# UNIVERSIDADE DE SÃO PAULO INSTITUTO DE QUÍMICA Graduate Program in Chemistry

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## **Transparent Films Featuring Persistent Luminescence**

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## Filmes transparentes apresentando a propriedade luminescência persistente

Tese apresentada ao Instituto de Química da Universidade de São Paulo para obtenção do Título de Doutor em Ciência (Química)

Orientador: Prof. Dr. Lucas Carvalho Veloso Rodrigues Coorientador: Prof. Dr. Everton Bonturim

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"Filmes transparentes apresentando a propriedade luminescência persistente"

## **DOUGLAS LOURENÇO FRITZEN**

Tese de Doutorado submetida ao Instituto de Química da Universidade de São Paulo como parte dos requisitos necessários à obtenção do grau de Doutor em Ciências - no Programa de Química.

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#### **Dedicatória / Dedication**

Dedico o seguinte trabalho a vocês leitores, que ao lerem minhas descobertas, dividem seu tempo comigo, independente de crenças, religiões, gêneros e sexualidades.

Obrigado por dividir seu tempo comigo.

//

I dedicate the following work to you readers, who, while reading my findings, are sharing your time with me, regardless of our beliefs, religion, gender or sexuality.

Thank you for sharing your time with me.

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#### **RESUMO**

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Luminescência Persistente é um fenômeno visual no qual um material é capaz de absorver luz, armazená-la, e então emitir luz própria no escuro. Dentre as aplicações para materiais com luminescência persistente (PersL), a mais comum é seu uso em sinalização de segurança, que podem ser encontradas em prédios de quase qualquer lugar do mundo. No entanto, outras aplicações mais complexas estão emergindo para esta classe de compostos. Porém, certas aplicações requerem propriedades especificas, que não são necessariamente intrínsecas de materiais persistente conhecidos, o que dificulta o avanço do uso de luminescência persistente no campo interdisciplinar. Uma propriedade com potencial de mudança para essa classe de compostos é a transparência. Materiais persistentes e translúcidos podem expandir grandemente as possibilidades de aplicações dessa classe compostos. A investigação presente nessa tese de doutorado é baseada no desenvolvimento de um novo composto, que combina a translucidez com a luminescência persistente. Para isso, síntese dos seguintes materiais persistentes: Sr<sub>2</sub>MgSi<sub>2</sub>O<sub>7</sub>:Eu<sup>2+</sup>,Dy<sup>3+</sup>, ZnGa<sub>2</sub>O<sub>4</sub>:Mn<sup>2+</sup> e Y<sub>2</sub>O<sub>2</sub>S:Eu<sup>3+</sup>,Ti,Mg<sup>2+</sup> foram otimizadas e descritas, e os produtos obtidos foram incluídos numa matriz de hidroxipropilmetilcelulose. Por fim, a relação entre as propriedades de persistência e de transparência foram avaliadas e três filmes diferentes foram produzidos - um com persistência no azul, um no vermelho e outro no verde. Para uma melhor caracterização da dispersão das partículas nos filmes, uma nova técnica de mapeamento por fluorescência e absorção de raios X nanofocados, baseada em luz Síncrotron foi aplicada.

**Palavras-chave:** Luminescência persistente, Filmes transparentes, Nanomateriais, Celulose.

#### ABSTRACT

Fritzen, D.F. **Transparent Films Featuring Persistent Luminescence**. 2022. 100p. Ph.D. Thesis – Graduate Program in Chemistry, Instituto de Química, Universidade de São Paulo, São Paulo.

