PRESSURE-TEMPERATURE SENSORS: SOLUTION DEPOSITION
OF RARE EARTH DOPED GARNET FILMS

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PRESSURE-TEMPERATURE SENSORS: SOLUTION DEPOSITION OF RARE EARTH DOPED GARNET FILMS

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ABSTRACT

An aqueous route to the deposition of multicomponent metal oxide films is based upon the complexation of precursor metal nitrate salts by glycine, or other organic complexant, followed by spin-coating the homogenous solution onto pretreated silica substrates. Glycine serves to frustrate the formation of cation oxides, thus precipitation. Upon dehydration, a glassy matrix results through which metal cations and nitrate anions are homogeneously dispersed. Subsequent heating of coated substrates initiates an oxidation-reduction reaction, which removes the organic matrix and residual nitrate leaving behind a film of the desired oxide composition. Using this method, Sm:YAG ($\text{Sm}:\text{Y}_3\text{Al}_5\text{O}_{12}$ - garnet) films about 150 nm thick have been deposited. The respective phases have been confirmed by powder XRD measurements and fluorescence spectroscopy. Analogous studies using powders generated by the same technique provided the parameters for optimizing processing conditions to generate phase pure YAG films. The fluorescence emission wavelength and related lifetime of certain electronic transitions arising from metal cation dopants vary as a function of pressure and temperature suggesting their use as optical sensors. This work suggests the possible application of these films as pressure-temperature sensors in a planar waveguide configuration or as a coating material for optical fibers.

INTRODUCTION

An aqueous synthesis route, the glycine-nitrate process or GNP, has been developed previously to generate fine, ceramic, homogenous metal oxide powders [1,2]. This process begins with the dissolution of metal nitrates and glycine, or other simple amino acid, in an aqueous solution. Upon heating, the now viscous solution autoignites; the nitrates serve as oxidants and the glycine serves a dual role: both as fuel for the combustion reaction and as a complexant for the metal cations. During the oxidation-reduction reaction, water, glycine, and the nitrates decompose and are driven off as H_2O , CO_2 , and N_2 . The resulting fine metal oxide ash can be amorphous or crystalline. Amorphous ash can be pressed into pellets and sintered at elevated temperatures where it densifies and crystallizes. The crystalline structure, or mixture of structures, which results is critically dependent upon the stoichiometry of the precursor solution and the sintering temperature. In related work, it has been demonstrated that these same solutions can be concentrated and then spin-cast to form amorphous thin films [3]. Upon heating, the amorphous phase crystallizes into a clear, polycrystalline film approximately 100 nm in thickness. The crystalline structure of the films can be verified using x-ray diffraction techniques, and for doped materials, by comparing the characteristic fluorescence spectra for the film to that measured for the single crystal material [4].

The ability to generate crystalline garnet films and coatings via an aqueous solution route is of interest to the electro-optics, optical communications, and sensor industries. As a material, Sm:YAG is of special interest as an optical sensor. The laser-induced fluorescence

wavelength of this material shifts as a function of pressure but is virtually insensitive to temperature [5]. In addition, the Sm:YAG fluorescence lifetime exhibits a temperature dependence, but negligible pressure dependence. The pressure and temperature dependence of the fluorescence behavior of Sm:YAG single crystal material has been calibrated [6,7]. In this paper, we demonstrated that the glycine nitrate process can be used as a means of generating polycrystalline planar waveguide films which may have application as optical pressure and temperature sensors.

EXPERIMENTAL

Preparation of Precursor Solution and Samples. Aqueous stock solutions of known concentration were prepared using the following metal nitrates: $\text{Al}(\text{NO}_3)_3$, $\text{Y}(\text{NO}_3)_3$, and $\text{Sm}(\text{NO}_3)_3$. The stock solutions were mixed in the correct molecular proportion to achieve the appropriate stoichiometry for the cubic garnet phase $\text{Y}_3\text{Al}_5\text{O}_{12}$. The Sm dopant level was calculated in terms of the percent atom replacement of Y and Al, respectively. A less than stoichiometric (fuel-lean) amount of glycine was added to the solution. Previous work has demonstrated that the amount of glycine added can affect the temperature and the extent of oxidation during autoignition [1,2].

In initial work [8], powders were used to determine the optimum sintering parameters for generating phase pure YAG films. Approximately 0.5 g samples of amorphous ash were

placed in covered Pt crucibles and heated in air in a preheated furnace for set period of time, then removed from the furnace and allowed to cool to room temperature. The phase composition of the powders was determined using XRD and fluorescence spectroscopy.

For the films presented here, the Sm dopant level was 0.5 atomic % Y. The precursor solution was then stirred over low heat to attain the correct viscosity for spin-casting and cooled to room temperature. Fused silica substrates were cleaned by dipping in heptane to remove organic surface contaminants and dried in air. The cleaned substrates were then etched lightly in concentrated HF followed by a thorough rinse in distilled H₂O. Thin films were cast by flooding the surface of the prepared substrate with the concentrated glycine-nitrate solution and spinning at 3000 rpm for 60 seconds. The coated substrates were placed in a furnace pre-heated to 1000°C for 10 to 60 minutes then quenched rapidly to room temperature. The crystalline structure of the resulting films was determined using fluorescence spectroscopy and x-ray diffraction.

