CHEMICAL PREPARATION OF YIG (Yttrium Iron Garnet) AND YAG (Yttrium Aluminum Garnet) POWDERS BY SELF-PROPAGATING COMBUSTION SYNTHESIS (SPCS)

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Abstract

The preparation of transparent magnetic fluids is necessary for both research on and practical applications of the magnetooptics of magnetic fluids. It was recently found that yttrium iron gamet $(Y_3Fe_3O_{12})$ or YIG is suitable for colloidal particles of transparent magnetic fluids. Phosphors are known as materials that emit light when bombarded with an energy source such as photons or an electron beam. These luminescent materials are used in such applications as fluorescent lamps, cathode-ray tubes, and electron microscope screens. They are composed of a host lattice which is doped with a small amount of impurity ions which activate the luminescence. Typically, YAG:Nd (or :Cr) phosphors are synthesized by a solid-state reaction between the component oxides, which requires long heat treatments at high temperatures. On the other hand, YAG:Nd compositions are utilized as laser materials. We have prepared the YIG and YAG:Nd compositions all completed their crystallization in the temperature range 1000 to 1250°C. The phase purities, particle sizes and morphologies, and crystallographic features of the sub-micron particulated powders were investigated by powder XRD, EDXS, SEM, and Rietveld Analysis, respectively.

1. Introduction

Previously Taketomi et al. [1-3] found that the preparation of transparent magnetic fluids is necessary for applications of the magnetooptics of magnetic fluids. It was also found that yttrium iron garnet ($Y_3Fe_5O_{12}$) or YIG is suitable for colloidal particles of transparent magnetic fluids [2, 4]. Several researchers have prepared YIG ultrafine particles about 10 nm in size. For example, Abe and Gomi prepared particles by the coprecipitation technique [5], while Matsumoto and Fujii used mist pyrolysis [6,7]. Generally speaking, inhomogeneity in the stoichiometry of the particles often occurs with these techniques [6-8]. The alkoxide method readily lends itself to preparing metal oxides which are hard to synthesize by the conventional techniques (solid-state reactive firing, coprecipitation, sol-gel, etc.) [9] and it also allows preparation of homogeneous ultrafine particles in stoichiometry [8]. Taketomi et al. have recently prepared YIG powders by the alkoxide method [10] and synthesized particles in the size range of 10 to 40 nm at temperatures below 800°C, with a low crystallinity. It was found that the ultrafine particles grow and fuse together, and eventually form polycrystalline particles of about 400-500 nm during calcination above 800°C.

Since Maiman [11,12] discovered the ruby laser in 1960, the solid-state laser has been rapidly developed. In recent years, especially, solid-state lasers have been applied with remarkable success in various industrial capacities such as for taking physical measurements and for medical uses. Although many kinds of solid-state lasers exist [13-16], the yttrium aluminum garnet $(Y_3Al_5O_{12})$ or YAG single crystal is the best laser host material. As a luminescent element, Nd plays a more important role than do Ho, Tm, Er, etc. Because a solid-state laser demands severe optical requirements, however, synthesizing Nd YAG laser

material of polycrystalline cerstate laser materials from polhave been reported by Greskic de With and van Dijk [20], experiments of both de With optical applications and unan polycrystalline, transparent Nsingle crystal, by solid-state in mixtures of Nd₂O₃, Y₂O₅, an were revealed, for the first superior to those of an Nd Y et al. were reported [23] to os

The present work and Nd-doped), at significantly researchers, by using the self-

2. Experimental Procedure

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The sintering charact obtained were studied in an (for peak temperature scalar, and 3 mm thickness were synthesized powders in harde

Powder X-ray ciffact sintered pellets for phase diffractometer was used with second for the runs performe of the synthesized/heated NT material of polycrystalline ceramics is technically very difficult. Attempts to synthesize solidstate laser materials from polycrystalline ceramics such as Nd-doped Y_2O_3 -ThO₂ ceramics have been reported by Greskovich and Wood [17-19], and attempts from YAG ceramics by de With and van Dijk [20], Mudler and de With [21], and Sekita et al. [22]. In the experiments of both de With and Sekita et al., polycrystalline YAG proved inadequate for optical applications and unable to emit a laser beam. Yoshida et al. [23] have produced polycrystalline, transparent Nd:YAG with optical characteristics nearly equal to those of a single crystal, by solid-state reactive firing (1750°C, 50 hours, *in vacuo*) of the appropriate mixtures of Nd₂O₃, Y₂O₃, and Al₂O₃. The laser characteristics of the Nd:YAG polycrystal were revealed, for the first time, by the Yoshida et al. study to be nearly equivalent or superior to those of an Nd:YAG single crystal. The Nd:YAG samples produced by Yoshida et al. were reported [23] to oscillate successfully by diode laser excitation.

The present work attempts to produce powders of YIG and YAG (both pure and Nd-doped), at significantly lower temperatures than those reported by the previous researchers, by using the self-propagating combustion synthesis method.

