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Journal of Alloys and Compounds 300–301 (2000) 147–151

Journal of ALLOYS AND COMPOUNDS

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Fluorescence study of zirconia films doped by Eu^{3+}, Tb^{3+} and Sm^{3+} and their comparison with silica films

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Abstract

Zirconia oxide and silica oxide films doped by europium, terbium and samarium were prepared by the sol gel method and deposited on quartz slides. Fluorescence and excitation spectra of the samples were measured using species with the same number of ions per unit thickness. Europium excited into the charge transfer band and terbium excited into the f–d band showed enhanced fluorescence in the zirconia matrix. When samarium was excited into the intra f–f transitions bands it exhibited luminescence in zirconia only but not in silica films. For Eu and Tb higher luminescent intensities of the rare earth ions were obtained in zirconia films. The advantages of zirconia films is discussed.

Keywords: Fluorescence; Zirconia films; Silica films

1. Introduction

There exists an interest in designing new materials for active wave guides. Based on mechanical and optical properties of zirconia films deposited on transparent substrates we believe that these materials have a potential application if they will be doped by highly luminescent rare earth ions.

In our previous paper [1] we have described the preparation and physical properties of zirconia and zirconia–ormosil films suitable for planar waveguides. The films as well as the intermediate products for their formation were characterized by UV-visible spectra, Fourier transferred infrared spectra (ETIR), X-ray photoelectron spectra (XPS), differential thermal analysis and thermal gravimetry (DTA/TG), differential scanning calorimetry (DSC) and X-ray diffraction (XRD). Organic laser dyes incorporated into planar waveguides based mainly on TiO_2 prepared by the sol gel method have been shown to be a good active laser and amplifier medium [2,3], however titanium based materials are subjected to photochemical damage after long exposure to high intensity exciting light. Zirconia coatings due to their chemical and photochemical stability, high refractive index and low phonon energy seem to be an ideal medium for preparation of active waveguides. While zirconia–ormosil based waveguide prepared at room temperature and doped by laser dyes Rhodamine 6 was described recently [4], in the present paper we report on zirconia films doped by the rare earth ions europium, terbium and samarium.

Rare earth ions Nd^{3+}, Er^{3+} and Ho^{3+} are well known laser activators in a variety of crystal and glass media. The lasers based on these ions are active in the infrared part of the spectrum between 1.06 and 2 μm. The fibre waveguides especially doped by erbium are widely used for telecommunication [5] as amplifiers and repeaters. The planar waveguide based on ions emitting in the visible range on the other hand may find a number of applications such as active optical windows, optical switches, new generation television screen nonlinear materials, etc. It is well established that in the luminescence of rare earth ions the highest phonon frequencies of the host lattice are responsible for nonradiative relaxations [6–8]. In accordance with the energy gap law, the presence of large gaps between emitting and the terminal level reduce the probability of nonradiative decay. The lower the energy of the host phonons the larger is the number of phonons connecting the emitting level with the next lower layer. The more phonons needed to gap the energy will decrease the

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0925-8388/00/$ – see front matter
PII: S0925-8388(99)00714-8

nonradiative relaxation probability and increase the quantum yield of luminescence.

Since the stretching frequency of silica matrix is about 1100 cm^{-1} and for zirconia matrix is about 470 cm^{-1} we may expect much higher efficiencies of luminescence in zirconia films than in silica films for ions with small energy gaps. This does not hold for Eu^{3+} and Tb^{3+} where the gaps are large.

Preliminary studies on luminescence of terbium-doped ZrO_2 thin films prepared by the sol gel method [9] do indeed show the terbium luminescence. It was of interest to compare the luminescence intensity of rare earths in zirconia films with that in silica films. Thin films of zirconia have been prepared by different deposition techniques [10–13] but the sol gel technique offers unique advantages such as an ease of doping and controlling of the concentration of the dopants. Also the resistance to atmospheric moisture has been shown to be superior in the zirconia films [14].

