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Solubility limit of Si in YAG at 1700 °C in vacuum

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ABSTRACT

Measurement of the solubility limit of Si in yttrium aluminum garnet (YAG-$Y_3Al_5O_{12}$) is crucial for understanding the mechanisms by which Si influences grain boundary mobility, and the mechanisms by which grain boundaries migrate. In the present work, the solubility limit of Si in YAG at 1700 °C in vacuum (5×10^{-6} Torr), which are the most common sintering temperature and environment for YAG, was measured for the first time. Measurements were conducted by wavelength dispersive spectroscopy (WDS), using polished YAG specimens with 3700 ppm Si (0.8 wt% SiO_2). Si content to ensure saturation with Si. The accuracy of the WDS result was confirmed by using a series of doped specimens and by comparing to inductively coupled plasma mass spectrometry ICP-MS results. The results indicate that the solubility limit of Si in YAG at 1700 °C (5×10^{-6} Torr), is 980 ± 60 ppm. The measured Si solubility was found to significantly depend on the cooling rate, where for furnace cooled specimens the measured Si solubility was 650 ± 60 ppm. A second phase in triple junction was repeatedly observed when higher content of Si was used, confirming this work results.

1. Introduction

Yttrium aluminum garnet (YAG-$Y_3Al_5O_{12}$) is considered to be an important host material for solid state laser applications due to its unique optical and mechanical properties [1,2]. The reduced cost of manufacturing, larger sizes of sintered parts, and the possibility to achieve higher doping levels, makes the use of polycrystalline YAG attractive for laser applications, as compared to single crystals. Since Ikesue et al. [3] demonstrated for the first time the possibility to obtain lasing polycrystalline Nd:YAG, several works demonstrated that transparent polycrystalline Nd:YAG is equivalent, in terms of laser applications, to single crystal Nd:YAG, grown by the Czochralski method [4–10]. In the vast majority of these works, SiO_2 was used as a sintering aid to achieve fully dense, transparent polycrystalline Nd:YAG.

The presence of dopants at levels below or above the solubility limit can dramatically change the properties of a material. In the case of polycrystalline Nd:YAG, doping with Si at increasing concentrations below the solubility limit can lead to a higher densification rate without deterioration of the Nd:YAG optical and lasing properties [11,12]. However, doping at levels above the solubility limit is expected to result in Si enrichment of the grain boundaries and secondary phase precipitation, reducing the transparency and lasing sustainability [13]. Moreover, as demonstrated by Ikesue et al. [14], SiO_2 solubility in YAG decreases as temperature decreases, hence second phase appears at grain boundaries when low cooling rate is used (hence, applying low cooling rate will lead to the appearance of a second phase at the grain boundaries). Therefore, it is critical to determine the solubility limit of key dopants in YAG at the sintering temperature and atmosphere of interest.

Recent studies have investigated the influence of silica on sintering of Nd:YAG and its mechanism. Salle et al. [15] claimed that the positive effect of silica on densification is linked to the appearance of secondary phases, resulting from a reaction with YAG, and suggested that liquid-phase sintering occurs. They showed a dramatic effect on densification when a relatively high SiO_2 content was added (0.3 wt%). No transmission electron microscopy (TEM) characterization was performed to support this claim. Boulesteix et al. [16] explored the densification rate dependence on the silica content from 0 to 0.3 wt%, and demonstrated that the densification rate obtained with 0.3 wt% SiO_2 increased by two orders of magnitude compared to pure YAG. Boulesteix et al. related this to the effectiveness of silica in promoting liquid-phase sintering in Nd:YAG. Maitre et al. [17] detected a small endothermic peak at 1663°K in a Nd:YAG specimen containing 0.3 wt% SiO_2 using differential thermal analysis (DTA). The peak was related to liquid phase formation based on the Al_2O_3-Y_2O_3-SiO_2 ternary phase diagram. Despite this finding, no intergranular film or intergran-

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ular phase was observed using transmission electron microscopy (TEM) characterization, nevertheless some intergranular spherical inclusions were detected, which correlated with secondary phases detected by scanning electron microscopy (SEM) conducted by the same authors. In a different study, Stevenson et al. [12] did not detect any endothermic peak by DTA on a YAG specimen containing lower SiO_2 content (0.14 wt%). This was explained by the low content of liquid (50% less compared with the study of Maitre et al.). Kochawattana et al. [11] also demonstrated significant densification enhancement and grain growth when doping with SiO_2 (0.14 wt%) relative to pure YAG, as a result of liquid phase sintering. In a different study by Stevenson et al. [12] nuclear magnetic resonance (NMR) was used to show that the Si^{4+} in polycrystalline Nd:YAG is coordinated in a highly crystalline environment and occupies the tetrahedrally coordinated Al^{3+} sites. Moreover, high resolution transmission electron microscopy (HRTEM) revealed that the grain boundaries and triple lines are free of crystalline or amorphous secondary phases. Electron energy loss spectroscopy (EELS) was used by Stevenson et al. to detect Si in the solid solution, at grain boundaries and triple junctions. These observations provided further evidence that Si^{4+} forms solid solution in the Nd:YAG lattice during sintering and Si affects grain growth by solute mechanisms as described in previous work [12,18].

It is important to mention that none of these studies included measurements of the solubility limit of Si in YAG, or mentioned the importance of this parameter while discussing the densification mechanisms.