2. Experimental Procedure

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Pure and 1.1 at% Nd-doped YIG (Y₃Fe₅O₁₂), and pure and 1.1 at% Nd-doped YAG (Y3Al3O12) powders were synthesized by using the self-propagating combustion synthesis The starting stock solutions (0.4 M) of $Y(NO_3)_3$, $Al(NO_3)_3$ and $Nd(NO_3)_3$ were prepared from high-purity Y2O3 (99.9%, Ames Laboratory, ISU, USA), Nd2O3 (99.9%, Molycorp, USA) and Al(NO₃)₃.9H₂O (99.9%, Riedel de Haen, Germany). The oxides were dissolved in pure nitric acid to form the desired nitrate stock solutions. Stoichiometric amounts of nitrate stock solutions were mixed (for homogenizing the solutions) in a glass beaker with a stirrer for about 20 minutes. A proprietary amount of Urea was then added to the cations solutions. Following the dissolution of urea in the solution, the beaker contents were transferred into a 250-ml capacity Pyrex beaker. The Pyrex beaker with the liquid mixture was placed in a muffle furnace maintained at 510 \pm 10°C. Initially, the mixture boils and undergoes dehydration followed by decomposition with swelling and frothing resulting in a foam which ruptures with a flame and glows to incandescence. The entire combustion process was complete in less than 15 minutes. The product of combustion was a voluminous, foamy and amorphous precursor of the YIG (or YAG) phase. The foamy precursors were ground in an agate mortar into a fine powder and calcined on α -alumina plates in air over the temperature range of 1100 to 1250°C for 24 hours to yield the desired, crystalline and pure phases.

The sintering characteristics of both pure and Nd-doped YIG and YAG powders obtained were studied in an air atmosphere over the temperature range of 1250 to 1500°C (for peak temperature soaking times of 5 to 24 hours). The circular pellets of 1 cm diameter and 3 mm thickness were prepared by cold-uniaxial pressing (2000 kg/cm²) of the synthesized powders in hardened-steel dies.

Powder X-ray diffraction spectra were obtained from the synthesized powders and sintered pellets for phase characterization purposes. A Rigaku DMax/B powder diffractometer was used with FeK_{α} radiation at the step size of 0.03° and a preset time of 1 second for the runs performed to accomplish phase characterization and to check the purity of the synthesized/heated YIG or YAG powders.

Particle size and morphology of the powders and sintered pellets were monitored from the photomicrographs taken with a JEOL/ JSM6400 scanning electron microscope. The samples were, first, sputter coated with an approximately 25 nm-thick layer of gold-palladium alloy. EDXS (Kevex, USA) analysis were carried out on the samples to perform a semi-quantitative analysis for the determination of the elemental distribution in the powder samples. The EDXS runs were believ d to be accurate to about ± 3 wt%.

3. Results and Discussion

(A) Synthesis of Pure and 1.1 at% Nd-doped YIG and YAG Powders

The voluminous, dark foams, of pure or 1.1 at% rare-earth (i.e., Nd)-doped $Y_3Fe_5O_{12}$, recovered from the Pyrex beakers (containing the solutions) heated at about 510°C for 15 minutes were found to be amorphous. They begin to crystallize out the YIG phase in the temperature range of 900 to 1050°C, in a dry air atmosphere, over a calcination period of 6 to 12 hours. The color of the synthesized powders turns emerald green with increasing calcination temperature and time. Figure 1 shows the typical XRD spectrum of powders calcined at 1100°C for 24 hours. The structure of pure YIG is cubic with the unit cell edge (i.e., a) of 12.398 Å (Z=8), and a space group of Ia-3d (# 230). The addition of 1.1 at% Nd did not cause a detectable change (by Rietveld Analysis [24]) either in the individual d-spacings or the lattice parameter of the YIG structure. The procedure utilized here for the synthesis of sub-micron YIG powders represents an alternative over the conventional methods (such as solid-state reactive firing of oxides of Y_2O_3 , Fe₂O₃ and/or Nd₂O₃) of powder synthesis. The process of "self-propagating combustion synthesis [25-28]" is believed to yield YIG powders of higher chemical purity and homogeneity over a shorter time of synthesis.

The voluminous foams, of pure (white) or 1.1 at% rare-earth (i.e., Nd)-doped (pink) Y3Al5O12, recovered from the Pyrex beakers (containing the solutions) heated at about 510°C for 15 minutes were found to be amorphous. They begin to crystallize out the YAG phase in the temperature range of 1000 to 1150°C, in a dry air atmosphere, over a calcination period of 10 to 24 hours. Figure 2 shows the typical XRD spectra of pure YAG powders calcined at 1100 and 1250°C, for 24 hours. The XRD peak intensities (in Cps) were found to increase with increasing calcination temperature and time. The structure of pure YAG is cubic with the unit cell edge (i.e., a) of 12.053 Å (Z=8), and a space group of Ia-3d (# 230). The addition of 1.1 at% Nd did not cause a detectable change (by Rietveld Analysis [24]) either in the individual d-spacings or the lattice parameter of the YAG structure. The Miller indices of the planes giving rise to individual reflections were indicated, in Figures 1 and 2, over the XRD spectra of YIG and YAG phases. The procedure utilized here for the synthesis of sub-micron YAG powders represents an alternative over the conventional methods (such as solid-state reactive firing of oxides of Y2O3, Al2O3 and/or Nd₂O₃) of powder synthesis. The process of "self-propagating combustion synthesis" is believed to yield YAG powders of higher chemical purity and homogeneity (at a lower temperature of compound formation) over a shorter time of synthesis.

