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Review Article

Sol-Gel Processing of Nanostructured Inorganic Scintillating Materials

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The development of scintillating materials is believed to reach a new step by controlling their preparation on a nanometric level. Sol-Gel chemistry offers very unique tools for nanoscale mastering of the materials preparation. In particular, shaping of the materials as thin films or nanoparticles offers new application in medical imaging. The control of doping ions dispersion thanks to soft chemistry is also a great advantage of such synthetic routes. In this paper, we will review recent work devoted to the sol-gel preparation of inorganic scintillating materials. We will focus on the new possibilities and advantages offered by sol-gel chemistry for the preparation of new scintillators and improvement of existing ones.

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1. INTRODUCTION

Since the discovery of X-ray by Röntgen and the concomitant use of the first scintillator, research directed towards materials that can convert high-energy radiations (X-rays, γ -rays, neutrons) into UV-visible light, easily detectable with conventional detectors, is in constant development [1–7]. These materials spread over various applications such as medical imaging, high energy physics, and nondestructive testing (airport security, industrial control, etc.).

During the past twenty years, numerous materials have been proposed to be used as scintillators. Among them, a lot of oxides materials have successfully been developed up to industrial applications. In order to provide efficient scintillators for X or γ rays, the choice of the oxide matrix is crucial. Since the first step of the scintillation mechanism involves absorption of high-energy photon (from a few KeV to several MeV), photoelectrical effect has to be favored. To do so, materials with high $\rho \cdot Z_{\text{eff}}^4$ are required. In this formulation, ρ is the density of the material and Z_{eff} is the effective atomic number defined as [8]

$$Z_{\text{eff}}^4 = \sum_i w_i Z_i^4, \quad (1)$$

where w_i is the mass fraction of atom i and Z_i is its atomic number. More recently, research focused more on improving the performances of known scintillators rather than de-

veloping new materials. It appears that a good way to improve scintillators is to get a control of the material on a nanometric scale. It is indeed very important to control the dispersion of doping ions in the matrix and to control the size of the grains in case of powders. The possibility to prepare nanocrystals could allow the preparation of transparent ceramics that could replace advantageously single crystals. Another very attractive solution is the direct preparation of scintillating thin films. Thin scintillating films are particularly valuable in fundamental spectroscopic studies when the absorption coefficient of the material is high or when the excitation energy is close to the absorption edge. They are also very interesting for high-resolution imaging where the scintillator is required as a homogeneous coating. Both solutions provide low-cost substitutions for single crystals. The use of sol-gel processes for the preparation of scintillating materials seems to be a very interesting way to reach these objectives. In effect, the use of molecular precursors is the guarantee of very high chemical homogeneity which is usually also observed in the final material. Furthermore, the high versatility of the sol-gel process allows to reach various compositions and to vary the nature and the concentration of the doping ion easily. This cannot be usually done for single crystal growth. Even if sol-gel chemistry appears to be a valuable way to prepare new scintillators and scintillators with enhanced properties, not so many works propose such an approach. This paper tries to summarize the state-of-the-art on sol-gel processing

of scintillating materials and in particular scintillating thin films. Only crystalline materials will be considered, obviously sol-gel process is also very valuable for amorphous materials like glasses and hybrid materials incorporating organic molecules. Because this point will not be developed in the following, we would like to list the main tendencies.

Sol-Gel chemistry has been initially developed as an alternative route to glasses. Sol-Gel derived glasses in particular doped with Ce^{3+} ions have been considered as scintillating materials; see for instance work from Chiodini et al. [9, 10] or Nogues et al. [11] and references therein. Another interesting possibility is offered by the intrinsic porosity of sol-gel-derived glasses. In this case, the porous glass or gel can be used as a host for active species. If the guest species is organic, the resulting material is an inorganic-organic hybrid material. Depending on the interaction between the two components, class I and class II hybrids can be found [12]. Molecules classically used in liquid scintillators can be embedded in the silica framework [13] and in the case of PPO and POPOP the active molecules can be covalently grafted to the silica network [14]. An important axis concerns the development of cationic complexes mainly of rare-earth ions and their incorporation in inorganic sol-gel-derived networks. A lot of work can be found in the literature including the incorporation of various rare-earth complexes [15], covalently grafted or not and including recently cryptates [16] and podates [17].

