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Influence of (Nd+Y)/Al ratio on sintering behavior and optical features of $Y_{3-x}Nd_xAl_5O_{12}$ ceramics for laser applications

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ABSTRACT

In this study, Nd:YAG ceramics with different (Nd+Y)/Al ratios around the stoichiometric one ((Nd+Y)/Al = 0.6000) with high accuracy (better than 0.1%) were elaborated by solid-state reactive-sintering under vacuum. The influence of (Nd+Y)/Al ratio on sintering behavior, microstructural and optical properties of as-obtained ceramics were systematically studied. This study shows that Al-excess strongly promotes mass transfer by diffusion, and consequently, densification and grain growth processes whereas Y-excess lead to opposite behavior. Results were interpreted by considering several parameters such as local chemical composition, intrinsic/extrinsic crystalline defects, and interactions between pores, secondary phases and grain boundaries. Finally, exact stoichiometry or Y-excess appear to be more favorable to obtain highly transparent Nd:YAG ceramics suitable for laser operation.

1. Introduction

Neodymium-doped Yttrium Aluminum Garnet (Nd:YAG) ceramics are attractive materials to use as amplifier media in high energy solid-state lasers. Ikesue et al. [1] has shown in 1995 the feasibility of Nd:YAG ceramics with high level of transmittance and effective laser oscillation, similar to Nd:YAG single-crystals [2,3]. Besides, the high mechanical strength and the high thermal conductivity, the possibility to incorporate high amount of rare-earth ions (Nd^{3+}, Yb^{3+}…) [4], the feasibility to manufacture high dimensions and/or complex architectures (*i.e.* dopant gradient) with the ceramic route are the main advantages of this material [5–8]. Moreover, Nd:YAG ceramics manufacturing requires elaboration conditions less severe than single-crystal ones [9,10]. Nevertheless, transparent ceramics for lasers are still involved in limited industrial applications. This fact is partially due to the remaining technical issue of ceramics manufacturing without scattering defects. Porosity, impurities and so on are still hard to avoid that decreases laser performances. One type of defects, secondary phases like Al_2O_3 or $YAlO_3$ in Nd:YAG ceramics, is often due to a control of (Nd+Y)/Al ratio with insufficient accuracy [11].

Optical and laser performances of Nd:YAG ceramics are mainly controlled by residual microstructural defects. Elimination of these defects like pores or secondary phases in ceramic matrix is necessary to reach good optical properties. Light is very effectively scattered because of the different refractive index n between the gas-filled pores, secondary phases and the main matrix ($n_{pore} \approx 1$; $n_{secondary\ phase} = 1.7–1.9$; $n_{Nd:YAG} = 1.815$). As a consequence, the optical transmittance T is often given by the following expression [12]:

$$T = T_0 \exp(-\alpha_{ext} h) \quad (1)$$

where α_{ext} is the extinction coefficient described by the relation: $\alpha_{ext} = \alpha_{pores} + \alpha_{secondary\ phases} + \alpha_{grain\ boundaries} + \alpha_{impurities}$, h is the sample thickness and $T_0 = \frac{2n}{1+n^2}$. This relation is a consequence of Fresnel reflectance for normal incidence and specular reflection (*i.e.* total reflection loss) [13]. For Nd:YAG, refractive index n = 1.815 at 1 μm, so Eq. (1) gives $T_0 = 84\%$. All of defects come from the different steps of the elaboration process: impurities in raw

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powders, control of Y/Al stoichiometric ratio, or elaboration process with steps like mixing, shaping, sintering, etc. with insufficient accuracy. For example, the influence of sintering on residual porosity content and related optical properties were extensively studied [13–15]. In our previous studies [16], it has been shown that a porosity value lower than 10^{-4}% is necessary to reach laser performance levels similar to single-crystal ones. Such low values remain attainable by simple natural sintering under vacuum for several hours [16] but can be also reached thanks to post-HIP treatment [17]. The influence of secondary phases on Nd:YAG ceramics optical properties have been much less studied as this issue is generally less critical. Moreover, most of these studies report the presence of secondary phases without any discussion of results taking into account their presence.

$Y_3Al_5O_{12}$ garnet phase (YAG) is a defined compound as shown on the Y_2O_3-Al_2O_3 binary phase diagram (Fig. 1) [18]. YAG phase is thus obtained for a defined Y/Al ratio equal to 0.6000. From this diagram one can see that this material doesn't accept any deviation from stoichiometric composition. For Y/Al ratio smaller than 0.6000, α-Al_2O_3 secondary phase is in equilibrium with YAG. For Y/Al ratio higher than 0.6000, the secondary phase in equilibrium with YAG is yttrium aluminum perovskite $YAlO_3$ (YAP). These two secondary phases were often reported to be encountered in sintered YAG or Nd:YAG ceramics (see for example [19,20]). Some studies were aimed at finding the influence of stoichiometry deviation on ceramics properties. Patel et al. [21] have highlighted by simulation the different mechanisms and the structural (intrinsic or extrinsic) defects linked to the deviation from stoichiometric Y/Al ratio. Huang et al. [22] were also interested in structural defects created by non-stoichiometry. Liu et al. [23] have shown the influence of aluminum or yttrium excess on crystallographic properties and grain size in YAG-based ceramics. In this study, Y/Al ratio appears to strongly influence the physicochemical properties and microstructure of Nd:YAG ceramics. Especially, grain growth kinetics were investigated but densification behavior was not discussed in regards to the presence of secondary phases, structural defects and sintering aids (*i.e.* SiO_2 and MgO). Sintering kinetics and mechanisms in a given material are well known to be dependent on several parameters including the presence of precipitates, their location (intra- or intergranular), the nature and content of intrinsic and extrinsic defects, etc. [24]. According to the literature, sintering behavior -densification and grain growth-of Nd:YAG ceramics is expected to depend on the Y/Al ratio. Consequently, this work aimed at better understand the influence of its atomic ratio on sintering ability of Nd:YAG ceramics. In this study, densification, grain growth and overall microstructural evolution during sintering with corresponding final optical properties of Nd:YAG ceramics were investigated.