X-ray Diffraction. The crystalline structure of the sintered films and powders were verified by x-ray diffraction measurements using a Philips APD 3620 diffractometer. The x-ray source was a fixed Cu anode operated at 40 KeV, 25 milliamp. The anode was equipped with a graphite monochromator which allowed separation of the Cu-K α_1 and K α_2 radiation and a 2 θ compensating slit which maintained a 13 by 13 mm spot size throughout the 2 theta scans. Two-theta scans were conducted from 10 to 70 degrees using a step size of 0.02 degree in 2 θ . The diffracted x-rays were detected with a scintillation detector. Since the

films were quite thin, data were collected at rates of both 10 sec/step and 75 sec/step to increase the signal-to-noise ratio.

Fluorescence Measurements. Fluorescence spectra of the Sm:YAG films and powders were excited with 488.0 nm radiation from an argon ion laser. The fluorescence was collected and dispersed by a 1.0 m scanning double spectrometer and detected using a photo-multiplier tube. The fluorescence lifetime was measured using the phase modulation technique [9]. A mechanical chopper operating at 500 to 1000 Hz was placed in the probe laser beam path. The output from the photo-multiplier tube was detected synchronously using a lock-in amplifier from which the phase delay between the probe excitation and the fluorescence signal measured by the photo-multiplier tube could be determined.

Atomic Force Microscopy. A Digital Instruments Nanoscope III atomic force microscope was used to probe the morphology of the as-cast YAG films as well as those that had been sintered at 1000°C for 30 minutes. A standard square pyramidal Si_3N_4 tip was used and all images were acquired in "constant force" or "constant deflection" mode. Two piezoelectric scanners were used dependent on the scale of the feature to imaged. The largest scan area was a 265 μm square. For features less than 1 μm , a smaller scanner was chosen. In sintered films where a granular texture was observed, the grain diameter determinations were based on a vertical relief measurement as opposed to the measurement of the grain diameter in the plane of the image. For imaging features that are on the order of a few tens of nanometers, the vertical sensitivity of the AFM is much greater than its planar

resolution.

RESULTS AND DISCUSSION

For the YAG materials produced, XRD of the GNP combustion product, ash or as-spun film, yielded very broad peaks as shown in Figure 1(a). After heat-treat at 1000°C for 60 minutes, the diffractogram exhibited substantially narrower diffraction peaks indicative of particles having a mean diameter of 20 nm. These diffractograms are compared to the reference diffraction pattern for the YAG structure in Figure 1(c). The results of samples sintered for various times at several different temperatures is summarized in the Time-Temperature plot in Figure 2. At temperatures between 875°C and 1000°C, the YAG structure coexists with a second crystalline phase YAlO_3 , a hexagonal perovskite, and amorphous alumina. Within this temperature range, if the powder is heated for longer durations, phase pure YAG powder results. Earlier work [8] suggested that the appearance of the second crystalline phase results from the temperature dependence of the competitive nucleation and growth rates; however, at sustained temperature the transformation of hexagonal YAlO_3 to phase pure YAG powder is controlled by a diffusion limited process.

The diffraction pattern of the Sm:YAG film sintered at 1000°C for 30 minutes is shown in Figure 3. A substantial broad background contribution from the amorphous silica substrate is observed due to the thinness of the Sm:YAG film (ca. 150 nm). However, upon comparison of the diffractograms of an uncoated silica substrate, small peaks characteristic of the cubic garnet structure and a minor phase, hexagonal YAlO_3 , can be resolved. The presence of hexagonal YAlO_3 , indicates that the crystallization to the garnet structure had not reached completion. Formation of a phase pure garnet film is achieved by heating at 1000°C for longer time periods or heating at higher temperature. No significant difference in the sintering behavior was observed between the powder and the thin film samples.

Atomic Force Microscope images of the heat-treated Sm:YAG films at 1000°C reveal a

granular microstructure that is loosely packed as shown in Figure 4. The grains are approximately 20 to 50 nanometers in diameter. From SEM measurements, this grain size is directly comparable to the grain size seen in powders generated by the same precursor solution. This similarity in grain size between the powder and film samples is consistent with the similarity in the crystallization kinetic behavior observed for the two sample types. As suggested previously, the transformation of hexagonal YAlO_3 to YAG is a diffusion limited process and thus susceptible to grain size effects.

