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PREPARATION AND THERMOLUMINESCENCE PROPERTIES OF ALUMINIUM OXIDE DOPED WITH EUROPIUM

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Abstract — There is little information concerning the use of rare earths as dopants of Al_2O_3. This paper presents the preparation method and the results of studying the thermoluminescence characteristics of Al_2O_3:Eu exposed to ultraviolet light. Phosphor powder was obtained by the evaporation method. Optimum dopant concentration was 10% at an evaporation temperature of 700°C. The powder obtained was submitted to thermal treatments at high temperatures in order to stabilise the traps. Diffraction patterns showed amorphous powder up to 500°C; as the temperature was raised crystalline phases of Al_2O_3 appeared. The photoluminescence spectrum induced by 250 nm UV light exhibited four well defined peaks characteristic of the Eu^{3+} ion. The glow curve exhibited two peaks at 180 and 350°C. The sensitivity of Al_2O_3:Eu was 10 times lower than Al_2O_3:C. The thermoluminescence response was linear from 2.4 to 3000 μJ.cm^{-2} of spectral irradiance, and the fading 2% in a month. From these results it can be concluded that Al_2O_3:Eu has potential as an UV dosemeter.

INTRODUCTION

The increased use of ionising radiation in the diagnosis and therapy of some diseases as well as the modern radiation diagnosis and radiotherapy equipment available make necessary the use of a highly reliable dosemeter which is able to measure more and more low energy radiation. On the other hand, it is known that humanity is constantly exposed to the UV natural radiation reaching the earth's surface. An important part of the UV spectrum is considered to be low energy ionising radiation. This makes it necessary to make an adequate evaluation of the dose absorbed by man due to UV radiation.

One of the former materials studied for possible use as a dosemeter is aluminium oxide (Al_2O_3). However, the study of this material was forgotten for a long time, because of its low sensitivity compared with that of TLD-100[1]. Recently the research on this material has been increased due to the development of Al_2O_3:C crystals[2]. Thermoluminescence induced by UV radiation in Al_2O_3:C has been reported by several authors[3,4]. However, there is no evidence on the use of rare earths as dopants. This paper presents the preparation method, the structural, morphological and luminescence characteristics and the results of studying the thermoluminescence (TL) properties of europium-doped aluminium oxide (Al_2O_3:Eu) exposed to ultraviolet (UV) light.

X ray diffraction and sweep electron microscopy measurements showed that as the annealing temperature is increased, crystalline phases are formed. Photoluminescent emission of the powders exhibited a characteristic spectrum which is associated with radiative transitions among electronic energy levels of europium. Dependence of luminescent intensity as a function of annealing temperature and of impurity concentration is also reported.

EXPERIMENTAL PROCEDURE

Phosphor powder of Al_2O_3:Eu was obtained using the solvent evaporation method by mixing 12 g of aluminium nitrate with europium fluoride at the following concentrations: 5, 10, 15 and 20% dissolved in 5 ml of ethanol. This mixture was heated at 250°C for half an hour, then evaporating 700°C for half an hour. In order to stabilise the traps, powder obtained was then submitted to thermal treatments of two hours at the following annealing temperatures: 500, 700 and 900°C. The final product was crushed and sieved to select powder with grain sizes between 200 and 500 μm. To obtain Al_2O_3:Eu + PTFE pellets of 5 mm in diameter and 0.8 mm thickness, a mixture 2:1 of Al_2O_3:Eu powder and PTFE resin powder was placed in a stainless steel die to be pressed at room temperature at about 100 MPa. Pellets thus obtained were thermal treated for a period longer than 5 h in a nitrogen oven at a temperature slightly lower than that of PTFE fusion for sintering them.

Previously to production of the pellets, the crystalline structure of Al_2O_3:Eu powder was determined by means of X ray diffraction. The crystalline structure of the

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powder was determined using an X ray diffractometer Siemens D-5000 which emits a radiation of $\lambda = 0.15406$ nm from a Cu target. Morphological characteristics were observed with a sweep electronic microscope JEOL JSM-6300 using a voltage of 15 kV and an amplification of 5000×.

