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METAL OXIDE PLANAR WAVEGUIDES DEPOSITED
FROM AQUEOUS SOLUTIONS

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LASER-INDUCED FLUORESCENCE IN DOPED METAL OXIDE PLANAR WAVEGUIDES DEPOSITED FROM AQUEOUS SOLUTIONS

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ABSTRACT

An aqueous route to the deposition of complex metal oxide films is based upon the complexation of the corresponding metal nitrate salts by glycine, followed by spin-casting the concentrated solution onto silica substrates. The presence of glycine serves to frustrate precipitation and leads to the formation of a glassy matrix through which metal cations 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, ruby ($\text{Cr}:\text{Al}_2\text{O}_3$) and Sm:YAG ($\text{Sm}:\text{Y}_3\text{Al}_5\text{O}_{12}$) films on the order of 150 nm thick have been deposited. The respective phases have been confirmed by XRD data and from the measured fluorescence spectra.

The red fluorescence exhibited by these materials under 488 nm excitation is dependent upon the ambient temperature and pressure. A marked shift in wavelength is observed as a function of increasing pressure. Ruby also exhibits a temperature dependent wavelength shift in contrast to Sm:YAG where a negligible shift is seen to temperatures near 1200 K. Fluorescence lifetimes of both materials exhibit a temperature dependence which varies with dopant concentration. 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. Details of the deposition process will be reviewed and the fluorescence response of both types of films will be summarized.

INTRODUCTION

An aqueous synthesis route has been developed previously to generate fine ceramic powders consisting of a homogenous mixture of metal oxides [1,2]. This process begins with the dissolution of metal nitrates and glycine in an aqueous solution. Upon heating, the solution autoignites; the nitrates serve as oxidants and the glycine acts as both 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 . A fine metal oxide ash remains which can be pressed into pellets and sintered at elevated temperature to develop crystallinity. The crystalline structure, or mixture of structures, that results is critically dependent upon the stoichiometry of the precursor solution. 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, Raman spectroscopy, 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 planar waveguides via an aqueous solution route is of interest to the electro-optics and sensor industries. Two materials of special interest as optical sensors are ruby ($\text{Cr}^{3+}:\text{Al}_2\text{O}_3$) and Sm:YAG ($\text{Sm}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}$, garnet). The laser-

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induced fluorescence wavelength of each material shifts as a function of pressure [5,6]. In addition, both the ruby and Sm:YAG fluorescence lifetimes exhibit a temperature dependence [7,8]. The pressure and temperature dependence of both ruby and Sm:YAG single crystal material has been calibrated. In this paper, we have utilized the glycine nitrate process as a means of generating polycrystalline planar waveguide films which may have application as optical pressure and temperature sensors.

EXPERIMENTAL

Preparation of Precursor Solutions. Aqueous stock solutions of known concentration were prepared using the following metal nitrates: $\text{Al}(\text{NO}_3)_3$, $\text{Y}(\text{NO}_3)_3$, $\text{Cr}(\text{NO}_3)_3$ and $\text{Sm}(\text{NO}_3)_3$. The stock solutions were mixed in the correct molecular proportion to achieve the appropriate stoichiometry for either $\text{Y}_3\text{Al}_5\text{O}_{12}$ or Al_2O_3 . The Sm and Cr dopant level was calculated in terms of the percent atom replacement of Y and Al, respectively. For the films presented here, the Sm dopant level was 0.5 % Y and the Cr dopant level was 1.0 % Al. 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]. The precursor solution was then stirred over low heat to attain the correct viscosity for spin-casting and cooled to room temperature. Silica substrates were cleaned by dipping in heptane to remove organic material and dried in air. The clean substrates were then etched lightly in concentrated HF followed by a thorough rinse in distilled H_2O .

The waveguides were cast by flooding the surface of the prepared substrate with the concentrated glycine-nitrate solution and spinning at 8000 rpm for 60 seconds. The coated substrates were placed in a furnace pre-heated to 1000 °C or 1400 °C for 10 minutes for the Sm:YAG structure or the $\alpha\text{-Al}_2\text{O}_3$ structure, respectively, and 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 glycine-nitrate films 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 $\text{Cu-K}\alpha_1$ and $\text{K}\alpha_2$ radiation and a 2θ 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 2θ . The diffracted x-rays were detected with a scintillation detector. Due to the thinness of the films, 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 ruby and Sm:YAG films 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.

