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Synthesis of Nd/Si Codoped YAG Powders via a Solvothermal Method

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We report the synthesis of single-phased Nd/Si-doped yttrium aluminum garnet powder via a solvothermal method by using ethanol as the solvent. The obtained powder exhibits a spherical shape, no agglomeration, and an average particle size of ~300 nm, suitable for conventional powder processing. The effect of heat treatment on the lattice parameter and optical properties of the powder is also studied. The results are discussed in terms of Nd/Si solubility.

I. Introduction

Garnet crystals constitute a very important class of laser materials due to their excellent thermo-mechanical properties and high stability. The materials exhibit high transparency over a wide wavelength range that encompasses the absorption favorable for pumping and the emission for most of the laser-active ions from the transition to the rare-earth groups. Their energy-band structures and electron–phonon interactions are suitable for laser emission.[1,2] Recently, transparent fully dense polycrystalline yttrium aluminum garnet (YAG) has attracted extensive attention due to its potential applications in high-power solid-state lasers.[3–5] Compared with its single-crystal counterpart, ceramic YAG with high dopant concentrations and large dimensions is easier and less expensive to fabricate. In order to obtain high-quality ceramics for laser applications, it is preferable to start with preformed YAG powders rather than simple oxides.

YAG powders can be synthesized by various technologies, such as coprecipitation,[6,7] sol–gel,[8,9] combustion,[10] and solid-state reaction.[11–13] Although the solid-state reaction method is a simple process suitable for large-scale production, the YAG powders synthesized by the solid-state reaction usually form hard agglomerates and possess non-uniform composition, thus making them difficult to sinter. Recently, pure YAG powders have been synthesized using a solvothermal technique.[14] By using an organic solvent, YAG powders of excellent quality can be obtained at relatively low temperatures.

In this study, we report the synthesis and optical properties of Si/Nd codoped YAG powders using the solvothermal technique. The underlying promise of this research is that the preformed Si/Nd-doped YAG powders could have improved sintering capability and uniformity of dopant distribution. The powders as synthesized and heat treated are characterized using X-ray diffractometry (XRD) and transmission electron microscopy (TEM). The photoluminescence (PL) spectra and fluorescence decay times of the powders are measured. The effects of heat treatment on the structure and optical properties of the powders are discussed.

II. Experimental Procedure

The aluminum, yttrium, and neodymium sources are yttrium oxide (99.99%), neodymium oxide (99.99%), and $Al(NO_3)_3 \cdot 9H_2O$ (>99%), respectively. An aluminum nitrate solution was prepared by dissolving $Al(NO_3)_3 \cdot 9H_2O$ in distilled water. Yttrium and neodymium nitrate solution was obtained by dissolving the Y_2O_3 and the Nd_2O_3 in HNO_3 (1 mol/L). The above three solutions were then mixed uniformly according to the stoichiometry of Al:Y:Nd = 5:2.88:0.12 (corresponding to 4 at.% Nd-doped YAG). The hydroxides were precipitated by the addition of excess NH_4OH (10%) to the mixture under continuous stirring. The precipitates were repeatedly washed with distilled water to remove the residual nitric and ammonia ions. The washed hydroxides were dried at 50°C for 6 h and dispersed in ethanol with TEOS additives according to 0.3 wt% of solids. A small amount of Si doping can facilitate Nd-doping concentrations and improve the sinterability of YAG.[3,15] The solution was then placed in an autoclave for the solvothermal reaction. The reaction was carried out at 300°C and 18.2 MPa, which are higher than the supercritical temperature and pressure of ethanol (243°C and 6.3 MPa). After reaction for 6 h, the autoclave was cooled to room temperature. The resulting powder was filtered and repeatedly washed with ethanol, and then dried at 80°C for 1 h. Some of the synthesized powders were heat treated at various temperatures and times.

The as-synthesized and heat-treated powders were characterized using XRD (Rigaku, Tokyo, Japan) with Cu$K\alpha$ radiation and TEM (JEOL JEM 2010F, Tokyo, Japan). PL spectra of the powders were obtained under excitation of the 808 nm line of a laser diode using a TRIAX-550 spectrometer (Jobin Yvon, Long-jumeau, France) equipped with a GaInAs diode detector. Fluorescent decay time was measured on the same spectrometer using a TDS 3052 digital oscilloscope that had a time resolution of 0.1 μs. The excitation source is a 532 nm laser with a pulse duration of 10 ns.