2. SOL-GEL PROCESSING OF MATERIALS

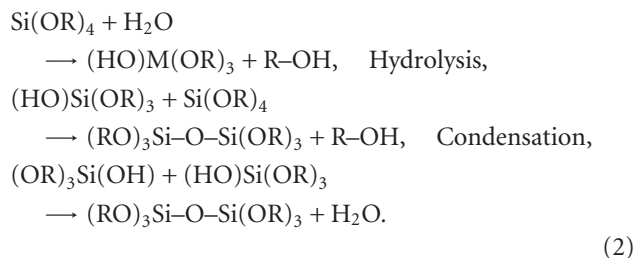
Numerous excellent reviews can be found in the literature concerning the sol-gel processing of materials. In this section, we would like to summarize the main features and to underline the major advantages in the view of producing scintillators.

During the last 30 years, sol-gel processes have been widely used for the preparation of glasses and ceramics. Usually, starting with molecular precursors like alkoxides or acetates, the sol-gel process takes place in solution. This provides definitive homogeneity for multicomponent systems. In the particular case of doping, the sol-gel process provides an ideal way to control the level and the homogeneity of doping. For luminescent materials, this is crucial since the light emission is usually due to doping ions like rare-earth or transition metals ions. Quenching concentrations are usually found higher for sol-gel-derived materials because of better dispersion of doping ions and thus higher average distance between emitting centers. Several authors have also developed heterometallic precursors associating different elements through chemical bonding and thus providing the highest homogeneity [18, 19]. As far as alkoxides chemistry is concerned, it is useful to distinguish the case of silicon alkoxides (Si being a semimetal) and the case of metal alkoxides.

2.1. Silicon alkoxides

The sol-gel process involving silicon alkoxide can be described in two steps, the hydrolysis of the alkoxide and its polycondensation. For a given alkoxide of general formula

$Si(OR)_4$, R being an alkyl chain, these reactions can be written as follows:



Usually, silicon alkoxides are very stable against hydrolysis. Step 1 thus requires catalysis usually performed by using acids or bases. Excellent review can be found in [20]. Briefly, base-catalyzed hydrolysis occurs through an S_N2 mechanism involving a 5-fold coordinated silicon atom. On the other hand, acid catalysis proceeds through a limiting step corresponding to the protonation of an oxygen atom resulting in an S_N1 mechanism. Acidic catalysis leads to a much quicker hydrolysis than basic catalysis resulting in different final structures for the gels networks.

2.2. Metal alkoxides

Contrary to silicon alkoxides, metal alkoxides react very quickly with water in absence of catalysts. In particular, transition metal alkoxides are very reactive because of the presence of highly electronegative OR groups that stabilize the central atom in its highest oxidation state. This in turn makes the metal atom very susceptible to nucleophilic attack. An excellent review presents the chemical reactivity of metal alkoxides [21]. Recently, some controversy appeared with respect to the well-acknowledged mechanism of hydrolysis condensation of metal alkoxides [22] supported for instance by the recently demonstrated impossibility of S_N2 mechanism [23] classically invoked to explain the higher reactivity of metal alkoxides.

In any case, both for silicon and metal alkoxides, the ongoing polycondensation process leads to the formation of a 3D network. The point where this network extends throughout the reactor is described by the percolation theory and named the gel point. The obtained wet gel can be dried in various conditions leading a xerogel with residual porosity. Further heating of the xerogel in controlled conditions allows obtaining the desired glass or ceramic.

Before the gel point, the colloidal solution can be stabilized and used directly to coat various substrates by classical techniques like dip coating, spin coating, laminar induction or spray. This provides a low cost and efficient way to produce nanometric thin films with good homogeneity.

Furthermore, the temperatures required for the full densification and crystallization of the desired glass/ceramic are usually lower than the ones required by classical melting or solid-state processes. This can be interesting from an economical point of view but also because in some cases, the obtained phases can differ from the one obtained by classical procedures. By this way, new phases can be obtained or high-temperature phases can be stabilized at room temperature. In the following sections, we will propose an exhaustive

overview of literature works specifically aiming the developments of scintillating materials by sol-gel chemistry.

3. YTTRIUM AND RARE-EARTH SESQUIOXIDES

Yttrium, lutecium, and gadolinium sesquioxides have been acknowledged as efficient scintillating materials when activated with rare-earth ions.

