

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/23276164>

# HfO<sub>2</sub>:X (X = Eu<sup>3+</sup>, Ce<sup>3+</sup>, Y<sup>3+</sup>) Sol Gel Powders for Ultradense Scintillating Materials

ARTICLE in THE JOURNAL OF PHYSICAL CHEMISTRY A · OCTOBER 2008

Impact Factor: 2.69 · DOI: 10.1021/jp803339n · Source: PubMed

CITATIONS

14

READS

46

4 AUTHORS, INCLUDING:



**Maricela Villanueva**

Universidad Politécnica de Pachuca

20 PUBLICATIONS 161 CITATIONS

SEE PROFILE



**A. Pillonnet**

Claude Bernard University Lyon 1

53 PUBLICATIONS 380 CITATIONS

SEE PROFILE



**Christophe Dujardin**

Claude Bernard University Lyon 1

234 PUBLICATIONS 2,915 CITATIONS

SEE PROFILE

Article

## HfO:X (X = Eu, Ce, Y) Sol Gel Powders for Ultradense Scintillating Materials

C. LeLuyer, M. Villanueva-Ibanez, A. Pillonnet, and C. Dujardin

*J. Phys. Chem. A*, **2008**, 112 (41), 10152-10155 • DOI: 10.1021/jp803339n • Publication Date (Web): 24 September 2008

Downloaded from <http://pubs.acs.org> on February 20, 2009

### More About This Article

Additional resources and features associated with this article are available within the HTML version:

- Supporting Information
- Access to high resolution figures
- Links to articles and content related to this article
- Copyright permission to reproduce figures and/or text from this article

[View the Full Text HTML](#)



ACS Publications  
High quality. High impact.

The Journal of Physical Chemistry A is published by the American Chemical Society, 1155 Sixteenth Street N.W., Washington, DC 20036

# HfO<sub>2</sub>:X (X = Eu<sup>3+</sup>, Ce<sup>3+</sup>, Y<sup>3+</sup>) Sol Gel Powders for Ultradense Scintillating Materials

C. LeLuyer, M. Villanueva-Ibañez, A. Pillonnet, and C. Dujardin\*

LPCML CNRS UMR 5620, Université Claude Bernard Lyon I, 10 rue A. M. Ampère,  
F-69622 Villeurbanne Cedex, France

Received: April 17, 2008; Revised Manuscript Received: June 9, 2008

Hafnium dioxide (HfO<sub>2</sub>) presents a high crystalline density which makes it attractive for host lattice activated by rare earths for applications as scintillating materials. HfO<sub>2</sub> powders doped with Eu<sup>3+</sup> or Ce<sup>3+</sup> luminescent ions are prepared by sol gel process. The annealing temperature and the concentration of doping ions are optimized to provide the powder presenting the best scintillation yield. The powders are crystallized in monoclinic phase whatever annealing temperature above 800 °C. The emission spectra are characterized by a white broadband between 400 and 600 nm. After optimization, the most efficient composition, namely HfO<sub>2</sub>:2.5% Eu 1% Y (molar percent) exhibits a scintillation yield about 31 000 photons/MeV, which is about 3.8 times that of the standard Bi<sub>3</sub>Ge<sub>5</sub>O<sub>12</sub> (BGO) commercial powder.