Thermodynamically calculated phase diagrams of the SiO_2-Y_2O_3-Al_2O_3 system showed that SiO_2 forms a liquid phase with YAG at temperatures above 1400 °C [19,20]. However, the solubility of SiO_2 into the YAG lattice was not included in the thermodynamic models.

Despite the importance of understanding the Si solubility limit with regards to densification and microstructural development of transparent polycrystalline YAG, to the best of the author's knowledge no measured values at common sintering temperatures and atmospheres has been published. Most researchers in the field of transparent YAG refer to the solubility limit of Si in YAG published in 1984 by Sun et al. [21]. In their work, Sun et al. reported quantitative analysis of electron microprobe measurements of highly doped (17000 ppm Si) polycrystalline YAG, air-sintered at 1550 °C for 1hr: Y:Al:Si = 1.00:1.64:0.02 (corresponds to 2800 ppm Si). The specimen had a relatively fine grain size, and as a result the microprobe analysis was taken from grain aggregates. Another work dealt with the measurement of Si solubility in YAG was reported in 2008 by Kuru et al. [22] which reported that the solubility limit of Si in YAG powder is 560 ppm. This value was obtained using electron probe microanalysis. The powders were calcined in air at a relatively low temperature of 900 °C for 2 h. In their work the average grain size was approximately 1 μm therefore (as Kuru et al. mentioned) it is reasonable to assume that grain boundaries, and perhaps grain boundary inclusions, had an effect on the analysis results.

Furthermore, Kochawattana et al. [11] have shown that at 1650 °C no change in grain size occurs due to SiO_2 additions in the range of 0.035–0.28 wt.%; hence, most research regarding grain growth kinetics is performed at higher temperatures. Therefore, it seems that measurement of Si solubility limit in YAG at sintering temperature can significantly contribute to the understanding of the effect of Si on microstructure development.

A straight forward approach to measure the solubility limit of dopants in polycrystalline ceramics, based on wavelength dispersive spectroscopy (WDS) of super saturated polycrystalline specimens (similar to the approach described by Sun et al.), was comprehensively described in previous published studies [23–26]. There are several mandatory requirements before using this approach: the starting dopant content should be higher than the solubility limit to ensure saturation; the sintering duration has to be long enough to achieve a homogeneous distribution of the dopant; rapid cooling should be used to limit diffusion of the dopant from/to the matrix grains resulting from the change of the solubility limit at lower temperatures; and specimen preparation for SEM-WDS should not include processes such as thermal or chemical etching that may affect the measured content.

The goal of the present work was to determine the solubility limit of Si in YAG at 1700 °C in vacuum, which is the most common sintering temperature and environment for the YAG sintering process. Furthermore, the solubility limit of Si in 1 at.% Nd doped YAG was measured.

2. Experimental procedures

2.1. Specimen preparation

Pure (99.99%) nanocrystalline YAG powder formed by spray pyrolysis (Nanocerox Inc., Michigan) was used. Another pure (99.99%) YAG powder (Baikowski) was used to corroborate the measured values of the solubility limit of Si in YAG and its potential sensitivity to minor changes in background-level impurities. The composition of both powder sources, as characterizedvia inductively coupled plasma mass spectrometry ICP-MS, is presented in Appendix A. Si was introduced as oxide using SiO_2 powders (Sigma Aldrich, 7 nm). A relatively high content of SiO_2 (0.8 wt.%) was used to obtain saturation of the YAG grains with Si. In additional specimens, 1 at.% Nd_2O_3 powder was added as a co-dopant to Si doped YAG in order to explore the influence of Nd on the solubility limit of Si. Four more mixtures were prepared for evaluating the accuracy of the method, containing 0.4 wt.%, 0.2 wt.%, 0.1 wt% and 0.07 wt.% of SiO_2 doped YAG.

The YAG and additive powders were mixed by wet ball-milling, using alumina milling balls (99.9% Tosoh Japan) for 24 h in ethanol, in polyethylene containers. The slurry was dried, sieved and uniaxially pressed at 10 MPa into 10 mm diameter and 5 mm thick pellets, followed by cold isostatic pressing at 300 MPa. The green compacts were fired in air at 900 °C for 8 h.

Specimens were sintered in a 5×10^{-6} Torr vacuum furnace (MRF Inc.) at 1700 °C for 6 h and cooled at a rate of 1000 °C/h. A custom designed vacuum furnace which enables water-quenching of specimens was used for the preparation of second set of four specimens which were quenched from 1700 °C. The cooling time from 1700 °C to room temperature was less than 10 s (estimated cooling rate of ~200 °C/s). Specimens were polished to a 0.1 μm surface finish using diamond polishing media. No additional chemical or thermal etchings were performed.

2.2. Characterization methods

In order to confirm the presence of a second phase (indicating that YAG grains contains Si at the solubility limit), specimens for TEM (Titan 80–300 FEG-S/TEM, FEI) were prepared using a dual beam focused ion beam (FIB) microscope Strata 400s, FEI using the in-situ "lift-out" method [27]. Although no etching was performed, grain boundaries could be identified due to residual pores and second phase at grain boundaries. Nevertheless, electron backscattered diffraction (EBSD; Oxford Instruments PLC) was used to ensure grain boundary detection. Additional TEM specimens were prepared by conventional mechanical thinning, followed by dimpling, and ion-milling (Gatan PIPS, Pleasanton, CA) until perforation.

The Si content was measured using WDS (Oxford Instruments, High Wyecombe U.K.) mounted on a SEM (FEI Quanta, FEI Electron Optics, Eindhoven, The Netherlands). A TAP crystal (Thallium

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