In 2003, Montes et al. proposed a new sol-gel route to Nd^{3+} doped Y_2O_3 thin films [24]. Authors have used Yttrium and Neodymium nitrates together with coconut water to prepare the sol that has been deposited by dip coating on glass substrates. After annealing at 500°C , the films are crystallized with crystallite size ranging between 17 and 23 nm depending on the densification conditions. The radioluminescence of the films is observed but not quantified.

Gd_2O_3 powders and thin films have been prepared by García-Murillo et al. in 2001 [25] and later by Guo et al. [26]. In the first reference, the authors used gadolinium isopropoxide $\text{Gd}(\text{iOPr})_3$ as precursor and acetylacetone as chelating agent to control hydrolysis/condensation of the very reactive alkoxide. Thin films of good optical quality have been obtained by multistep dip-coating operation on various amorphous substrates. In the second reference, the authors used gadolinium acetate as precursor and diethylenetriamine as complexant. García-Murillo et al. paid particular attention to the material formation by using several complementary techniques like TEM, Raman, and m-lines spectroscopies. Raman spectroscopy performed in the waveguiding configuration [27] allowed a detailed study of crystallization of Gd_2O_3 thin films. The films begin to crystallize around 650°C in the cubic phase and transform partially to the monoclinic phase above 800°C [28].

For scintillation purpose, Eu^{3+} doped films (5%) have been prepared by the same group [29]. Emission spectra were dominated by europium $^5\text{D}_0$ to $^7\text{F}_2$ transition around 611 nm and in agreement with the cubic structure of the gadolinium oxide. Under X-ray excitation, the films showed intense emission (Figure 1) estimated by comparison with $\text{NaI}(\text{Tl})$ with the photopeak method [30]. Lightyield of 18500 photons/MeV was found with an afterglow of 0.1% after 10 milliseconds which remains too high for medical imaging.

Due to its high atomic number, lutecium containing materials have been widely considered for scintillation application. Complex oxides will be described in the following section. Lutecium sesquioxide Lu_2O_3 is isostructural to Gd_2O_3 but presents a much higher density ($8.4 \text{ g}\cdot\text{cm}^{-3}$ instead of $7.1 \text{ g}\cdot\text{cm}^{-3}$). Starting from Lutecium 2,4 pentanedionate in isopropanol, García-Murillo et al. prepared Lu_2O_3 powders and thin films by dip coating [31]. The reported work and results are indeed very similar to the ones reported for Gd_2O_3 . Activation of Lu_2O_3 thin films with Eu^{3+} ions results in good scintillation performances (Figure 1), 19750 photons per MeV under X-ray excitation but still an afterglow of about 0.1% after 10 milliseconds. Codoping with Tb^{3+} ions for instance can reduce this afterglow.

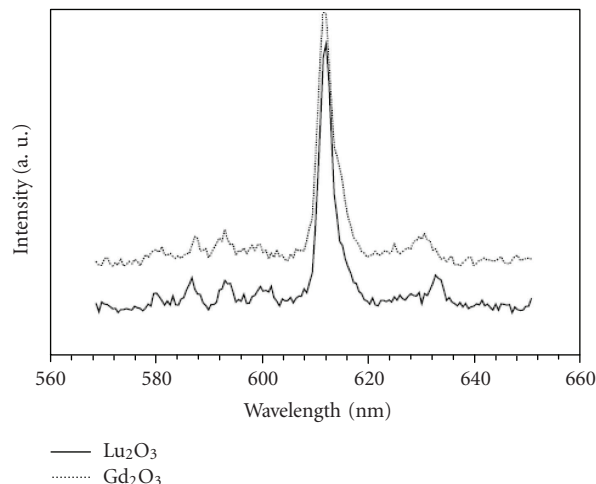


FIGURE 1: Emission of $\text{Gd}_2\text{O}_3 : \text{Eu}^{3+}$ 5% and $\text{Lu}_2\text{O}_3 : \text{Eu}^{3+}$ 5% thin films under X-ray excitation, reproduced from [15] © 2002 with permission from Elsevier.

4. LUTECIUM OXIDES

As stated above, lutecium oxides have received considerable interest to be used as host matrices for scintillators applications. Lutecium oxides are obviously very dense materials and rare-earth substitution can easily be performed in these materials. Among all rare-earth ions, Ce^{3+} occupy a specific situation because of its electronic scheme and the subsequent allowed 5d-4f transitions lying in the UV-visible range (300–500 nm). These transitions are also very fast (20–60 nanoseconds) and very intense.