## 1. Introduction

Nowadays, new inorganic scintillating materials are studied for various applications. The primary requirements of scintillating materials are high density and high effective atomic number linked to high atomic numbers of its constituents. The sol gel process has proved to be very efficient to synthesize such pure and homogeneous materials doped on a molecular scale like powders and thin films for scintillation applications. For instance, sol gel Gd<sub>2</sub>O<sub>3</sub> and Lu<sub>2</sub>O<sub>3</sub> powders and films doped with Eu<sup>3+</sup> ions have already been successfully obtained with very high optical quality and with high scintillating performance for X-ray imaging.<sup>1,2</sup> HfO<sub>2</sub> presents interesting physical and chemical properties. It is widely used in optical fields because of its high refractive index<sup>2</sup> and low optical losses and scatter in the near UV (below 300 nm) and IR (10 μm) regions. The high density of HfO<sub>2</sub> (with atom number of 72), 9.68 g/cm<sup>3</sup>, makes it an attractive host for heavy scintillators.<sup>3</sup> The undoped HfO<sub>2</sub> lattice has already been studied by Kirm et al. who has proved the high X-ray absorption efficiency of the materials.<sup>4</sup> Various studies only dealing with luminescence properties of rare earth doped HfO<sub>2</sub> have also been reviewed.<sup>5,6</sup> Moreover, effective scintillating properties can be expected after doping HfO<sub>2</sub> with luminescent ions. More particularly, Eu<sup>3+</sup> ions are considered to be very efficient luminescent centers emitting in red (f–f radiative transitions) and Ce<sup>3+</sup> is well-known for its fast d–f emission. In this paper, the attractive physical properties of HfO<sub>2</sub> materials are exploited and combined with the luminescence properties of Eu and Ce ions to produce highly performing sol gel scintillators. The aim of this work is to determine the required doping concentration and the best thermal treatment to optimize the powders in terms of scintillation properties. Structural and optical analyses are performed on each sample to determine the most efficient composition.

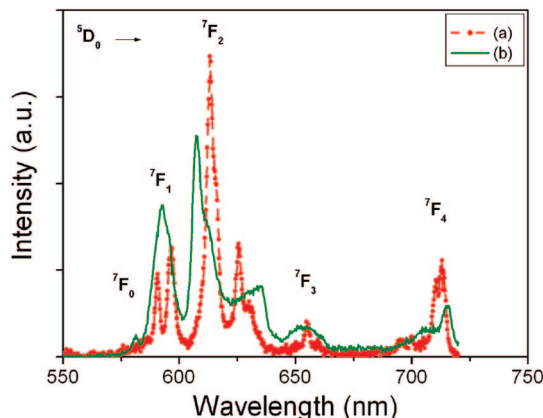
## 2. Sol Gel Elaboration

The powders are elaborated using the sol gel process because it is an excellent option to prepare high purity materials by drying the solution. Starting materials to prepare the solution

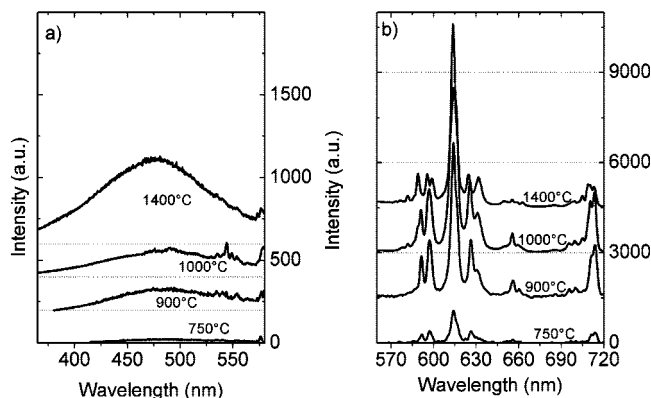
are hafnium tetra-ethoxide (Hf(OC<sub>2</sub>H<sub>5</sub>)<sub>4</sub>). The sol gel technique to elaborate the hafnia solution is described in detail in ref 8. Briefly, (Hf(OC<sub>2</sub>H<sub>5</sub>)<sub>4</sub>) is dissolved in ethanol. A solution of acetylacetonate (acac) and ethanol is added with a Hf(OC<sub>2</sub>H<sub>5</sub>)<sub>4</sub>/acac = 1 mol ratio to chemically stabilize the alcoxide. The doping ions are introduced as nitrates salts after the hydrolysis of the solution in different proportions (mole percent). The powders are obtained by slowly drying the solution for 24 h at 100 °C and are heat-treated during 4 h at different temperatures from 600 up to 1400 °C under oxygen ambient atmosphere. Fourier transform infrared spectroscopy (FTIR 2000, Perkin-Elmer) analyses of powders are carried out between 4000 and 500 cm<sup>-1</sup> to determine the thermal decomposition of the material and the temperature of crystallization. For all prepared compounds, the FTIR spectra (not presented here) corresponding to the doped HfO<sub>2</sub> powders heat-treated between 600 and 1000 °C to indicate that the organic compounds are completely eliminated at 900 °C. The crystallization of the samples characterized by the bands located between 410 and 770 cm<sup>-1</sup> begins at 600 °C.<sup>9</sup>