Persistent Luminescence is a visual phenomenon in which a material can absorb light, store it, and then emit light of its own in the dark. Among the applications for materials with persistent Luminescence (PersL), the most common is its use in safety signs, which can be found in buildings almost anywhere in the world. However, other more complex applications are emerging for this class of compounds requiring specific properties, which are not necessarily intrinsic to known persistent materials, making it difficult to advance the use of PersL in the interdisciplinary field. One potentially changing property for PersL materials is transparency. Persistent and transparent materials can greatly expand the application possibilities of this class of compounds. The investigation of the referred doctoral thesis is based on the development of new compounds, which combines transparency with persistent luminescence. For this, the syntheses of the following persistent luminescent materials Sr<sub>2</sub>MgSi<sub>2</sub>O<sub>7</sub>:Eu<sup>2+</sup>,Dy<sup>3+</sup>, ZnGa<sub>2</sub>O<sub>4</sub>:Mn<sup>2+</sup> e Y<sub>2</sub>O<sub>2</sub>S:Eu<sup>3+</sup>,Ti,Mg<sup>2+</sup> were optimized and described, and the products obtained were included in a matrix of hydroxypropyl methylcellulose. Finally, the relationship between persistence and transparency properties was evaluated, and three different films were produced - one with blue persistence, one with red, and one with green. To better understand the nanoparticles dispersion in the films, a new nanofocused X-ray absorption and emission mapping technique based on Synchrotron radiation was applied.

Keywords: Persistent luminescence, Transparent films, Nanomaterials, Cellulose.

### SUMMARY

Chapter 1: Introduction	
1.1 Contextualization	
1.1.1 Persistent Luminescence	
1.2 Persistent Luminescence with Different Emission Co	lors
1.2.1 A Blue Emitter Material - Sr <sub>2</sub> MgSi <sub>2</sub> O <sub>7</sub> :Eu <sup>2+</sup> ,Dy <sup>3+</sup>	
1.2.2 A Green Emitter Material – ZnGa <sub>2</sub> O <sub>4</sub> :Mn <sup>2+</sup>	
1.2.3 A Red Emitter Material – Y <sub>2</sub> O <sub>2</sub> S:Eu <sup>3+</sup> ,Ti,Mg	
1.3 PersL Films and Composites	
1.4 Possible Applications for Persistent and Transparent	Composites24
Chapter 2: Objectives	
2.1 General Objectives	
2.2 Specific Goals	
Chapter 3: Characterization Techniques	
3.1 Characterization Techniques Chapter 4: Synthesis and Characterization of Sr <sub>2</sub> N	
4.1 Synthesis of SMSO	
4.1.1 Co-Precipitation Synthesis for SMSO obtention	
4.1.2 Materials	
4.1.3 Procedure	
4.2 Results	
4.2.1 Synthesis Optimization	
4.2.2 Structural and Morphological Characterization.	
4.2.3 Spectroscopic Characterization	
4.3 Conclusion	
Chapter 5: Synthesis and Characterization of ZnG	
	a2O4:Mn <sup>2+</sup> (ZGO) 40
5.1 Synthesis of ZGO	a2O4:Mn <sup>2+</sup> (ZGO) 40
5.1 Synthesis of ZGO 5.1.1 Hydrothermal Synthesis for ZGO obtention	a2O4:Mn <sup>2+</sup> (ZGO) 40
<ul><li>5.1 Synthesis of ZGO</li><li>5.1.1 Hydrothermal Synthesis for ZGO obtention</li><li>5.1.2 Materials</li></ul>	a2O4:Mn <sup>2+</sup> (ZGO) 40 41 41 41

5.2 Results	42
5.2.1 Structural and Morphological Characterization	42
5.4.2 Spectroscopic Characterization	44
5.5 Conclusion	46
Chapter 6: Synthesis and Characterization of Y2O2S:Eu <sup>3+</sup> ,Ti,Mg (YOS)	47
6.1 Synthesis of YOS	48
6.1.1 Microwave-Assisted Synthesis for YOS obtention	48
6.1.2 Materials	48
6.1.3 Procedure	49
6.2 Results	49
6.3 Conclusion	52
Chapter 7: Transparent Thin-Films Featuring Persistent Luminescence	53
7.1 HPMC/PersL Films Preparation	54
7.1.1 HPMC/SMSO	55
7.1.2 HPMC/ZGO	68
7.1.3 HPMC/YOS	72
Chapter 8: Conclusions	77
8.1 Conclusion	78
Chapter 9: References	81
Appendix: Supplementary Information	95
Academic Curriculum Vitae	98

# **Chapter 1: Introduction**

#### **1.1 Contextualization**

This work has the purpose of obtaining transparent composites, based on Persistent Luminescence (PersL) materials within a polymer matrix. The research field of science related to PersL material as continuously increasing in the last three decades. During this time, the knowledge on the synthesis of these compound became well established, with known PersL materials widely studied and obtained. Also, the mechanism behind the afterglow phenomenon become well understood, but with a few gaps remaining, as each material may have a different set of elements, which leads to small variations on the mechanism. Nevertheless, the development produced during the last three decades has led the research field to a new set, in which the applicability of this compounds has been being the focus on state-of-art reports. As it will be seen, the most recent reviews on PersL materials tend to focus on its current and possible applications, rather than its obtention and raw proprieties.