(B) Sintering Behavior of Combustion Synthesized YIG and YAG Powders

Figure 3 shows the SEM micrographs of pure YIG $(Y_3Fe_5O_{12})$ pellets (1 cm diameter, 3mm thick, cold-uniaxial pressing at 2000 kg/cm²) heated at 1300°C (A and B)

Figure 1. Typical XRI

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450

5000











Figure 2. Typical XRD spectrum of YAG (Y₃Al₅O₁₂) powders calcined in air

Figure 3. SEM metrogram



theta (Fe-K-alpha)



and 1500°C (C and D), for 5 hours, in an air atmosphere. The pellets were cooled to room temperature (from the peak temperatures) in the shut-off furnace. Micrographs of Figures 3A and 3B do show that at 1300°C necking and bonding of sub-micron spherical particles of the YIG phase have significantly proceeded. Further increase in sintering temperature to 1500°C (Figures 3C and 3D; as-sintered surfaces) has led to complete densification, with an average grain size of about 10 µm in the sintered microstructure of the dark green pellets.

Figure 4 shows the SEM micrographs of 1.1 at% Nd-doped YIG ($Y_3Fe_5O_{12}$) pellets (1 cm diameter, 3mm thick, cold-uniaxial pressing at 2000 kg/cm²) heated at 1300°C (A and B) and 1500°C (C and D), for 5 hours, in an air atmosphere. The pellets were cooled to room temperature (from the peak temperatures) in the shut-off furnace. The micrographs given in Figures 4A and 4B seem to suggest that a slightly higher level of densification has been achieved in the heating of the pellets at 1300°C. This immature suggestion warrants further research on the influence of rare-earth ions on the sintering behavior of YIG phase. On the other hand, as can be followed from the micrographs of Figures 4C and 4D, the increase of the sintering temperature to 1500°C has led to complete densification, again, with an average grain size of about 10 μ m in the sintered microstructure of the dark green, Nd-doped YIG pellets.

The sintering behavior of Nd-doped (1.1 at%) YAG $(Y_3AI_5O_{12})$ solid-state laser powders were depicted in Figure 5, as a function of peak temperature. It was quite visible from this figure that the maximum sintering temperature of 1500°C of this study was not sufficient for the sub-micron particles of the YAG phase to proceed to complete densification, on cold-uniaxially pressed samples. One may even claim that there was no notable difference between heating the YAG pellets at 1250°C for 24 hours (Fig. 5B), and heating them at 1500°C for 5 hours (Fig. 5D). It became apparent from this study that the YAG powders synthesized by the SPCS method did require temperatures higher than 1500°C for complete densification to be achieved.

4. Conclusions

Pure and rare-earth (Nd) doped powders of YIG $(Y_3Fe_5O_{12})$ and YAG $(Y_3Al_5O_{12})$ phases were prepared by the self-propagating combustion synthesis, at 1100°C. The cubic lattice parameters of the synthesized garnet phases did exactly match those of the previously reported phases produced at much higher temperatures via the conventional preparation routes. The SPCS technique was hereby shown to be an economical alternative for the manufacture of garnet phases of technological importance. $Y_3Fe_5O_{12}$ powders reached full densities, in the form of polycrystalline pellets, over the temperature range of 1400 to 1500°C. However, even the sub-micron, spherical particles produced by this method did not suffice to reach to complete densification state in the cold-uniaxially pressed $Y_3Al_5O_{12}$ pellets over the above temperature range of sintering. Further studies on the densification of YAG phase (with these powders) will employ higher sintering temperatures, such as 1600-1700°C.

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Figure 4. SEM more







Figure 5. SEM micrographs of 1.1 at% Nd-doped YAG pellets heated in an air atm. (A: 1100°C, 20h, B: 1250°C, 24h, C: 1300°C, 5h; D: 1500°C, 5h)

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PREPARATION AND

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Ceramic membranes for g outer surface of tubeline of then calcined to --alumin This layer was modified to silicate. The precaration is given and the gas seen gas mixture composed of

1. Introduction

A membrane is a sem be solid, liquid or gas. selective way. This can b in solubility and difference be used for separation of manupilation of chemi commercially available to offer a significant flexibilit requirements. However, Inorganic membranes. advantages over polyme non-porous. Paladium o non-porous membranes membranes, carbon h membranes are also imo Carbon membranes coa used for microfiltration an macroporous support of a 10-100 µm thickness and ceramic membranes are

The new and interest of vapours and gases in to obtain efficient seten literature studies reports permeation. Separation performed in these studies

2. Experimental Proceed 2.1. Preparation of the bo butoxide (Merck %97) to TÜRK SERAMİK DERNEĞİ



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