various precipitation agents (ammonium carbonate, ammonium hydrogen carbonate and ammonia) and commercial micropowder purchased from Alfa Aesar. It can be noticed that their morphology differs strongly. In the case of all precipitation agents, the obtained Tm_2O_3 powders consist of nanoparticles clustered around large agglomerates of different shapes. Ammonium carbonate and ammonium hydrogen carbonate precipitations lead to the agglomeration of powders to form large thin platelets. In contrast, ammonia precipitated powder consists of relatively small, irregular shape agglomerates of Tm_2O_3 nanoparticles. This difference can result from differences in pH during precipitation with different agents. In the case of AHC and AC pH oscillated in the range 7.8–8.3 while with ammonia pH was around 9.8–10. It is known that layered rare-earth hydroxides are usually of plate-like shapes [27]. Unfortunately, the assumption that LDHs are precipitated in the case of ammonium