Moreover, this current work aims to address this tendency, with just a little twist. Instead of aiming a single application, the main goal is to create a novel PersL compound, with a property unusual to these materials: transparency. For that, a set of PersL compounds was obtained, characterized, and further deposited as films within a polymeric matrix. This new property can increase the perspective of PersL materials applicability, bringing light current challenges on their applications, bringing new ideas to the surface, as well as advance the possible applicability of this class of material.

#### **1.1.1 Persistent Luminescence**

Persistent Luminescence (PersL) is a visual phenomenon in which a material features a glow-in-the-dark property for a few hours after being charged by a luminous radiation source <sup>1</sup>. Even though it is a phenomenon historically described millennia ago on old Chinese paintings <sup>2</sup>, and some centuries ago on the Bologna Stone <sup>3</sup>, only at the end of the 90s and the beginning of the 2000s PersL phenomenon started to become understood by scientists throughout the world. Only after this period new synthesis routes for PersL materials were optimized and described <sup>4</sup>, its electronical mechanism started to unravel <sup>5</sup>, and studies on PersL applications emerged in interdisciplinary fields <sup>6,7</sup>.

Nowadays, many materials have been developed, presenting an optimized afterglow on a wide range of wavelengths. The most common PersL materials show green emissions and can be easily found on safety-exit signs on airplanes, hospitals, and buildings (Figure 1).



Figure 1.1: Examples of PersL safety-exit signs under room light (upper row) and on dark (bottom row); (left column) exit sign symbol under room light; (right column) safety sign with caption "Em caso de incêndio, não use elevadores, use escadas" (In case of fire, do not use lift, use the stairs).

These safety signs are usually based on SrAl<sub>2</sub>O<sub>4</sub>:Eu<sup>2+</sup>,Dy<sup>3+</sup>, and the characteristic green emission comes from the Eu<sup>2+</sup>, which is the emission center (or activators) of the compound. Emitting centers are one key part of PersL compounds, as they are responsible for the colorful emissions aspect of these materials (Table 1). The emission centers are present in small doses on an inorganic matrix, and they are commonly called dopants and have energy levels within the matrix bandgap, responsible for the radiative transition resulting the glow-in-the-dark property. The energy levels of the emission center are important not only for the color emission, but also for the energy absorption wavelength, and energy storage/transfer within the bandgap.

The second key part of PersL phenomenon are defects. Defects are imperfections in a given inorganic matrix. They can be classified as extrinsic defects, in which the imperfections comes from a source foreign to the inorganic host (e.g. dopants), or as intrinsic defects, which means that the imperfections comes from a source native from the host (e.g. vacancies and structural). In order for a defect to play role in PersL phenomenon, it must have a energy level near the conduction or valence band within the band gap. This energy acts as traps, storing the electrons/holes that are released in function of thermal energy creating a delay in the electronic transition, leading to the persistent feature of the phenomenon.

For instance, in a general PersL mechanism, the following steps takes place: (1) the excitation of the emission center; (2) trapping of excited electrons into defects, which can occurs via conduction band (2a) or via tunneling (2b); (3) through thermal energy, the electron is released from the trap, and recombines with the emission center emitting levels via conduction band (3a) or via tunneling (3b); (4) the mechanism ends with the radioactive decay of, producing light (Figure 1.2). Certainly, the mechanism may differ in function of the emission center and the inorganic matrix intrinsic properties, but most

importantly, PersL mechanism always relies on the thermal release of trapped energy, which leads the enduring glow-in-the-dark phenomenon.