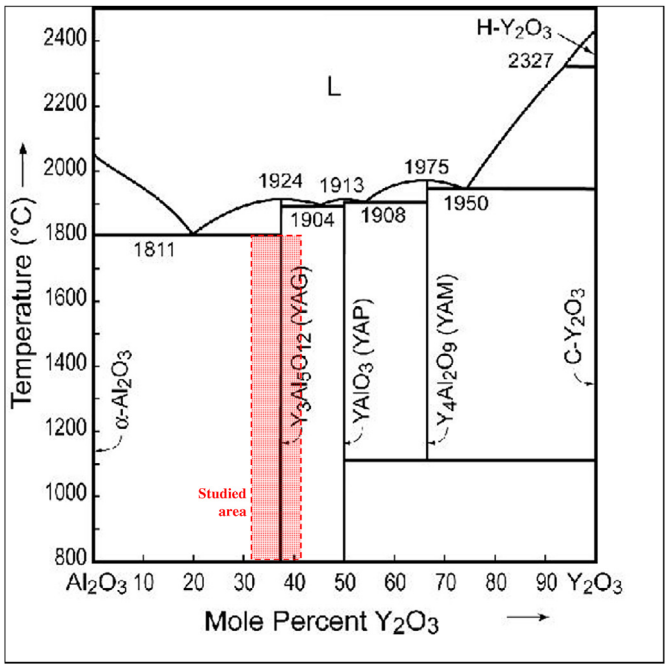

Fig. 1. Binary phase diagram Al_2O_3-Y_2O_3 with studied Y/Al ratio domain (area in red) [18]. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

2. Methods

2.1. Powder preparation and sintering

Nd:YAG-based ceramics were elaborated by a solid-state reactive sintering process as described elsewhere [25]. According to the flow chart reported in Fig. 2, Nd:YAG ceramics with different amounts of secondary phases ($YAlO_3$ or Al_2O_3) depending on Y/Al ratio were obtained after sintering. Commercial submicron α-Al_2O_3 (Ø < 0.5 μm; purity > 99.99%, Baïkowski, France), Y_2O_3 (Ø < 0.5 μm; purity > 99.99%, Solvay, France) and Nd_2O_3 (Ø < 1 μm; purity > 99.99%, Alfa Aesar, Germany) were blended together in deionized water and ball-milled with corundum balls. The ratio between Y_2O_3, Nd_2O_3 and Al_2O_3 powders was adjusted in order to obtain various (Nd+Y)/Al ratios ranging from 0.4000 to 0.7000, around the stoichiometric ratio equal to 0.6000. The (Nd+Y)/Al ratio accuracy was 0.05%. All the samples were doped with 1 at.% of neodymium (Nd/(Nd+Y) ratio equal to 0.01). Such doping content was chosen because higher neodymium concentration leads to increased collision decay and so, reduced laser lifetime [26]. 50 mm diameter green pellets were obtained by slip casting. Prior to sintering, samples were then calcined under air at T < 1173 K to remove organic residues. Sintering was conducted under vacuum in a tungsten mesh-heated furnace ($P \leq 10^{-3}$ Pa) at 1973 K for 10 h. Green bodies were placed in alumina crucible with heating and cooling rates of 5 K min^{-1}. In parallel, several dilatometric analysis (Thermal Mechanical Analyzer, TMA SETSYS, Setaram™, France) were carried out to establish the densification kinetics for Nd:YAG. Non-isothermal experiments were conducted under vacuum ($P \leq 10^{-3}$ Pa) with a heating rate equal to 5 K min^{-1} until 1973 K.

2.2. Characterizations

After thermal treatment at various temperatures between 973 K and 1673 K, the crystalline phases were identified and indexed by X-ray diffraction analysis (D8, Bruker, Karlsruhe, Germany) using monochromatic Cu $K_{\alpha 1}$ radiation. Indexation of crystalline phases was carried out by the DIFFRAC^{plus} EVA™ software and the PDFmain™ database. Sintered samples were then polished with 1 μm diamond paste and thermally etched under air at 100 K below the sintering temperature to investigate their microstructure by scanning electron microscopy (SEM, Phillips™ XL30, The Netherlands and FEG-SEM Quanta 450, FEI, Thermo Fisher Scientific, USA). BSE detector was used for better contrast between phases. The mean grain size of the different phases was determined thanks to image analysis software (ImageJ). The equivalent disc diameter was chosen as a parameter for size evaluation. For each composition, average grain size measurements were done over 300 grains. Grain size can be thus given with quite high accuracy with ±0.2 μm of uncertainty. Relative density of Nd:YAG-based ceramics after thermal treatment were determined by using the Archimedes method in anhydrous ethanol ($\rho_{ethanol} = 0.789$ at 293 K). The