The X-ray diffraction patterns (XRD) of powders are collected on a Siemens D500 X-ray diffractometer with Cu K radiation. The crystallites size is deduced from XRD data by using the Debye–Scherrer formula.<sup>9</sup> Thermogravimetric analyses experiments (TGA) have been performed in a SETARAM Tag 24 balance upon 20 mg of powder. Heating up to 1200 °C and cooling have been made at a rate of 2 °C/min under a flow of pure oxygen. For X-ray emission spectra measurements, an X-ray generator (XRD3000 INEL) is operated at 35 kV with a tungsten anode. The signal is detected using a monochromator triax 320 with a CCD detector. The different powders are pressed into a 10 mm diameter and 1 mm thick pellet. All measurements are conducted at room temperature in the same excitation and detection conditions. The scintillation yield is compared to a pellet of a standard Bi<sub>3</sub>Ge<sub>5</sub>O<sub>12</sub> (BGO) commercial powders for which the measured scintillation yield is 8000 photons/MeV. Such a protocol provides a good estimation of the scintillating properties as it was extensively done in refs 10 and 11.

\* Corresponding author. E-mail: dujardin@pcml.univ-lyon1.fr. Tel.: +33 4 72 43 12 08. Fax number: +33 4 72 43 11 30.



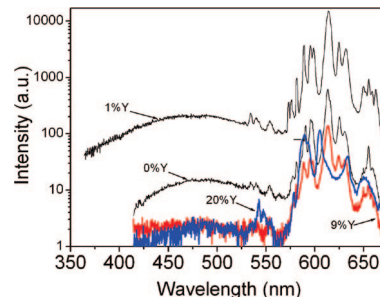
**Figure 1.** Room temperature emission spectra under X-ray excitation of (a) monoclinic HfO<sub>2</sub>:Eu (1% mol) and (b) tetragonal HfO<sub>2</sub>:Eu (25% mol) powders annealed at 900 °C.



**Figure 2.** Emission intensity under X-ray excitation of HfO<sub>2</sub>:Eu(1% mol) powder heat-treated at different temperatures under air: 750, 900, 1000, and 1400 °C. The measurements are performed at room temperature. The wavelength scale is adapted for the broad band (a) and the lines (b).