Photoluminescent spectra were obtained using a spectrophotometer (Perkin-Elmer LS50B) in the wavelength range from 400 to 800 nm using an excitation wavelength of 250 nm. Spectra were measured with a filtration of 430 nm to cut the excitation signal. The resultant spectrum was the average of three sweeps at 400 nm.min^{-1}.

Previous to the determination of dosimetric properties the samples were submitted to different thermal annealing treatments in order to erase any remaining information. Optimal thermal annealing consisted in heating at 300°C for 30 min. Dosimetric properties studied were: glow curve, sensitivity, linearity, repeatability and fading. Each experimental data point represents the

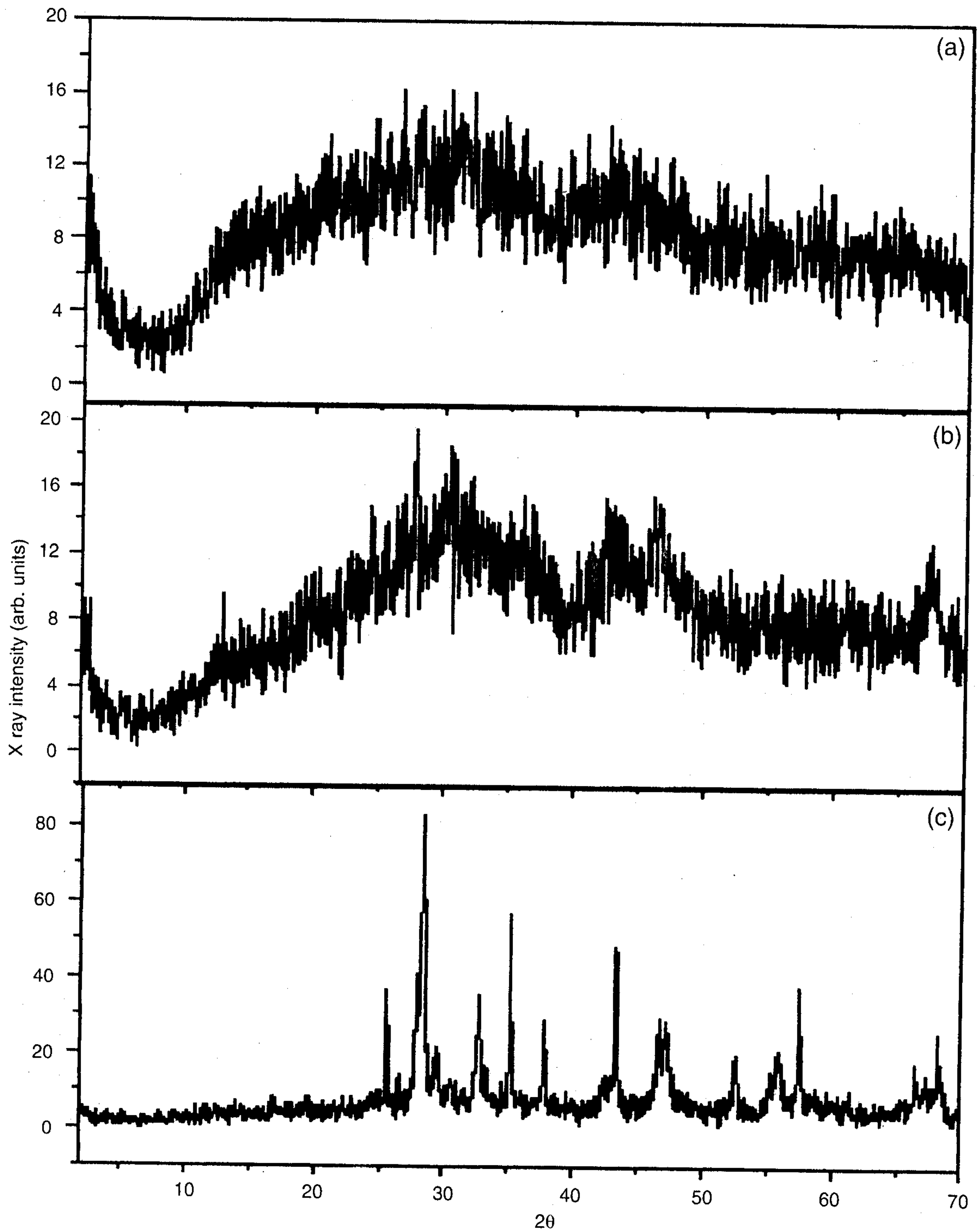

Figure 1. X ray diffraction patterns of Al_2O_3:Eu powder at three different temperatures: (a) 500°C, (b) 700°C and (c) 900°C.

average of at least ten measurements. To investigate the glow curve and other thermoluminescent properties of Al_2O_3:Eu, samples were individually exposed to a UV/light beam from a Xe lamp coupled with a monochromator to select different wavelengths between 200 and 400 nm. Sensitivity was determined by simultaneously exposing samples of Al_2O_3:Eu and Al_2O_3:C to 260 nm UV light. To determine the linearity, samples were exposed to a UV light beam of 260 nm wavelength by varying the exposure time. To investigate repeatability properties a set of samples was exposed repeatedly for five seconds to a UV light beam. Fading was determined by exposing samples to the UV beam and storing them in the dark at room temperature for different periods of time.

The TL measurements were made in a Harshaw 4000 TL analyser connected to a PC to record and process the data. The TL signal was integrated from room temperature up to 300°C using a heating rate of $10°C.s^{-1}$. All TL measurements were made in a nitrogen atmosphere in order to reduce the thermal noise resulting from the heating planchet of the TL reader.

