Temperature effect on the luminescent emission of hafnium oxide doped with europium ion.

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Abstract. Photoluminescent analysis of HfO2 doped with Eu3+, as a function of temperature is reported. Samples were synthesized by hydrothermal method at 200 °C of temperature and 120 minutes of reaction time, using chlorides as raw materials. The HfO2 was doped with trivalent europium ions (Eu3+) at concentrations 1, 2, 3, 5 and 10 % atomic. X-ray diffraction (XRD) showed synthesized material crystallized in monoclinic phase characteristic of HfO2. Scanning electron microscopy showed presence of particles of smaller size than 100 nm forming agglomerates. Photoluminescent analysis at room temperature for sample doped with Eu3+ (3%) display highest luminescent emission. Finally, photoluminescent analysis as a function of temperature, shown changes in luminescent intensity in 5D1 and 5D0 transitions, for 0 to 50 °C temperature range.

1. Introduction
Measurement of temperature has a crucial role in innumerable industrial processes, technology and scientific research. For this reason, sensors focused on this physical variable cover approximately 80% of sensor market worldwide [1]. Although, development of temperature sensors has evolved continuously for more than two centuries [2], nowadays technological advance and demand of sensors in areas such as nanomedicine, microelectronics, microoptics and photonics, has reached a level in where conventional sensors are unable to perform measurements with spatial resolution lower than submicrometer scale or in structure that change their temperature rapidly. In last decade luminescent thermometry has been proposed as an option to solve these problems of spatial and temporal resolution; this optical technique is based on luminescent properties which changes in function of temperature [2]. Among, luminescent materials, metal oxides doped with rare earth ions are predominant materials, due to their physical and chemical stability, narrow emission bands and absence of aging effects, as well as a low frequency of phonons and a wide gap [3]; therefore, rare earth ions are candidates for applications in temperature detection due to in some of them, exist thermally coupled energy levels, wich have a gap between 200cm⁻¹ and 2000 cm⁻¹ [5]. In last five years, are few reports in which metal oxides are used as luminescent hosts in nano-thermometry
applications. Brandão-Silva and collaborators successfully synthesize yttrium oxide (Y₂O₃) doped with europium Er³⁺, through the PVA assisted by sol gel, finding sensitivity in temperature is directly related with crystalline size [6].

Zhen Sun et al., synthesized nanoparticles of lanthanum oxide (La₂O₃) doped with Erbium (Er³⁺) by solvothermal method, found that electrons of thermally coupled levels, ²H₁₁/₂ and ⁴S₃/₂, shows a strong temperature dependence in range considered from 295 to 315 K [7]. Shaoshuai Zhou et al., proposed a new strategy to improve temperature detection of a large amount of yttrium oxide (Y₂O₃) doped with europium (Eu³⁺), synthesized by combustion method. This strategy consisted in doped additionally luminescent material with neodymium (Nd³⁺) to promote cooperative processes, improving luminescent intensity in range from 30 to 510 K [8].

In this work, we report synthesis of hafnium oxide (HfO₂) doped with europium (Eu³⁺), by hydrothermal method and its subsequent photoluminescent analysis as a function of temperature in range from 0 to 50 °C.

2. Experimental

Hafnium oxide (HfO₂) undoped and doped with europium was synthetized by hydrothermal method, using chlorides dissolved in deionized water. At first step was dissolved 0.1281g of HfCl₄ in 10 ml of deionized water and after dopant solution was added in an amount 1, 2, 3, 5 and 7 mL of EuCl₃·6H₂O. On the other hand, a 0.02M solution was obtained with 10 ml of HfCl₄ and 10 ml of FeCl₃ · 6H₂O. Final step was kept under magnetic agitation during 10 minutes, and pH was adjusted to 12 adding 1M of NaOH solution. Then, this solution was put into a polytetrafluoroethylene container in core of a stainless steel reactor; it was heated up at 200°C during 120 minutes; finally the reactor was cooled at room temperature. Samples were washed repeatedly with water deionized and dried at room temperature during 24 hours.

Structural analysis of synthesized material, was made by X-ray diffraction (XRD), using a Bruker diffractometer model D-8 Advanced, with the Kα radiation of the Cu (λ = 1.5406 Å) in steps of 0.05° and 0.5 seconds per step in range from 15° to 70°. Morphology was analyzed through of scanning electron microscopy (SEM) JEOL JSM-6390LV using 20 kV as accelerator voltage and the secondary electron detector. Elemental composition was obtained by energy dispersive X-ray analysis (EDX), using an Oxford, Si-Li detector model Pentafet installed on SEM previously mentioned. Analysis photoluminescent was performed on a FluoroMax-P Jobin Yvon Horiba spectrofluorimeter, with a 150 watts Xenon lamp as illumination source. Firstly, emission spectra were recorded at room temperature at different concentrations of europium (Eu³⁺) in order to know the dopant concentration that allows us to obtain greater intensity luminescent; after a cryostat Model S202 I-DMX-1SS was coupled by fiber optics to spectrofluorimeter previously mentioned to analyze luminescent response at different temperatures in range from 0°C to 50 °C.