### 3. Results and Discussion

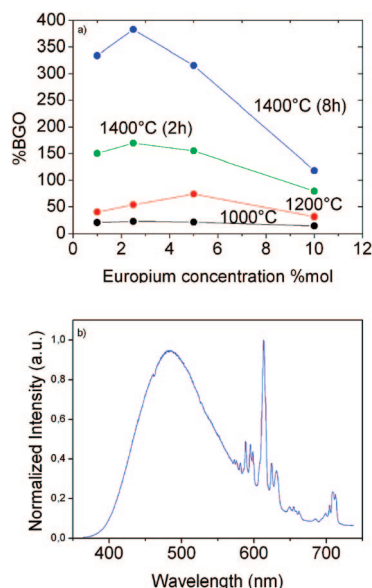
**3.1. Scintillating and Structural Properties of Eu Doped HfO<sub>2</sub> Powders.** The analysis of Eu doped HfO<sub>2</sub> indicates that the crystallization in the monoclinic or quadratric phase depends on the Eu concentration in HfO<sub>2</sub> powders. The Eu<sup>3+</sup> ions can then be used as structural probes because of its luminescent properties. The red emission spectra under X-ray excitation corresponding to the <sup>5</sup>D<sub>0</sub>–<sup>7</sup>F<sub>j</sub> transitions and characteristic to luminescence of Eu<sup>3+</sup> ions in the monoclinic and tetragonal phases are presented in Figure 1.<sup>7</sup> These results will be used in the following to simultaneously check the sample phase and the scintillating properties. Figure 2 exhibits the emission spectra of HfO<sub>2</sub>:1% Eu sample annealed at different temperatures. The powder crystallizes in the monoclinic phase after a 750 °C heat treatment. Since the experiment has been performed in the same condition of excitation and collection of light, the relative yield can be compared. The red emission in the 570–720 nm range shows a significant increase of the intensity (nearly a factor of 10) when the thermal treatment is performed from 750 to 1000 °C. It does not change significantly for thermal treatment up to 1400 °C. Two additional lines appear at 595.2 and 598.6 nm in the emission spectra for the 1400 °C treated sample. These lines are not attributed to the tetragonal phase because the XRD measurement of this sample shows pure monoclinic phase (in the limit of the XRD detection). The assignment of these lines still remains unknown. Surprisingly, an extremely broad white emission band ranging from 360 to



**Figure 3.** Emission intensity under X-ray excitation of HfO<sub>2</sub>:Eu(1% mol) codoped with 1%, 9%, and 20% of Y powders and treated 2 h at 1000 °C. The measurements are performed at room temperature.

about 600 nm appears and its intensity (area under the emission spectra) becomes more important to the red emission one when the annealing temperature increases. For powders annealed at 1400 °C, the decay times are measured under 308 nm excitation at 9.5 μs for white band emission and at 1 ms for Eu<sup>3+</sup> red emission. The formation of Eu<sup>2+</sup> when high thermal treatment is applied could partially explain the broad emission band because the substitution site state is 4+. Moreover, interstitial sites containing Eu<sup>2+</sup> could also be created. However, if the heat treatment changes the ratio of Eu ions from 3+ to 2+ states, the evolution of the yields ratio between the red lines area and the white broadband emission should be anticorrelated. The decrease of the Eu<sup>3+</sup> red emission in respect with the increase of the white broadband emission is not observed, which suggests that the origin of the broad emission band is multiple. Structural changes like crystallinity and the formation of defects associated species could also be considered. Although the origin of this emission is not clearly established, we focused our attention to the optimization of its intensity in terms of thermal treatment and Eu concentration. Doping with Y<sup>3+</sup> is proposed to enhance the 3+ state of Eu ions in HfO<sub>2</sub> lattice. Moreover, Y doping is known to stabilize the crystalline phase at high temperature.<sup>7</sup> The emission spectra of HfO<sub>2</sub>:1% Eu:Y powders heat-treated at 1000 °C are presented on Figure 3 for various Y concentrations. The comparison of the amplitude points out a significant enhancement by adding 1% of Y (a factor of 14 more light as compared to the sample without Y). At 9%, the intensity decreases, and at 20% of Y, some typical emission lines of the Eu<sup>3+</sup> in HfO<sub>2</sub> tetragonal phase appear. It must be noted that the broad white emission band is present whatever Y concentrations. On the basis of this result, the optimization of europium concentration and thermal treatments are performed on the HfO<sub>2</sub>:1% Y. The results are presented in Figure 4. Each value corresponds to the calculated area under the emission spectra compared to the area under the emission spectra of a BGO pellet. The best sample corresponding to the composition HfO<sub>2</sub>:1% Y 2.5% Eu and heat-treated 8 h at 1400 °C (no longer time has been tested) exhibits a yield of 30 000–31 000 photons/MeV which is about 3.8 times that of BGO.