4.1. Silicates

Cerium-doped lutecium oxyorthosilicate Lu_2SiO_5 is actually used in the detection system of PET scanners. In 2000, Bescher et al. proposed the first sol-gel route to lutecium containing scintillator [32]. At this time, the inorganic phase was not clearly identified and embedded in an amorphous SiO_2 matrix. A few years later, Mansuy et al. proposed the first reported preparation of Lu_2SiO_5 (LSO) by sol-gel chemistry [33]. Due to the very high reactivity and cost of rare earth alkoxides, the authors proposed the in situ preparation of $\text{Lu}(\text{iOPr})_3$ by metathesis reaction between Lutecium chloride and potassium alchoolate. TEOS was used as the silicon precursor. Doping was achieved through the same procedure starting with europium, terbium, or cerium nitrates. The obtained multicomponent sol was stable and could be used to prepare thin films or destabilized to yield powders. Single phase materials were obtained and high scintillation efficiency under X-ray was measured (20 000 photons/MeV). Following this first paper, the same authors proposed a detailed study of rare-earth substitution in LSO using Eu^{3+} ion as a structural probe [34]. Combining X-ray absorption and luminescence spectroscopies, a clear preferential substitution on one of the two Lu sites has been evidenced. This behaviour was already described for Ce^{3+} but the attribution of the sites

was clearly wrong. This is a very nice example of the interest of the sol-gel process both from an applicative point of view (low-cost efficient alternative to single crystals preparation) and from the fundamental point of view (first preparation of Eu^{3+} doped LSO and detailed study of substitution).

Mansuy et al. also evidenced the sol-gel formation of lutecium pyrosilicate $\text{Lu}_2\text{Si}_2\text{O}_7$ [35]. This material has been recently studied for scintillation application and acknowledged as very interesting candidate in particular for medical imaging applications [36, 37].

4.2. Borates

Lutecium orthoborate LuBO_3 is also a good candidate for scintillation applications. Boyer et al. reported the first sol-gel elaboration of LuBO_3 thin films [38]. Using Boron triisopropoxide and Lutecium isopropoxide, the authors prepared amorphous powders and thin films that could be transformed into vaterite LuBO_3 around 700°C . In this first work, only Eu^{3+} doping was considered and was achieved for a single doping concentration. Using the same procedure, Mansuy et al. proposed a systematic study of scintillation properties of LuBO_3 powders and thin films doped with Eu^{3+} , Tb^{3+} , and Ce^{3+} ions with various concentrations.

Ce^{3+} doped LuBO_3 powders showed maximum scintillation yield for 0.5% doping concentration corresponding to a light yield under X-ray of about 8100 photons/MeV equivalent to commercial $\text{Bi}_4\text{Ge}_3\text{O}_{12}$ scintillator [39]. The afterglow was low, 0.2% after 1 second. For Eu^{3+} and Tb^{3+} doping, maximum emission under X-rays was observed for $\text{LuBO}_3 : \text{Eu}^{3+}$ 5% and $\text{LuBO}_3 : \text{Tb}^{3+}$ 5% with light output of 8900 and 4400 photons/MeV, respectively [40].

The evolution of the relative scintillation yield as a function of the doping level is displayed in Figure 2 for $\text{LuBO}_3 : \text{Eu}$, Tb , Ce . The rare-earth-doped LuBO_3 thin films were thoroughly characterized by XPS and RBS techniques demonstrating the good homogeneity of the coatings and an inter diffusion process between the layer and the substrate [41]. Scintillation was clearly evidenced but not quantified because of the inherent difficulty to get quantitative light yield for thin films.

4.3. Aluminates

Lutecium-aluminium garnet, $\text{Lu}_3\text{Al}_5\text{O}_{12}$, has been the subject of various works. Activated with Ce^{3+} ions, it turned to be a very promising scintillating material. Recently, Min et al. proposed a Pechini sol-gel route to Tb^{3+} doped LuAG films [42]. Combining Pechini method and dip coating, LuAG films doped with various concentrations of Tb^{3+} ions were coated onto silicon substrates. Crystalization begins around 900°C and the luminescence properties have been reported but not under high-energy excitation. Liu et al. reported in 2007 the preparation of nanosized cerium-doped LuAG phosphors by a sol-gel combustion process [43]. Aluminium, cerium, and lutecium nitrates were mixed in required proportions together with glycine (fuel). Upon stirring at 60°C , a gel is formed. This gel was then heated at 180°C where an autocombustion process took place. After annealing the final