Since Al_2O_3:Eu is sensitive to visible light it had always to be handled in conditions of darkness.

RESULTS AND DISCUSSION

Crystalline characteristics of Al_2O_3:Eu powder are shown in Figure 1. This figure shows the diffraction patterns for three different annealing temperatures. It can be seen that at temperatures up to 500°C the powder is amorphous. As the annealing temperature is increased, peaks associated with crystalline phases of Al_2O_3 appear. The results obtained by sweep electronics showed certain regular forms which are maintained for the three annealing temperatures. However, for the higher annealing temperature (700°C) some geometrical forms which could be associated with crystals are noticed. These results could be correlated with the X ray diffraction measurements suggesting an improvement in the ordering degree at higher temperatures.

Figure 2 shows the photoluminescence spectrum of Al_2O_3:Eu induced by 250 nm UV light which exhibited four well defined peaks at 587, 600, 611 and 648 nm corresponding to $^5D_0 \rightarrow {}^7F_0$, $^5D_0 \rightarrow {}^7F_1$, $^5D_0 \rightarrow {}^7F_2$ and $^5D_0 \rightarrow {}^7F_3$ characteristics of the Eu^{3+} ion.

Luminescence intensity of the main peak as a function of annealing temperature and the impurity concentration showed that the optimum concentration was 10% and the optimum annealing temperature 700°C (see Figure 3).

Figure 4 shows the glow curve of Al_2O_3:Eu+PTFE pellets exposed to a UV/light beam of 260 nm wavelength. This glow curve exhibited two peaks at 180 and 350°C respectively. Sensitivity of Al_2O_3:Eu was 10 times lower than Al_2O_3:C. The thermoluminescence response was linear in the range from 2.4 to 3000 $\mu J.cm^{-2}$ of spectral irradiance. Fading of Al_2O_3:Eu was 2% in a month. Repeatability was ±3% after 10 measurements.