**3.2. Scintillating and Structural Properties of Ce Doped HfO<sub>2</sub> Powders.** In the case of cerium doped samples, the spectroscopic behavior is not very characteristic of the sample phase. In this case, X-ray diffraction measurements have been systematically carried out to determine the structural phase of the powders. The phase remains pure monoclinic (JCPDS 43-1017) whatever the annealing temperature from 600 up to 1400 °C. The spectra are similar to those observed in a monoclinic HfO<sub>2</sub>:Eu<sup>3+</sup> sample<sup>7</sup> and are then not presented. A diffraction lines narrowing observed with increasing temperature indicated a crystallites growth. The crystallites sizes deduced using the



**Figure 4.** (a) Comparative scintillation yield measured under X-ray excitation (as compared to BGO) of HfO<sub>2</sub>:Eu 1% Y powder heat-treated at different temperatures. Each value corresponds to the area under the emission spectrum. The measurements are performed at room temperature. (b) Emission spectrum of the best sample containing Y (1% mol) and Eu (2.5% mol) and treated during 8 h at 1400 °C.

**TABLE 1: Crystallite Size Evolution of HfO<sub>2</sub>:Ce (1% mol) Sol Gel Powder, Deduced from X-ray Diffraction Data Using the Debye–Scherrer Formula**

temperature (°C)	crystallite size (nm)
800	29 ± 1
900	32 ± 2
1000	39 ± 2
1200	50 ± 3
1400	79 ± 4

Debye–Scherrer formula are reported in Table 1. As the temperature increases, the crystallites sizes increase from 29 ± 1 nm at 800 °C up to 79 ± 4 nm at 1400 °C. In order to optimize the cerium doped HfO<sub>2</sub> powder, various concentrations and thermal treatment have been performed and compared to a BGO pellet. Cerium activators have to be in the 3+ state to exhibit the required optical properties. The oxidation state of cerium ions in the HfO<sub>2</sub> lattice depends on ionic environment. The Ce<sup>4+</sup> form is in principle preferential and stable in HfO<sub>2</sub> lattice and will probably substitute to Hf<sup>4+</sup> ions. This small tetravalent ion would prefer eight-coordination as exposed by Orera et al.<sup>13</sup> TGA experiments (not presented here) are performed on powders in order to determine the evolution of cerium ions oxidation state depending on the heat treatment by studying the cerium ions oxido-reduction process (i.e., the variation of oxygen stoichiometry). Measurements are conducted on a high concentrated cerium (30% mol) doped HfO<sub>2</sub> sol gel powder and on a commercial CeO<sub>2</sub> powder. As the temperature increases, two mass changes are observed on the CeO<sub>2</sub> powder. The first weight loss around 200 °C is assigned to the elimination of all volatile compounds and the second weight loss which appears above 900 °C leads to the reduction process of cerium.<sup>12</sup> A similar weight loss phenomenon is observed on the cerium doped sol gel powder. As the temperature decreases, no significant mass change is observed, indicating that the 3+ valence state of cerium ions remains stable after cooling down the sample. Furthermore, the CeO<sub>2</sub> powder presents a yellow coloration when heat-treated at 800 °C whatever the Ce

concentration. A complete discoloration of powders is observed after heating in air above 1200 °C. The yellow color is characteristic of Ce<sup>4+</sup> ions<sup>13</sup> and the presence of a majority of Ce<sup>3+</sup> lies to a white color of the powder. In fact, the coloration change of the Ce : HfO<sub>2</sub> sol gel powder, induced by thermal treatment, confirms the reduction of Ce<sup>4+</sup> to Ce<sup>3+</sup> and the stability of ions three valence during sample cooling.<sup>14</sup> According to TGA measurements, the thermochemical and irreversible Ce<sup>4+</sup>–Ce<sup>3+</sup> reduction is performed at temperature above 1200 °C. The formation of preferential Ce<sup>3+</sup> form could be explained by the presence of perturbed network or defects related for example to oxygen vacancies generated at high annealing temperature. Under X-ray excitation, the cerium doped material exhibits a broad emission band peaking around 480 nm.