2. Experimental

The films were prepared by dipping quartz slides of optical quality from appropriate precursor sols. The quartz slides were pre-cleaned first in a liquid soap for 1 h at 60°C, rinsed in triply-distilled water then immersed in the solution containing seven parts of concentrated sulfuric acid and three parts of hydrogen peroxide This was followed by rinsing with triply distilled water until no residue of cleaning materials remained, drying at room temperature and finally heating at 300°C for 30 min.

2.1. Preparation of precursor sols

Three millilitres of glacial acetic acid was slowly added to 10 ml of zirconia tetrapropoxide $Zr(OC_3H_7)_4$ (TPOZ) and stirred for 30 min. Then 20 ml of *n*-propanol (C_3H_7OH) was added to the solution, which was further stirred for 15 min at room temperature. 4 ml of 50% diluted solution of acetic acid in deionized water was slowly added to the above solution under stirring. Following this step, the solution was stirred for another 30 min at room temperature; filtered and stored in a refrigerator for up to 4 days. The solution is transparent with a pale yellow colour. For the preparation of zirconia films, doped films with rare earth ion nitrates $Eu(NO_3)_3$, $Tb(NO_3)_3$ and $Sm(NO_3)_3$ were synthesized from the rare-earth oxides. The nitrates were dissolved in 10 ml of monomethoxyethanol added to the original sol and stirred for 15 min. The quantities of rare-earth oxides were calculated to obtain 3×10^{20} ions/cm^3 of Eu^{3+}, Tb^{3+} and Sm^{3+} in the final zirconia and silica matrix.

2.2. Preparation of the silica sol

Four drops of trimethoxychiorosilane were added to a stirred solution of 10 ml trimethoxyorthosilane (TMOS) in 20 ml *n*-proponal. The solution was then hydrolyzed by 3 ml of de-ionized water to obtain the silica sols. The desired quantities of rare earths nitrates dissolved in monomethoxiethanol were added to the silica sol and stirred for 15 min.

2.3. Film deposition, drying and thermal treatment

For both zirconia and silica films the quartz slides were dipped into the sols, dried at 40°C for 15 min and finally annealed at 500°C for 20 min in air. The thickness and refractive indices were measured by spectral ellipsometry using a WVASE 32™ ellipsometer (J.A. Woolam) at room temperature in the range 300–480 nm. The refractive index of the silica and zirconia films varied, depending on the wave lengths, between:

for silica $n(\mathrm{Si}) = 1.3245 \div 1.402$

and for zirconia $n(\mathrm{Zi}) = 1.8652 \div 2.020$

The thickness of the silica films is 0.463 ± 0.003 μm and for zirconia films $0.500\ 1\pm0.001$ μm.

2.4. Spectroscopic measurements

The excitation and emission spectra were recorded on a Jasco FP-750 spectrofluorimeter. All measurements were done at room temperature.

The spectra of the undoped films were subtracted by the computer analysis from the measured spectra of rare earth containing films. For europium and terbium the bandwidth was 10 nm for excitation and 5 nm for emission. The sensitivity was medium. For the samarium-containing samples the bandwidths were 10 nm for excitation and emission and the sensitivity was high. The ratio between the high sensitivity and the medium sensitivity is 14. Both the excitation and the emission spectra were obtained by subtracting the background emission of the undoped zirconia and silica films on quartz. In order to remove the second harmonic a yellow cutoff filter (ESCO Products Inc., [200–400] cut off, was used.