III. Results and Discussion

Figure 1(a) shows XRD patterns of the as-synthesized and heat-treated powders. The patterns reveal that all powders are single-

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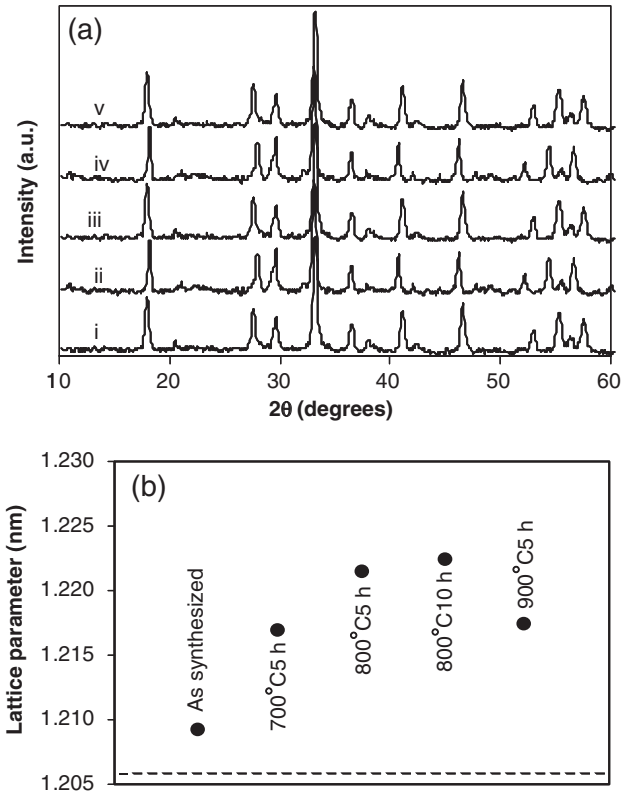

Fig. 1. (a) X-ray diffraction patterns of Si/Nd-doped yttrium aluminum garnet (YAG) powders as synthesized (i); annealed at 700°C for 5 h (ii); annealed at 800°C for 5 h (iii), 10 h (iv), and annealed at 900°C for 5 h (v). (b) Lattice parameter of Si/Nd-doped YAG powders annealed under different conditions as indicated.

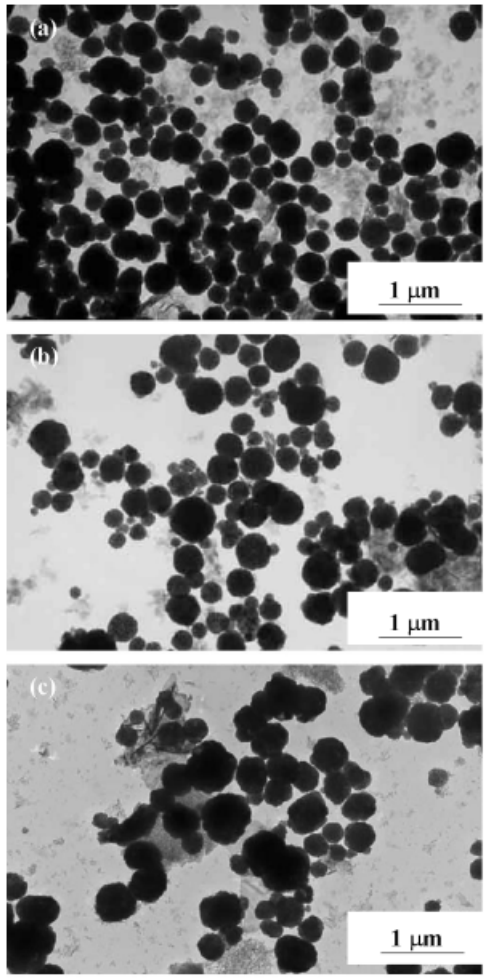

Fig. 2. Transmission electron microscopy images of (a) Si/Nd-doped yttrium aluminum garnet powders as synthesized, (b) annealed at 800°C for 5 h, and (c) annealed at 900°C for 5 h.

phase YAG. This result suggests that similar to pure YAG, single-phased-doped YAG powder can also be obtained via a solvothermal method when processing temperatures and pressures are higher than the supercritical temperature and pressure of the solvent. The lattice parameter of each powder is calculated from the corresponding diffraction pattern and summarized in Fig. 1(b). It can be seen that all powders obtained in the present study have a lattice parameter larger than the standard value of cubic YAG as indicated in Fig. 1(b) by a dashed line (PDF card #79-1892). The lattice parameter increases with heat treatment in the beginning and then decreases when heat treated at 900°C.

Figure 2 shows the TEM images showing the morphology of the powders as synthesized and heat treated at 800°C for 5 h, and 900°C for 5 h. It can be seen that regardless of the heat-treatment conditions, the powders are loosely dispersed without observable agglomeration. The particle size and size distribution are similar between 800° and 900°C heat-treated powders, suggesting that no significant grain growth and sintering occurred at the heat-treatment conditions. The average particle size is ~300 nm. A powder of this size is easy to handle for conventional powder processing.

The optical behavior of the powders was studied by measuring their PL and fluorescence decay time. Figure 3 shows the PL spectra of the powders as synthesized and heat treated. The light emission exhibited in the spectra is due to the $^4F_{3/2} \rightarrow {}^4I_{9/2}$ transition of Nd^{3+} ions dissolved in YAG.[16] It can be seen that the heat treatment has a significant effect on the PL behavior of the powders. The powder shows as-synthesized negligible light emission. The powder heat treated at 700°C for 5 h shows weak light emission, while the powder heat treated at 800°C for 5 h exhibits a strong PL signal. Increasing the heat-treatment time from 5 to 10 h at 800°C leads to a slight decrease in PL intensity. Finally, heat treating at 900°C for 5 h results in a significant decrease in light emission compared with that heat treated at 800°C for 5 h. Figure 4 shows the fluorescence decay time of the powders heat treated under different conditions. The result shows that the decay time continuously increases with heat-treatment temperature and time.