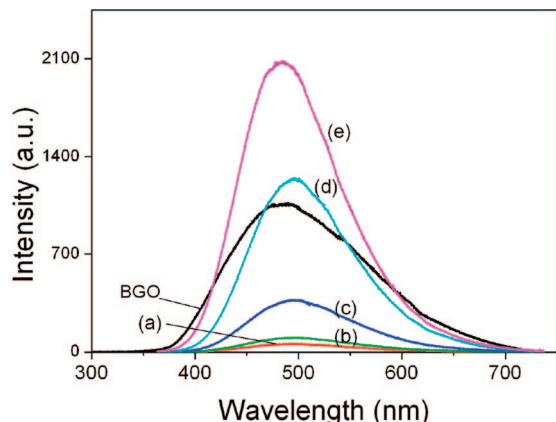
This result looks different than the emission peaking at 420 observed in ref 20. Nevertheless, in this patent, a mixture of pure HfO<sub>2</sub> with substantially pure Y<sub>2</sub>O<sub>3</sub> in a HfO<sub>2</sub>:Y<sub>2</sub>O<sub>3</sub> ratio of 3:1 has been prepared for cathodoluminescence applications and the final resulting phase is cubic material, which is not the case of our samples. More recently, García-Hipólito et al.<sup>21</sup> have prepared HfO<sub>2</sub>:CeCl<sub>3</sub> layers using spray pyrolysis method and have observed a blue–violet luminescence assigned to the traditional Ce<sup>3+</sup> 5d–4f luminescence. Besides, their analyses have indicated that the samples were containing a significant amount of Cl. Since the doping process has been performed using CeCl<sub>3</sub>, it can then be suspected that Ce<sup>3+</sup> is in a different environment close to a Cl ion. Since the 5d orbitals are extremely sensitive to the crystal field, this environment might be more favorable to the luminescence compared to the other nonradiative processes such as the autoionization process. It can thus be suspected that cerium was not properly incorporated in our sample. Nevertheless, several arguments discard this hypothesis. First, the same precursor salt used for Eu doped samples has been used for cerium doping, and it has been clearly shown that Eu ions were incorporated into the oxide lattice. There is then no chemical reason that the same doping procedure is not appropriate in case of cerium. Second, the scintillation yield clearly depends on the Ce contents, and this could not be explained if cerium was not present in the host. Finally, the TGA experiments as well as the color changed observed with thermal treatments obviously indicate that cerium ions have been properly incorporated.

In terms of scintillation yield, an optimum of concentration around 1% mol provides a yield about 180% of BGO measured in the same optical conditions. It is then clear that this luminescence is correlated to cerium. Nevertheless the measured decay time under 308 nm excitation is 7.7 s, and this value is too long to correspond to the 5d–4f emission band of Ce<sup>3+</sup> ions. Figure 5 presents the evolution of the emission spectra intensity under X-ray excitation for Ce (1% mol) doped HfO<sub>2</sub> sol gel powder annealed at different temperatures between 800 and 1400 °C. The shape of the emission band does not change with the thermal treatment. We observed that the emission intensities of sol gel powders increase with annealing temperature and become superior than BGO above 1200 °C. The best scintillating performance is observed after a heat-treatment at 1400 °C like the Eu doped sample.

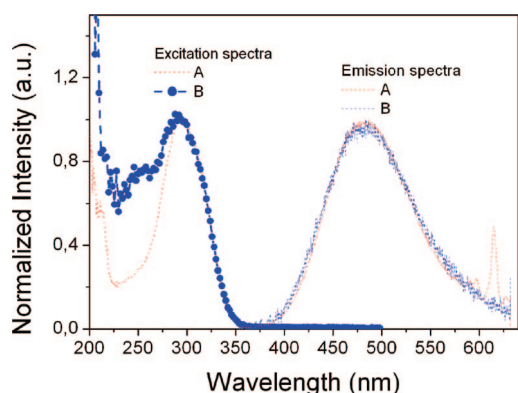
#### 4. Discussion

Similar broad bands emissions are observed for both Eu and Ce activated HfO<sub>2</sub> powders. In the case of Eu doped samples, this emission could be mainly connected to the 2+ state of Eu which exhibits broad 4f<sup>5</sup>5d–4f<sup>6</sup> fluorescence band. The observed decay time matches well with the order of magnitude observed for Eu<sup>2+</sup>.<sup>15</sup>