RESULTS AND DISCUSSION

The diffractogram of the Sm:YAG film is shown in Fig. 1(a,c). A substantial broad background contribution from the amorphous silica substrate is observed due to the

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Figure 1. Diffraction patterns 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 $\text{Y}_3\text{Al}_5\text{O}_{12}$ in the cubic garnet structure and for YAlO_3 are shown in 1(d) and 1(e), respectively.

thickness of the Sm:YAG film (ca. 150 nm). However, upon comparison of the diffractograms of an uncoated silica substrate in Fig. 1(b) to the Sm:YAG coated substrate, the small peaks diagnostic of the cubic garnet structure can be resolved. The diffractogram in Fig. 1(c), collected at the slower step-rate, indicates the presence of a minor phase, hexagonal YAlO_3 . The presence of hexagonal YAlO_3 , indicates that the crystallization to garnet structure had not reached completion. Formation of pure garnet film can be attained by heating at 1000 °C for longer time periods or heating at higher temperature.

The fluorescence spectra of single crystal ruby and Sm:YAG are shown in Figures 2(a) and 3(a). In both spectra, the most intense feature are doublets. In ruby, the doublet consists of the R1 peak at 694.24 nm and R2 at 692.90 nm. In Sm:YAG, there are numerous transitions extending from 555 to 770 nm; however, the most intense doublet consists of the Y1 peak at 617.77 nm and the Y2 peak at 616.04 nm. The fluorescence spectra of the ruby and Sm:YAG waveguides are shown in 2(b) and 3(b). Although the linewidths of the fluorescence transitions of the films are broader than that observed for the bulk 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 hundreds of angstroms, characteristic of the glycine-nitrate process. Powders that have been sintered for longer time periods exhibit fluorescence linewidths more characteristic to those of single crystal materials.

Figure 2. Fluorescence spectra of ruby single crystal, 2(a), and the ruby waveguide, 2(b).

Figure 3. Fluorescence spectra of Sm:YAG single crystal, 3(a), and the Sm:YAG waveguide, 3(b).

The pressure-induced frequency shift of the R1 and Y1 peaks is shown in 4(a). The shift of the R1 peak is used as the standard optical pressure sensor for high pressure diamond anvil cell experiments [10]. However, R1 and R2 transitions also display a significant temperature-induced shift [11], shown for R1 in Fig. 4(b); the intensity of the R1 and R2 transitions are difficult to detect above background at temperatures above 450 °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 [12,13]. The magnitude of the pressure-induced shift is comparable to ruby; however, unlike ruby, the temperature induced shift is negligible, and is shown for Y1 in Fig. 4(b). As a result, Sm:YAG is an attractive alternative pressure sensor to ruby for high temperature experiments.

Figure 4. The pressure-induced frequency shift exhibited by the ruby R1 and Sm:YAG Y1 peaks is displayed in 4(a). The temperature-induced shift for the same peaks is shown in 4(b). The pressure and temperature dependencies observed for the fluorescence lifetimes of ruby R1 and Sm:YAG Y1 are shown in 4(c) and 4(d).

The lifetime of the ruby [7,14] and Sm:YAG fluorescence transitions are temperature dependent as shown in Fig. 4(c). The magnitude of the ruby temperature derivative is substantially larger than that observed for Sm:YAG at temperatures less than 450 °C. At temperatures greater than 800 °C the Sm:YAG lifetime decreases precipitously with increasing temperature. However, if the Sm dopant concentration is decreased to 0.1% Y, the temperature at which the fluorescence lifetime begins to change rapidly is reduced to ca. 300 °C. Thus at low temperatures, the use of the ruby fluorescence lifetime is an effective thermal sensor; however, at much higher temperatures, Sm:YAG provides accurate temperature measurements and by varying the Sm dopant concentration the region of temperature sensitivity can be altered. The fluorescence lifetime of both ruby [14,15] and Sm:YAG also display a pressure dependence, shown in 4(d). However, the

pressure dependence of the lifetime measured for ruby is much larger than that exhibited by Sm:YAG.

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. The 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. The fluorescence wavelength and lifetime of ruby exhibit both pressure and temperature dependence and thus either the temperature or pressure must be determined independently. The fluorescence wavelength of Sm:YAG exhibits only a pressure dependence making it an ideal pressure sensor for high temperature experiments. The fluorescence lifetimes of both ruby and Sm:YAG can be used to determine temperature. However, unlike ruby, the Sm:YAG lifetime is pressure-insensitive and is well suited to high stress environments. In addition, the Sm dopant concentration can be optimized to provide tuning of temperature sensitivity.

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