Figure 1.2: Schematic diagram of simplified PersL mechanism. CB stands for conduction band, VB for valence band, and kt stands for thermal energy.  $^{8}$ 

Emission Center	Emission Color (average wavelength)	References
Defects	UV (260 nm) to NIR (1000 nm)	9–12
Gd <sup>3+</sup>	UV (313 nm)	13
Pb <sup>2+</sup>	UV (390 nm)	14
Hf <sup>4+</sup>	Blue (470 nm)	15
Dy <sup>3+</sup>	Blue (480 nm) to Red (667 nm)	16
Ce <sup>3+</sup>	Blue (430 nm); Green (550 nm)	17,18
Bi <sup>3+</sup>	Blue (448 nm); NIR (1000 nm)	19,20
Eu <sup>2+</sup>	Blue (400 nm) to Red (700 nm)	21,22
Eu <sup>3+</sup>	Red (610 nm)	23
Tb <sup>3+</sup>	Green (543 nm)	24–26
Mn <sup>2+</sup>	Green (500 nm); Yellow (576 nm); Red (650 nm)	27
Ti <sup>3+/4+</sup>	UV (380 nm); Blue (500 nm)	28,29
Sm <sup>3+</sup>	Red (550 nm to 610 nm)	30
Er <sup>3+</sup>	Red (650 nm) to NIR (1530 nm)	31,32
Pr <sup>3+</sup>	Red (620 nm); NIR (1100 nm)	33,34
Cr <sup>3+</sup>	NIR (730-1500 nm)	35,36
Ni <sup>2+</sup>	NIR (1200 nm)	37
Co <sup>2+</sup>	NIR (1200 nm)	38
Mn <sup>4+</sup>	NIR (730 nm)	39
Yb <sup>3+</sup>	NIR (1020 nm)	40,41

Table 1.1: Example of PersL Materials, Based on Emission Center and Their Color Range

Certainly, PersL application does not limit itself to exit signs, although further commercial applications are still being developed or are considered a challenge for the current state-of-art of PersL material. Poelman et al. (2020), reported an up-to-date review on the main challenges of persistent phosphors applications<sup>7</sup>. Well-established applications for PersL materials are safety signs and toy decoration, applications in progress are the ones related to the thermometer in extreme conditions, AC LEDs, road marking, and bioimaging. The current challenging applications are those related to photocatalysis and solar energy harvesting (Figure 1.3).



Figure 1.3: Diagram representation of PersL applications. Inspired on Figure from: <sup>7</sup>

One might notice that there is an evident diversity of PersL compounds, but still, most of its applications remain in progress or are considered a challenge. This mostly happens due to limitations from the intrinsic properties of PersL materials. For instance, in some cases, the materials are not well optimized regarding the afterglow properties - emitting only for a few seconds after ceasing the radiation source, as is the case of LaAlO<sub>3</sub>:Cr<sup>3+</sup>, which exhibits a relatively short afterglow in the red/NIR region<sup>36</sup>. In other cases, the materials may present a long and bright PersL emission, such as the Zn<sub>3</sub>Ga<sub>2</sub>Ge<sub>2</sub>O<sub>10</sub>:Cr<sup>3+</sup> that persists for up to 360 h after a few minutes of sunlight exposuring<sup>35</sup>, but are based on expensive precursors, which hamper commercial extensive applicability – 100 g of Ge<sub>2</sub>O<sub>4</sub> can cost up to \$1970, which is way more expensive when compared to Al<sub>2</sub>O<sub>4</sub>, which cost

less than \$133 (price tables from Alfa Aesar-2022) <sup>42</sup>. Other materials may present an intense glow at uncommon ranges, such as the red-emitter SrS:Eu<sup>2+</sup>,Sm<sup>3+</sup>, but are chemically unstable at ambient conditions, and its low stability to humidity does not make the material suitable for most general applications.<sup>43</sup>

The applicability of PersL materials, both in industrial scale and non-industrial scale (lab scale), usually requires more than just the pure powder. Even materials with well stabilized properties, such as  $SrAl_2O_4$ : $Eu^{2+}$ , $Dy^{3+}$ , require dispersion in a polymer to mitigate its hydrolysis and enhance its applicability. Moreover, the difficulty of using PersL materials as road markers (Figure 1.4), strongly relies on the chemical and physical stability of the PersL to non-controlled conditions, while caring for factors associated with paints, such as adhesion, durability, compatibility, and particle dispersion  $^{44-46}$ . A promising composition for PersL paintings focusing on road marking involves the use of a coater to protect the PersL particles from degrading (*e.g.* PVC, APTES, PAA) and to disperse the particles within the main polymer (*e.g.*PMMA).<sup>44</sup>