**Figure 5.** Comparison of the emission spectra under X-ray excitation of HfO<sub>2</sub>:Ce (1% mol) pellets annealed at different temperature compared to BGO pellets: (a) 800, (b) 900, (c) 1000, (d) 1200, and (e) 1400 °C.



**Figure 6.** Emission (under 290 nm excitation) and excitation (for 550 nm emission) spectra of white broad band for (A) HfO<sub>2</sub>:Y (1% mol):Eu (5% mol) and (B) HfO<sub>2</sub>:Ce (5% mol) powders heat-treated at 1400 °C.

In the case of the Ce doped sample, the emission band could correspond to the well-known 5d–4f emission band except that the decay time is too long for such transition. A charge transfer emission band can then be assumed, as observed in Sr<sub>2</sub>CeO<sub>4</sub> compounds.<sup>15</sup> Nevertheless, Figure 6 shows the comparison of the luminescence properties of the white band emission observed in HfO<sub>2</sub>:1% Y 2.5% Eu and HfO<sub>2</sub>:5% Ce powders heat-treated at 1400 °C, and surprisingly, the emission spectra under 290 nm excitation and the excitation band (300 nm) of the 550 nm emission have exactly the same shape. In addition, the measured decay times of all the samples are in the same order of magnitude. We can exclude then that the origin of the luminescence is due to the electronic states of the activator. It cannot also be assigned to intrinsic emission such as free exciton since the gap is too far from the blue (5.55 eV).<sup>18</sup> On the other hand it has been observed in ref 19, that undoped HfO<sub>2</sub>/SiO<sub>2</sub> thin films dedicated from a VUV mirror exhibit luminescence under ionizing radiation. Taking into account of the cutoff filter and the interferences due to the layer structure of their materials, a similar shape of emission spectra from our measurement and their measurement is observed. Their films are either contaminated or the emission is intrinsic to some defects. Nevertheless, it is clear from our data that the yield of the emission depends on the doping ion concentration whatever cerium or europium. A kind of impurity induced defect can then be assumed. The origin of the luminescence is not yet clearly established and further experiments such as Electron Paramagnetic Resonance (EPR) are in progress to figure out the nature of the emitting center.

## 5. Conclusion

We have synthesized different HfO<sub>2</sub> based sol gel powders at different annealing temperatures. The best scintillation efficiency is obtained on a sol gel powder doped with 1% Y and 2.5% Eu and heat-treated at 1400 °C which presents a scintillation yield (white broad emission band between 400 and 700 nm plus red lines) almost 3.8 times stronger than BGO. The corresponding decay time is 9.5 μs. In the Ce doped sample annealed at 1400 °C, the same emission band is observed but the origin of this emission band need further investigations to be clearly explained. Nevertheless, the high scintillation yield makes this composition very attractive for scintillation applications such as X-ray imaging or homeland security for which high density and high luminosity are the main criterion. In the last application, the use of the optimized compositions will depend on the possibility to obtain transparent forms such as large single crystals or transparent ceramics. Moreover, the broad spectral range of emission allows us to consider these compositions for white phosphors applications.

**Acknowledgment.** The authors are grateful to the CONACyT-SFERE Program 2001 for the mexican scholarship for M.V.-I. They thank Pr. S. Parola and Dr. G. Chadeyron for fruitful discussions.