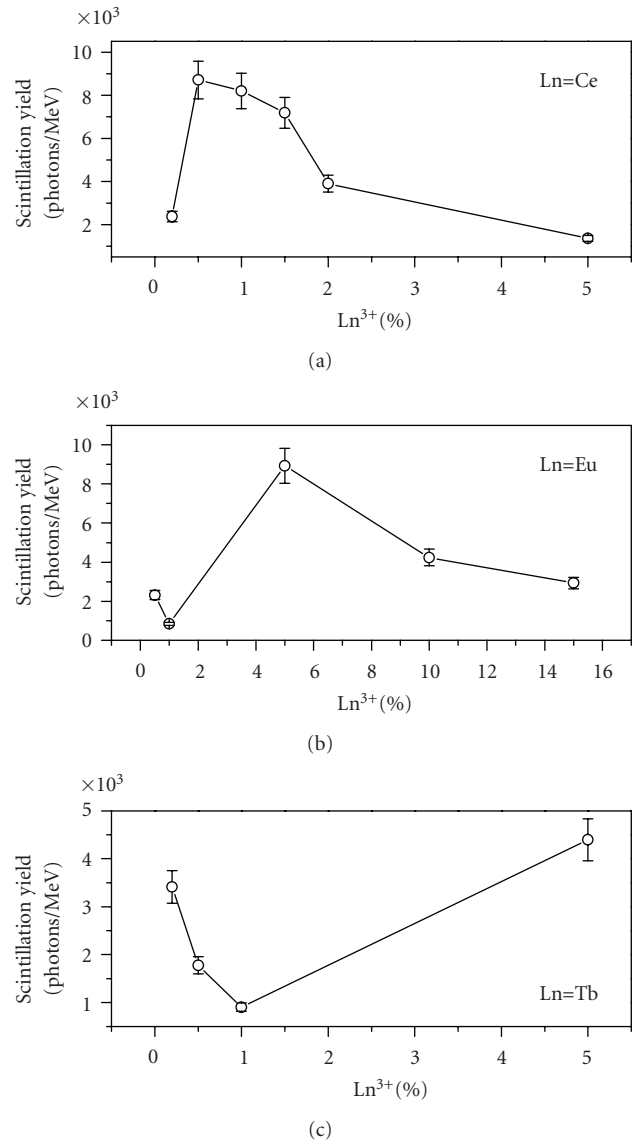


FIGURE 2: Scintillation yield under X-ray excitation for $\text{LuBO}_3 : \text{Ln}^{3+}$ ($\text{Ln} = \text{Ce}, \text{Eu}, \text{Tb}$) as a function of rare-earth concentration.

solid at $800\text{--}1000^\circ\text{C}$, the garnet phase is obtained. The radioluminescence was observed but not quantified.

4.4. Phosphates

Lutecium orthophosphate LuPO_4 is known as an efficient scintillator [44–47]. First, all-alkoxide sol-gel route to orthophosphate was described in 2002 [48]. In this procedure, phosphorous and rare-earth or yttrium oxides are formed in situ by reacting isopropanolate with P_2O_5 and rare-earth chlorides. Following the same procedure, LuPO_4 was prepared as nanometric powder and doped successfully with Eu^{3+} ions up to 5% mol [49]. Successful doping of $(\text{Y}, \text{Lu})\text{PO}_4$ with cations like Eu^{3+} or Ce^{3+} is not evident since EuPO_4 and CePO_4 crystallize in a different crystalline structure (monazite instead of xenotime). Once again, the use of sol-gel

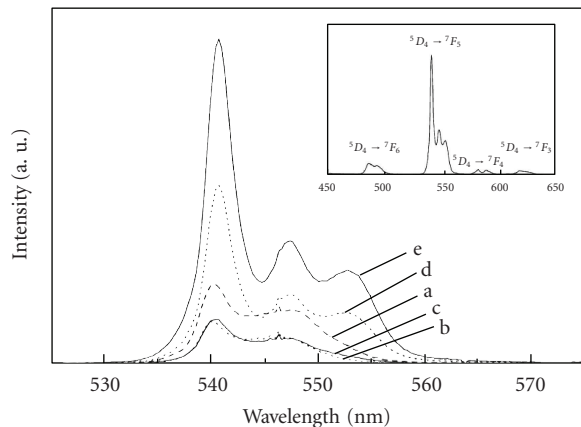


FIGURE 3: Room temperature emission spectra under X-ray excitation of 1% Tb^{3+} doped HfO_2 powders with (a) 0, (b) 1, (c) 4, (d) 9, and (e) 20% Y^{3+} . Reproduced from [34] © 2003 with permission from Elsevier.