Figure 1.4: Photography of road painted with Persistent Luminescence paint and examples of PersL compounds used to create the paint. Retrieved from: <sup>47</sup>

The list of examples of PersL materials that do not fit the right application is extensive, and it is an ongoing interdisciplinary topic being extensively researched worldwide. Nanoparticulated PersL Materials (PersLnano) are one of the promising classes of PersL compounds that could bring solutions to current challenges. For instance, the nanoscale could facilitate bioapplications and biofunctionalizations when compared to bulk materials <sup>8</sup>. Bio-imaging based on nano-persistent Luminescence has been proved by pioneer researches in the last decade, specially focused on near infrared (NIR) emitting persistent materials <sup>48</sup>. Certainly, the pure PersL material is not biologically compatible, so functionalization treatments are commonly used to make the compounds suitable for *in vivo* use. For instance, report of PEG- functionalized PersL nanoparticles shows *in vivo* 

images of tumor cells <sup>49</sup> (Figure 1.5) and PersL hydrogels based on NIR emitter within a polymer mixture successfully triggering photodynamic therapy within mouse tissue <sup>50</sup>.



Figure 1.5: (a) In vivo imaging obtained at 5 and 10 min after the injection of the PeL-NPs. (b) Emission intensity as a function of the time monitoring the whole body and liver during the first 10 min of experiment. From:  $^{49}$ 

The visual and electrical properties of PersL materials makes it suitable for electronic applications, being a promising main component of AC-driven LEDs and solar cells. Notwithstanding, the applicability of PersL materials on electronic devices requires the design of the storage capacity and trap depth distribution, to match the elevated temperature operation (higher than the ambient temperature) <sup>51</sup>

Regarding the solar-cell applicability, it remains a challenge to the current stateof-art of Persistent Luminescent Materials. Even though there were efforts on making PersL material to act as light source of solar cells during dark hours, the afterglow efficiency when compared to sunlight leads to disregarding the material as a suitable light source. For instance, recently Zhang *et al* studied the use of PersL dye on solar cells, and reported and enhancement of 0.0076% <sup>52</sup>, while Puntambekar *et al* reported that solar cell died with PersL ink can only generate power enough to maintain low powered electronic devices actives <sup>53</sup>. Moreover, PersL materials applied on solar cells can cause undesired phenomena that lowers the energy conversion efficiency, such as light scattering, and shadowing effects <sup>54</sup>.

Based on the aforementioned information, one might assume that the state-of-art of persistent luminescent materials has been committed to developing composites and/or functionalized PersL compounds to fit novel applications. Therefore, two courses of action might be considered in this research field. The first would be to study a particular application of PersL composites, attributing required properties to solve related challenges. The second is to research novel properties of PersL materials that could perform on diverse applications and be the foundation for further studies. Novel properties of PersL compounds could shed light upon applications that are not currently possible. One example of novel property for PersL materials is transparency. Transparent PersL materials could be applied on surfaces of devices or installation that requires the sunlight for an electronic or biological process (e.g. electric energy production or photosynthesis), avoiding undesired effects, such as light scattering or shadowing from particles, but still taking advantage of the light storage and light emitting of the PersL material. One might consider transparent PersL materials a promising advance for bioreactors, greenhouses, and photolytic reactors. Therefore, this current work aims to produce optimized and characterized PersL materials featuring a new property: transparency.

#### 1.2 Persistent Luminescence with Different Emission Colors

To address the first specific goal of the thesis, which is to produce PersL material with blue, red, and green emissions, featuring sharp size distribution, specific materials should be chosen regarding their PersL emission. Therefore, the choice of PersL materials for this work was based on up-to-date reported PersL (nano)materials, which feature optimized afterglow, persisting for at least one hour after ceasing the irradiation source. The chosen materials for this investigation are:  $Sr_2MgSi_2O_7$ :Eu<sup>2+</sup>,Dy<sup>3+</sup>, ZnGa<sub>2</sub>O<sub>4</sub>:Mn<sup>2+</sup>, and Y<sub>2</sub>O<sub>2</sub>S:Eu<sup>3+</sup>,Ti,Mg. The following subsections contain brief descriptions of these materials. More detailed information on their synthesis can be found in a dedicated chapter for each compound.