3. Results

Fig. 1 presents the emission spectra Eu^{3+} in zirconia and silica films. The excitation was performed at the charge transfer bands as seen from the maxima excitation in the figure. Four bands due to $^5D_0\rightarrow{}^7F_0$, $^5D_0\rightarrow{}^7F_1$, $^5D_0\rightarrow{}^7F_2$, $^5D_0\rightarrow{}^7F_3$ and $^5D_0\rightarrow{}^7F_4$ are observed between 580 and 700 nm. The intensities of the emissions are much higher

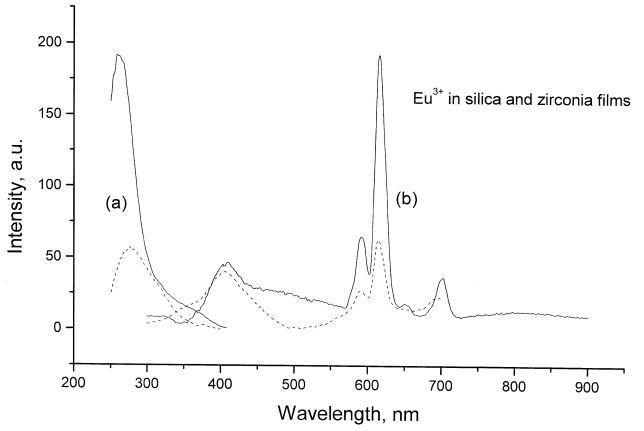

Fig. 1. P1 spectra of Eu^{+3} in zirconia and silica sol–gel film (exc 275 λ). a.excitation; b. emission. Full line, zirconia; broken line, silica.

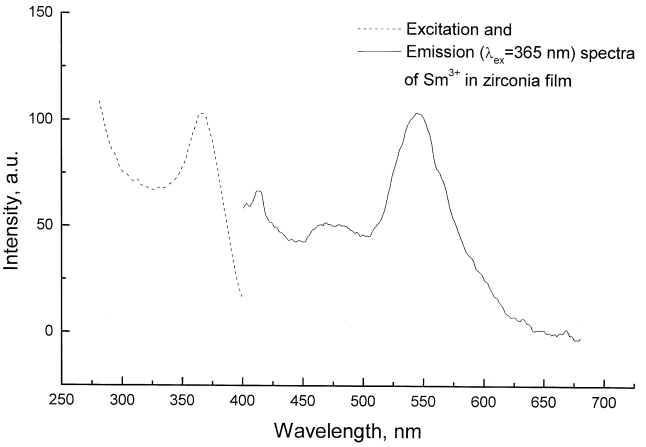

Fig. 3. P1 spectra of Sm^{+3} in zirconia (exc $\lambda = 365$). Full line, emission; broken line, excitation spectrum.

in the zirconia films. In addition a broader band is observed around 400 nm which may be due to Eu^{2+} created as a results of photoreduction [15,16].

Fig. 2 shows the emission spectrum of terbium in silica and zirconia films excited at the f→f transition as shown in the figure. The bands between 489 and 617 nm arise from $^5D_4 \rightarrow {}^7F_6$, $^5D_4 \rightarrow {}^7F_5$, and $^5D_4 \rightarrow {}^7F_4$ and $^5D_4 \rightarrow {}^7F_3$. The intensities of these bands is again stronger in the zirconia films. In addition in the zirconia films we observe a band picking at 420 nm due to the emission from higher $^5D_3$ to $^7F_5$ state. These can be explained by lower multiphonon relaxation between the $^5D_3$ to $^5D_4$ state as a result of lower phonon energy in the zirconia matrix.

Fig. 3 presents the excitation and emission spectrum of samarium in the zirconia film. No luminescence of samarium was observed in the silica film. The excitation in samarium is performed in the f→f transition.

Table 1 presents the wavelength of the transitions and their assignments and related intensities.

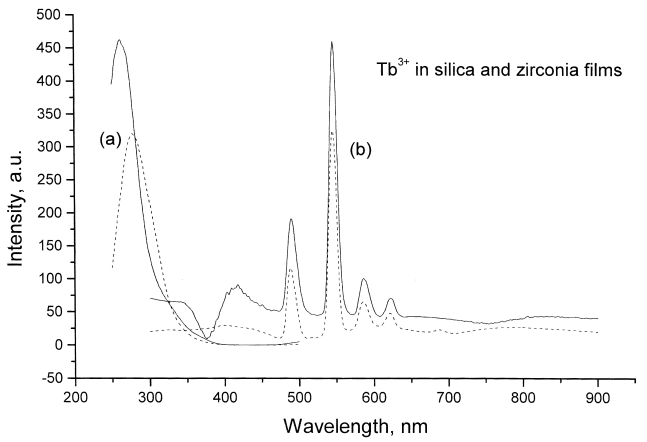

Fig. 2. P1 spectra of Tb^{+3} in zirconia and silica sol–gel film (exc 257 λ). a.excitation; b. emission. Full line, zirconia; broken line, silica.