process is responsible for the good homogeneity of the materials and the efficient dispersion of doping ions throughout the matrix. LuPO_4 powders doped with Ce^{3+} , Eu^{3+} , and Tb^{3+} ions at various concentrations were prepared and their scintillation properties reported [50].

The optima for scintillation yield were found to be 0.1, 10, and 5%, respectively for Ce^{3+} , Eu^{3+} , and Tb^{3+} (Table 1). An important afterglow was observed that could be limitative for some practical applications.

5. HAFNIUM OXIDES

Due to its rather large band gap and low-phonon energy, hafnia is a suitable host matrix for rare-earth doping. Rare-earth doped HfO_2 and SiO_2 - HfO_2 thin films have been prepared by sol-gel chemistry [51, 52]. In particular, Lange et al. studied Ln-doped HfO_2 thin films (Ln = Sm, Eu, Tb) as potential scintillators [53]. The sol was prepared by reacting Hafnium butoxide in hexane solution, doping was performed by adding rare-earth chlorides. Films were deposited by dip coating on quartz and silicon substrates. Strongly observed photoluminescence suggested an efficient transfer from the host material to the rare-earth ions.

In 2003, Villanueva-Ibañez et al. published a paper reporting the preparation of Yttrium-Hafnium oxide powders by sol-gel chemistry [54]. Yttrium was substituted to Hafnium from 0 to 20% yielding phase transformation and facilitating doping with Tb^{3+} ions (1%). Hafnium ethoxide and Yttrium and Terbium nitrates were mixed in ethanol in the presence of acetylacetonone. The xerogels were calcined up to 1000°C where complete crystallization was observed. The emission of the various samples has been measured under X-ray excitation (Figure 3). The most efficient materials are $\text{HfO}_2 : \text{Tb}^{3+}$ 1% and $\text{HfO}_2 : \text{Y}^{3+}$ 20% Tb^{3+} 1%. No quantitative information on the scintillation yield and afterglow is reported in the paper.

Strontium hafnium perovskite SrHfO_3 has been identified as potential scintillator in particular when activated with

Ce^{3+} ions [55]. Sol-gel preparation of SrHfO_3 films and powders has been reported recently [56]. The authors used in situ prepared strontium ethoxide and hafnium ethoxide in methoxyethanol for the preparation of a stable sol. Doping with Ce^{3+} ions was performed by adding cerium nitrate (1 mol% Ce^{3+}). Samples were annealed from 600 to 1100°C. Samples crystallize with the perovskite structure at 800° and 750°C for powders and films, respectively. Upon heating at higher temperature, monoclinic HfO_2 phase also appears. Ce^{3+} emission is detected under X-ray excitation on powders annealed at 1100°C but not for other conditions and not for the films. The same authors studied the influence of the Sr/Hf ratio on the scintillation properties of sol-gel-derived Ce^{3+} doped strontium hafnate powders [57]. Varying the Sr/Hf ratio from 0.66 to 1.63, it was shown that the best scintillation efficiency was observed for the perovskite stoichiometric ratio Sr/Hf = 1 and for powders annealed at 1200°C. At this temperature, the perovskite phase is well crystallized but HfO_2 monoclinic phase is also observed. It seems that optimization of the preparation procedure is still not achieved and that improvement is possible.

6. TUNGSTATES

Due to their high densities, tungsten oxides have received much attention from the scintillators community in particular lead tungstate [58, 59] and cadmium tungstate [60, 61]. These materials are intrinsically luminescent and do not require further doping with emitting ions.

Very few works can be found in the literature for the preparation of tungstate scintillators by sol-gel chemistry. In 2003, Lennstrom et al. proposed the sol-gel elaboration of CdWO_4 thin films by using WCl_6 and cadmium acetate in ethanol [62]. Stable sol was spin coated on various substrates. Powders and films were produced which showed photoluminescence corresponding to the CdWO_4 phase. No measurement was performed under high-energy excitation.