Nd^{3+} and Si^{4+} dopants have counteracting effects on the lattice parameter of YAG. Nd^{3+} ions, which replace Y^{3+} of YAG to form a substitutional solid solution, cause an increase in the lattice parameter as the ionic radius of Nd^{3+} (1.00 Å) is larger than that of Y^{3+} (0.89 Å),[17] while Si^{4+} ions, which replace the tetrahedral Al^{3+} of YAG, leads to a decrease in the lattice parameter because the ionic radius of Si^{4+} (0.26 Å) is smaller than that of Al^{3+} (0.39 Å)[17] and due to the formation of Al^{3+} vacancies. The effect of doping on the optical behavior of YAG is even more complex. While it increases the number of light emission centers, increasing Nd^{3+} doping concentration will lead to a decrease in fluorescence decay time due to the concentration quenching.[18,19] The characteristic quenching concentration is 2.8 at.% for Nd^{3+} in YAG.[18] The incorporation of Si^{4+} ions should also decrease the decay time as they lower the crystal symmetry in the vicinity of Nd^{3+} ions.[20] Therefore, both Nd^{3+} and Si^{4+} doping will lead to a decrease in fluorescence decay time. The PL intensity is determined by the combined effect of emission-center concentration and decay time.

Consequently, the continued increase in fluorescence decay time with heat treatment (Fig. 4) suggests that the incorporation of Nd^{3+} and Si^{4+} into the YAG lattice cannot occur during heat treatment. It is most likely that the Nd^{3+} and Si^{4+} ions are already incorporated into the lattice of the as-synthesized YAG powder. The lattice parameter of the as-synthesized powder being only slightly different from that of pure YAG can be

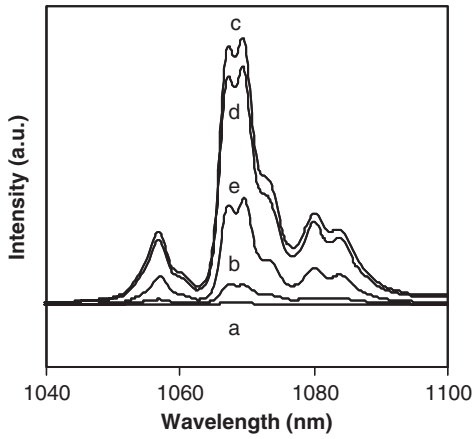

Fig. 3. Room-temperature photoluminiscence spectra of Si/Nd-doped yttrium aluminum garnet powders as synthesized (a); annealed at 700°C for 5 h (b); annealed at 800°C for 5 h (c), 10 h (d); and annealed at 900°C for 5 h (e).

explained by the copresence of Nd^{3+} and Si^{4+} in the lattice. The negligible PL intensity observed from the as-synthesized powder could be due to the concentration quenching of a high Nd^{3+} concentration, together with the low crystal symmetry caused by Si^{4+} doping. Heat treatment likely results in the extraction of both Nd^{3+} and Si^{4+} from the YAG lattice. In the beginning, the extraction of Si^{4+} dominates the process, leading to an increase in the lattice parameter, decay time, and PL intensity. The powder heat treated at 800°C for 10 h shows a further increase in lattice parameter and decay time, but a slight decrease in PL intensity. This suggests that the powder annealed at 800°C for 5 h reaches an optimized combination of Nd^{3+} concentration and decay time, leading to the maximum PL intensity. Further annealing at 900°C for 5 h causes a significant decrease in PL intensity and lattice parameter, but a further increase in the decay time, suggesting a further decrease in Nd^{3+} concentration.

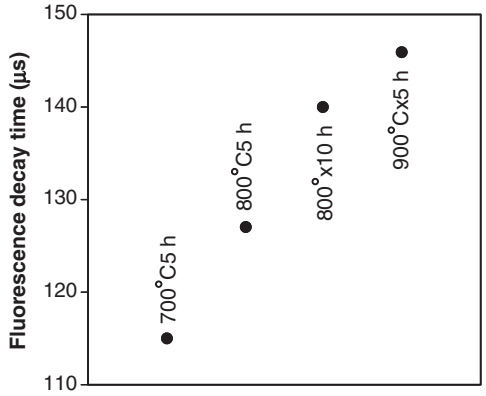

Fig. 4. Fluorescence decay time of the Si/Nd-doped yttrium aluminum garnet powders annealed under different conditions as indicated.

IV. Summary

In summary, we demonstrate that Nd/Si codoped YAG powders can be obtained via a solvothermal method. The XRD and TEM characterizations reveal that the lattice parameter and optical properties of the powder varied significantly with heat treatment. We propose that such a change is due to the extraction of Nd^{3+} and Si^{4+} dopants from the YAG lattice.

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