4. Discussion

Thin films made by the sol–gel process are promising materials for wave guides [17–19]. In the present paper we have compared the emission properties of zirconia and silica films doped by three rare earth ions. The wavelengths of transitions and their assignments are presented in Table 1. The spectra clearly show an in homogeneous broadening unlike the sharp lines of europium in zirconia crystals [20] indicating that the films are of amorphous nature.

In the case of zirconia and silica the highest absorption of europium is via the charge transfer state (CTS) between the host lattice oxygen atoms and Eu. This may vary slightly from one oxide to another oxide host as seen in the figure. The transition probabilities are high and the resulting luminescence appreciable.

In the case of terbium the $4f^8$–$4f^75d^1$ transition dominates the high absorption in the range 200–300 nm, the resulting luminescence from the f states is again high.

In the case of samarium both the charge transfer state and f–d state are positioned at energies much above the present measuring range and the ion is excited into f–f transition with much lower probabilities [6]. The luminescence of Sm is not observed in the silica films and only detected in the zirconia films.

In the case of Eu^{3+} and Tb^{3+} the energy gap between the emitting ^5D and the terminal levels is 12 000 cm^{-1} and 15 000 cm^{-1} equivalent to more than five matrix phonons even in the case of silicate matrix. Therefore the increased intensity of luminescence of these ions measured at comparative concentration of ions per optical path is due to higher refractive index and higher dielectric constant of the zirconia matrix. The same phenomenon is responsible for higher reflection of zirconia as evident in its higher base line.

Table 1
Observed transitions of Eu^{3+}, Sm^{3+} and Tb^{3+} in zirconia and silica films. The relative intensities are given in parenthesis

Tb^{3+}		Sm^{3+}		Eu^{3+}	
Wavelength nm	Transition	Wavelength nm	Transition	Wavelength nm	Transition
489	$^5D_4 \rightarrow {}^7F_6$	540	$^4G_{5/2} \rightarrow {}^6H_{5/2}$	590	$^5D_0 \rightarrow {}^7F_1$
546	$^5D_4 \rightarrow {}^7F_5$			612	$^5D_0 \rightarrow {}^7F_2$
Si (669)				Si (145)	
Zr (993)				Zr (352)	
589	$^5D_4 \rightarrow {}^7F_4$			652	$^5D_0 \rightarrow {}^7F_3$
617	$^5D_4 \rightarrow {}^7F_3$			700	$^5D_0 \rightarrow {}^7F_4$
420	$^5D_3 \rightarrow {}^7F_5$				

The low (or absent) luminescence of Sm in the silica matrix may arise from aggregation of this ion in silica [21,22] and resulting cross relaxation by the mechanism. $^4G_{5/2} \rightarrow {}^6F_{1/2} = {}^6H_{5/2} \rightarrow {}^6F_{7/2}$. From the measured luminescent life times of Eu and Sm under nitrogen excitation which are lower than the natural life times at least by a factor of two [23] we conclude that there exists also an aggregation of these ions in the films. This phenomenon needs to be taken into account when designing the wave guides.

In conclusion it can be seen that the zirconia films are quite a suitable material for active wave guides, as the luminescence of the rare earth activators in it is quite high and the stability and optically quality of the films very good.

Acknowledgements

The authors are grateful for the grant from the Israeli–Indian agreement and the Israeli Ministry of Science. Michael Zevin has kindly helped us with the computer work of the correction of the spectra and Shlomo Yitzhaik's group, V. Burtman and E. Vaganov for the ellipsometric measurements.

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