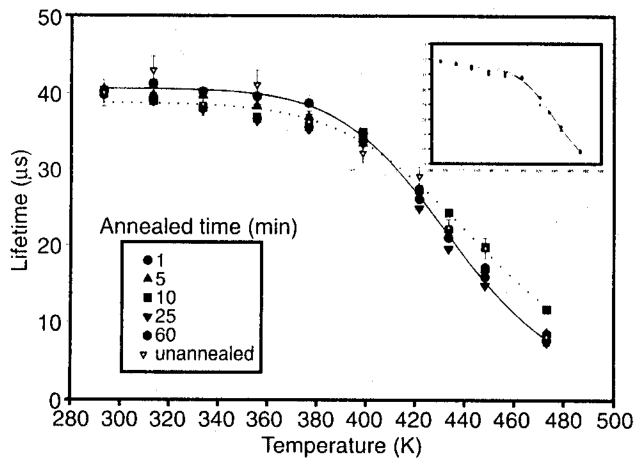

Figure 3. Luminescence intensity of Al_2O_3 powder as a function of dopant concentration at three different temperatures. (- -●- -) 500°C, (— ■ —) 700°C, (- -▲- -) 900°C.

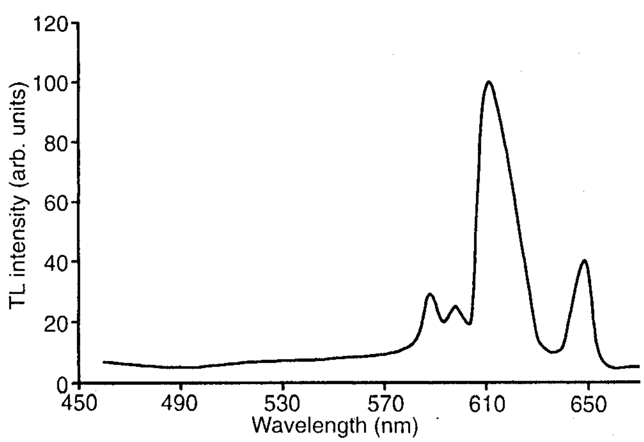

Figure 2. Photoluminescent spectrum of Al_2O_3: Eu induced by 250 nm UV/light.

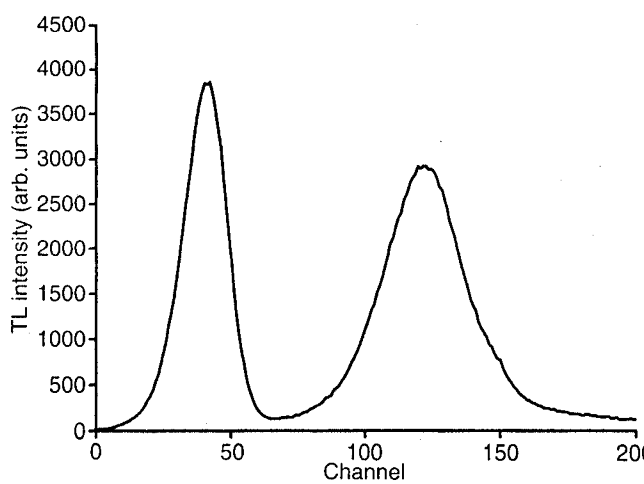

Figure 4. Glow curve of Al_2O_3+PTFE exposed to UV light of 260 nm.

CONCLUSIONS

Aluminium oxide doped with europium powder was obtained, of which the luminescent characteristics showed that Eu is incorporated in the matrix material as an atomic centre. The observed spectra exhibited characteristic peaks associated to radiative transitions among the electronic energy levels of the Eu ion. Diffraction patterns suggested amorphous powder at low annealing temperatures. As the annealing temperature increases an increase in the crystallinity is observed making evident the presence of crystalline phases corresponding to Al_2O_3.

Notwithstanding the sensitivity of Al_2O_3:Eu was 10 times lower than Al_2O_3:C. its very low fading compared with those of Al_2O_3:C makes this material appropriate for radiation dosimetry.

Pellets of Al_2O_3:Eu+PTFE made with this powder presented good dosimetric properties and can be re-used many times with non-apreciable changes in sensitivity if an apropriate annealing procedure is given and they are handled in darkness since this material is light sensitive.

Taking into account the above results, it can be concluded that the thermoluminescence dosemeters based on Al_2O_3:Eu+PTFE are very promising for use as a dosemeter for UV radiation.

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