More recently, Shang et al. studied the effect of doping in nanostructured CdWO_4 films [63]. Tungsten isopropoxide was prepared from WOCl_4 and reacted with cadmium nitrate. Solution was doped with either lithium, boron or bismuth. The doped sols were then used to prepare thin films by spin coating or hydrolyzed to yield powders. Study of photoluminescence (UV excitation) showed that doping with Li^+ , Bi^{3+} , or B^{3+} enhanced the luminescence of the material. This has been associated with diminution of grains size and higher density. Here again, no scintillation measurement has been performed.

7. CONCLUSIONS

Through an exhaustive survey of recent literature, it has been shown that sol-gel chemistry is an efficient tool to prepare various scintillating oxides. Available data have been reported and summarized in Table 1. As observed for other domains, the possibility to prepare thin films is considered the most important advantage of sol-gel process. The other important advantage brought by sol-gel chemistry is the possibility to easily vary the composition and to dope the

TABLE 1: Compositions, form, and scintillation yield (when available) of sol-gel-derived scintillating materials.

Compound	Emitting ion	Form	Light yield (Photons/MeV)	Reference
Y ₂ O ₃	Nd ³⁺ (1%)	Films	—	[11]
Gd ₂ O ₃	Eu ³⁺ (5%)	Powders, films	18500	[17]
Lu ₂ O ₃	Eu ³⁺ (5%)	Powders, films	19750	[17]
LuBO ₃	Eu ³⁺ (5%)	Powders, films	8900	[27]
	Tb ³⁺ (5%)		4400	[27]
	Ce ³⁺ (0.5%)		8100	[26]
LuPO ₄	Eu ³⁺ (10%)	Powders	5400	[34]
	Tb ³⁺ (5%)		9200	
	Ce ³⁺ (0.1%)		7400	
Lu ₂ SiO ₅	Eu ³⁺ (2%)	Powders, films	2900	[22]
	Tb ³⁺ (1.5%)		13100	[22]
	Ce ³⁺ (0.5%)		20000	[20]
Lu ₃ Al ₅ O ₁₂	Tb ³⁺	Powders, films	—	[29]
	Ce ³⁺ (1%)	Powders	—	[30]
HfO ₂	Sm ³⁺ , Eu ³⁺ , Tb ³⁺ (0.4%)	Films	—	[37]
	Y ³⁺ (20%)/Tb ³⁺ (1%)	Powders	—	[38]
SrHfO ₃	Ce ³⁺ (1%)	Powders	< 4000	[40, 41]
CdWO ₄	—	Films	—	[49]
	Li ⁺ , B ³⁺ , Bi ³⁺ (0.5–10%)	Powders, films	—	[50]

materials. In most cases, the emission of scintillators comes from doping ions like rare earth ions. Efficient doping with such ions can be achieved by sol-gel chemistry. It is indeed striking to note that optimal doping concentration is usually found much higher for sol-derived materials when compared to solid-state-derived synthesis. In our opinion, this comes from the conjunction of two opposite effects. The light yield of sol-gel derived materials is usually found lower than the ones prepared by solid state reaction for a given doping level, see [48] for instance. This is usually associated with residual hydroxyl groups provoking luminescence quenching. On the other hand, sol-gel derived materials are known to present a better dispersion of doping ions. This allows higher doping concentration to be reached without concentration quenching and thus higher emission efficiency. These two effects going into opposite directions somehow compensate each other and the optimum light yield is usually found equivalent for the different synthesis routes but with different doping levels (see Table 1).

In the specific case of Ce³⁺ doping which is a very important case for scintillation applications, a detailed study has been proposed by combining X-ray photoelectron spectroscopy (XPS) and X-ray absorption spectroscopy (XANES) [64]. Considering various materials, it has been shown that mixed oxidation state Ce³⁺/Ce⁴⁺ was clearly observed for sol-gel-derived materials. This tends to lower the scintillation efficiency but this lowering is compensated by higher doping concentrations without quenching.

In conclusion, the sol-gel process appears to be a very valuable way to prepare scintillators with enhanced properties and to develop new scintillators thanks to the versatility of this chemical route. In particular, thin films applications

are very attractive. The sol-gel process also allows fundamental studies by changing easily the nature of the doping ions or the composition. Finally, the possibility to prepare hybrid materials, not reported in this work, is a new opportunity to develop new generation scintillation materials for medical imaging.

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