The fluorescence spectra of single crystal Sm:YAG consists of numerous transitions extending from 555 to 770 nm that arise from the lowest excited state level, $^4\text{G}_{5/2}$, and terminate in the groundstate manifold. A portion of the spectrum containing the most intense fluorescence transitions terminating in the $^6\text{H}_{7/2}$ multiplet is shown in Figure 5(a). This multiplet is dominated by an intense doublet that consists of the Y1 peak at 617.77 nm and the Y2 peak at 616.04 nm. The fluorescence spectrum of the Sm:YAG thin film is shown in 5(b). Although the linewidths of the fluorescence transitions of the film are broader than those observed for the single crystal material, the structure of the fluorescence spectra are directly comparable. The broad linewidths most likely originate from the small crystallite size, typically on the order of tens of nanometers, characteristic of the glycine-nitrate process. For example, powders that have been sintered for longer time periods, and have larger crystallite size, exhibit fluorescence linewidths more characteristic to those of single crystal materials.

The pressure-induced frequency shift of the Y1 peak is compared to the shift of the ruby R1 peak at 632 nm in Figure 6(a). The shift of the R1 peak is used as the standard optical pressure sensor for high pressure diamond anvil cell experiments [10]. However, the R1 transition displays a significant temperature-induced shift [11] unlike that observed for the Sm:YAG Y1 peak as shown in Figure 6(b). In addition, the intensity of the R1 transition is difficult to detect above background at temperatures above 400°C. As a result of these temperature effects, an alternative pressure sensor is desired for experiments carried out under simultaneous high temperature-pressure conditions. Recently, the pressure-induced

frequency shift of the Y1 and Y2 peaks has been calibrated at temperatures from 6 to 900 K [6,7]. The magnitude of the pressure-induced shift is comparable to ruby; however, unlike ruby, the temperature induced shift is negligible. As a result, Sm:YAG is an attractive alternative pressure sensor to ruby for high temperature experiments.

The lifetime of the Y1 Sm:YAG fluorescence transition exhibits a temperature dependence as shown in Figure. 6(c). At temperatures greater than 800°C, the Sm:YAG lifetime decreases precipitously with increasing temperature. However, if the Sm:YAG is co-doped with a small amount of Cr, the temperature at which the Sm fluorescence lifetime begins to change rapidly is reduced to as low as 400°C. Thus by varying the Cr:Sm ratio and the absolute Sm concentration, the thermal region in which Sm fluorescence can be used as an effective thermal sensor can be tuned. The fluorescence lifetime Sm:YAG also displays only a minor pressure dependence, shown in 6(d).

CONCLUSIONS

The glycine-nitrate synthesis route is a quick and cost-effective method for generating refractory oxides doped with fluorescence species. Using the same precursor solution either powders or films can be prepared. Thin films can be spin-cast onto planar substrates or dip-coated onto optical fiber tips. The fluorescence behavior of both ruby and Sm:YAG exhibit pressure and temperature dependencies that make them attractive optical sensors in extreme experimental environments. However, the fluorescence wavelength and lifetime of ruby display both pressure and temperature dependencies, and thus either the temperature or pressure must be determined independently in order to effectively use this material as a sensor. In contrast, the fluorescence wavelength of Sm:YAG exhibits only a pressure dependence and the fluorescence lifetime displays only a minor pressure dependence making it an ideal pressure-temperature sensor for experiments allowing only optical access.

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CAPTIONS

- Figure 1. 1(a), X-ray diffractogram of glycine-nitrate ash having $Y_3Al_5O_{12}$ stoichiometry; 1(b), diffractogram of powder heated treated at 1000°C for 60 minutes; and 1(c), reference diffraction pattern of YAG structure.
- Figure 2. Time-Temperature plot showing crystalline phases for starting materials having $Y_3Al_5O_{12}$ stoichiometry. The dashed lines are boundaries indicating approximate minimum time at temperature to result in a given structural phase composition.
- Figure 3. Diffractograms of the Sm:YAG waveguide on a silica substrate, 1(a,c), compared to an uncoated silica substrate, 1(b). The reference diffraction patterns for $Y_3Al_5O_{12}$ in the cubic garnet structure and for $YAlO_3$ are shown in 1(d) and 1(e), respectively.
- Figure 4. Atomic Force Microscopy image of the surface of Sm:YAG film sintered at 1000°C for 60 minutes. Image is $2\text{ }\mu\text{m}$ square. The grains are approximately 30 nm in diameter.
- Figure 5. A portion of the fluorescence spectra of Sm:YAG single crystal, 5(a), and the Sm:YAG thin film, 5(b).
- Figure 6. The pressure-induced frequency shift exhibited by the ruby R1 and Sm:YAG Y1 peaks is displayed in 6(a). The temperature-induced shift for the same peaks is shown in 6(b). The pressure and temperature dependencies observed for the fluorescence lifetimes of ruby R1 and Sm:YAG Y1 are shown in 6(c) and 6(d).

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Hess & Exarhos, Figure 1 (a), (b), & (c)

Atomic Force Microscopy

Image is 2.0 μm across

Crystalline YAG films consist of well defined 10 to 20 nm spheres.

Hess + Exarhos, Figure 5