## References and Notes

- (1) Garcia-Murillo, A.; LeLuyer, C.; Dujardin, C.; Martin, T.; Garapon, C.; Pedrini, C.; Mugnier, J. *Nucl. Instrum. Methods Phys. Res.* **2002**, A 486, 181.
- (2) Mansuy, C.; Nedelec, J. M.; Dujardin, C.; Mahiou, R. *Opt. Mater.* **2007**, 29, 697–702.
- (3) Van Eijk, C. W. E. *Nucl. Instrum. Methods* **2001**, A 460, 1.
- (4) Kirm, M.; Aarik, J.; Jürgens, M.; Sildos, I. *Nucl. Instrum. Methods Phys. Res.* **2005**, A 537, 251.
- (5) Kelsey, V. P., Jr. Yb Activated Hafnium Oxide Phosphor and Methods, US Patent 4006097, 1977.
- (6) Schipper, W. J.; Piet, J. J.; DeJager, H. J.; Blasse, G. *Mater. Res. Bull.* **1994**, 29, 23.
- (7) Villanueva-Ibanez, M.; LeLuyer, C.; Dujardin, C.; Mugnier, J. *Mater. Sci. Eng.* **2003**, B105, 12.
- (8) Villanueva-Ibanez, M.; LeLuyer, C.; Marty, O.; Mugnier, J. *Opt. Mater.* **2003**, 24, 51.
- (9) Villanueva-Ibanez, M. Hfo<sub>2</sub> SrHfO<sub>3</sub> Dopés Terres Rares Réalisés par le Procédé Sol-Gel: Analyses Structurales, Propriétés Optiques et Potentialités en Scintillatiox. Ph. D. Thesis Université Lyon1, 2005.
- (10) Derenzo, S. E.; Moses, W. W.; Cahoon, J. L.; Perera, R. C. C.; Litton, J. E. *Nucl. Sci., IEEE Trans.* **1990**, 37 (2), 203–208.
- (11) Derenzo, S. E.; Moses, W. W.; Cahoon, J. L.; Perera, R. C. C.; Litton, J. E. *Prospects for New Inorganic Scintillators*, *IEEE Trans. Nucl. Sci.* Vol. NS-37, pp 203–208, 1990.
- (12) Yi, K. Ceria-Zirconia Oxide High Temperature Desulphurization. Ph. D. Thesis, Louisiana State University, 2004.
- (13) Orera, V. M.; Merino, R. I.; Peña, F. *Solid State Ionics* **1994**, 72, 224.
- (14) Blasse, G.; Grabmaier, B. C. *Luminescent Materials*; Springer-Verlag: Berlin Heidelberg, 1994.
- (15) van Peterson, L.; Sovarna, S.; Meijerink, A. *J. Electrochem. Soc.* **2000**, 147, 4688.
- (16) Minardi, A.; Garapon, C.; Mugnier, J.; Champeaux, C. *Lumin. Mater. Symp. Mater. Res. Soc. Proc.* **2001**, 667, G3.10.1G3.10.6.
- (17) Ledoux, G.; Mercier, B.; Louis, C.; Dujardin, C.; Tillement, O.; Perriat, P. *Radiat. Meas.* **2004**, 38, 763.
- (18) Goldburg, E. T.; Kulkarni, B.; Bhargava, R. N.; Taylor, J.; Libera, M. J. *Lumin.* **1997**, 72–74, 190.
- (19) Aarik, J.; Mändar, H.; Kirm, M.; Pung, L. *Thin Solids Films* **2004**, 466, 41–47.
- (20) Begon, C.; Rigneault, H.; Albrand, G.; Bois, E.; Nuti, D.; Sermet, F. *Appl. Opt.* **1999**, 38, 5458–5463.
- (21) García-Hipólito, M.; Caldiño, U.; Alvarez-Fragoso, O.; Alvarez-Pérez, M. A.; Martínez-Martínez, R.; Falcony, C. *Phys. Stat. Solid. a* **2007**, 204, 2355–2361.
- (22) Klein, P. H.; Addamiano, A.; Allen, R. Luminescent Hafnia Composition, US Patent 4,295,989, 1981.