3. Results and Discussion

Figure 1 shows the X-ray diffraction pattern of hafnium oxide doped with Eu³⁺ (3%), peaks centered in 2θ = 23.8, 28.4, 31.7 and 50.5 can be observed, correspond to monoclinic structure with space group P21/c, characteristic of HfO₂ according to diffraction chart PDF-34-0104. Crystals size was determined by mean of the Scherrer’s equation, using peak centered in 2θ = 28.4, having obtained an average size of 16.73 nm.

Figure 2 show SEM micrograph of HfO₂, where it is possible to appreciate nanoparticles smaller than 20 nm forming micrometric agglomerates, which are observed repeatedly throughout the sample. Particle size matches that obtained from the Scherrer equation.
Figure 1. X-ray diffraction pattern of HfO$_2$: Eu$^{3+}$ (3%).

Figure 2. SEM micrography of HfO$_2$.

Figure 3 shows characteristic X-ray spectrum of HfO$_2$: Eu$^{3+}$ (3%), where peaks associated with different elements can not be observed. No elements different from constitute HfO$_2$:Eu$^{3+}$ are seen.

Figure 4 shows emission spectra obtained from photoluminescent analysis was carried out at room temperature in samples with different concentrations of Eu$^{3+}$, in order to determine higher luminescent intensity. Material was excite a wavelength of $\lambda=396$ nm, where spectra show emission bands correspondent to trivalent europium in the yellow-orange (550 nm to 670 nm) and violet (700 nm) regions. Sample with highest luminescent intensity is doped with Eu$^{3+}$ (3%), with a decrease in intensity for higher values due to quenching by concentration.

Once concentration of dopant has highest luminescent intensity was determined, [HfO$_2$:Eu$^{3+}$(3%)], luminescent analysis was carried out as a function of temperature. Figure 5 show luminescent emission spectra of HfO$_2$:3%Eu$^{3+}$ at temperatures in range from -30 to 50°C, where appear bands corresponding to electronic transitions $^5\text{D}_0 \rightarrow ^7\text{F}_1$ centered at $\approx592$ nm and transition $^5\text{D}_0 \rightarrow ^7\text{F}_2$, centered at $\approx 614$ nm. Last transition presents a higher luminescent intensity, with a strong dependence on temperature, due to changes in electrons between these energy levels, driven by changes in temperature. This means, if transition $^5\text{D}_1$ increase electronic transitions with temperature is to be expected transition to $^5\text{D}_0$ decrease electronic transitions in equal proportion, in other words, exist a dependency between luminescent intensity and changes of temperature in levels thermally coupled.
Figure 4. Photoluminescent emission spectra of HfO$_2$:Eu$^{3+}$ at different Eu$^{3+}$ concentrations

Figure 5. Emission spectra of HfO$_2$: Eu$^{3+}$ (3%) as a function of temperature

For to use of luminescent emission in measurement of temperature, is necessary to obtain calibration curves, in other words, a curve allows to know temperature value associated with luminescent intensity. This calibration curve (Figure 6) was obtained in temperature range from -30 to 50°C, using curves obtained in $^5$D$_0 \rightarrow ^7$F$_2$ transition centered at 614 nm (Figure 5), which showed highest luminescent intensity. Figure 7 shows calibration curve focusing only at interval of 0 to 50°C, where a linear trend was observed. This straight line was adjusted to equation given by $y = -1465.9x + 401117$ with a correlation coefficient of $R^2 = 0.9984$.

Figure 6. Calibration curve for $^5$D$_0 \rightarrow ^7$F$_2$ transition in range from -30 to 50°C

Figure 7. Calibration Curve with linear approximation, in range from 0 to 50°C

4. Conclusions
Analysis photoluminescent as a function of temperature showed use of hafnium oxide doped with Eu$^{3+}$ presents two thermally coupled electronic transitions, $^5$D$_0 \rightarrow ^3$F$_1$ and $^5$D$_0 \rightarrow ^7$F$_2$, which can be used for temperature determination, being the transition $^5$D$_0 \rightarrow ^7$F$_2$ which showed highest intensity to changes of temperature. After heating and cooling the luminescent material several times, it showed always same results. A calibration curve was obtained from luminescent intensity in function of temperature spectra, in a range from 0 to 50 °C, shown a linear behavior, which is adjusted to equation $Y = (401117)X -1465.9$, where dependent variable corresponds to luminescent intensity and independent variable to temperature. Thereby, we can consider HfO$_2$: Eu$^{3+}$ (3%) is a candidate for development of nanoluminescent thermometer.
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