#### 1.2.1 A Blue Emitter Material - Sr<sub>2</sub>MgSi<sub>2</sub>O<sub>7</sub>:Eu<sup>2+</sup>,Dy<sup>3+</sup>

Europium and Dysprosium-codoped Di-strontium magnesium disilicate, Sr<sub>2</sub>MgSi<sub>2</sub>O<sub>7</sub>:Eu<sup>2+</sup>,Dy<sup>3+</sup> (SMSO), was reported as a PersL material in 2001 by Lin *et al*<sup>55</sup>. Since then, SMSO was the basis for many studies involving PersL mechanisms and application, such as in LED devices <sup>56</sup>, forensic chemistry <sup>57</sup>, and light source for catalytic processes <sup>58</sup>. A recent work reported by Merizio (2021), reported several synthesis methods for SMSO production, including microwave-assisted (MW) solid synthesis, ceramic synthesis (CM), and co-precipitation method (CPC). The author reported the production of SMSO with a sharpe size distribution (ca. 260 nm), and a blue afterglow persisting up to 120 min after 5 min UV charging <sup>59,60</sup>. In this work, it was developed a novel route for SMSO obtention, based in a combination of CPC method with MW annealing. The CPC method allows control of the precursor particle size, which can further allow the production of small and homogenous particles. While the MW annealing process is a fast-heating and energy-saving methodology in comparison to conventional heating using a muffle furnace. Since the MW process takes only a few minutes, it hampers the aggregation and agglomeration of particles, ensuring that the final material will have a similar size to the precursor.

#### 1.2.2 A Green Emitter Material – ZnGa<sub>2</sub>O<sub>4</sub>:Mn<sup>2+</sup>

ZnGa<sub>2</sub>O<sub>4</sub>:Mn<sup>2+</sup> (ZGO) materials feature a bright green emission at 500 nm under UV-light irradiation energy, with a ca. 1 hour afterglow <sup>61</sup>. As for SMSO, ZGO is a promising material for diverse applications, including LEDs, FEDs, UV photodetectors, and dosimeters <sup>61,62</sup>. In 2015, Srivastava *et al*, reported a biphasic hydrothermal approach synthesis for the production of Cr-doped ZGO producing 10 nm size particles with longemission in the NIR region <sup>63</sup>. In light of this, a similar approach was taken for the production of Mn-doped ZGO, aiming for the obtention of PersL nanoparticles with green emission. One major advantage of ZGO is its chemical and thermal stability, as well as its water-resistance property which makes it suitable for further applications on films based on a water-soluble matrix <sup>64</sup>. In this work, we developed an adapted ZGO obtention based on reported biphasic hydrothermal synthesis, combined with a novel annealing method consisting of MW treatment.

#### 1.2.3 A Red Emitter Material – Y<sub>2</sub>O<sub>2</sub>S:Eu<sup>3+</sup>,Ti,Mg

Even though red-emitter PersL materials are commercially available, they are not the common choice for everyday applications, such as those seen on safety signs and toy decoration. The lack of applications might be due to the shortage of those compounds in the early stages of PersL studies. Another possible explanation relies on the fact that one of the most optimized red-PersL materials,  $SrS:Eu^{2+},Sm^{3+}$  is not chemically stable and easily reacts with moisture in the atmosphere <sup>43</sup>. A suitable alternative for red phosphor is rare-earth-doped oxysulfide, which has been gathered much attention since its first report in 1999, due to its high stability to moisture and water <sup>65–69</sup>. Recently, Machado *et al.* reported a novel, rapid, energy-saving synthesis of Y<sub>2</sub>O<sub>2</sub>S (YOS) materials through a microwave annealing process <sup>41</sup>. Bearing this in mind,  $Y_2O_2S$ :Eu<sup>3+</sup>,Ti,Mg will synthesized through a microwave-assisted solid-state synthesis, aiming the obtention of material with strong afterglow red-emitting phosphors with enduring afterglow, as previously reported on literature.

#### **1.3 PersL Films and Composites**

In order to produce transparent PersL materials, different approaches could take place as the main methodology. First is the production of PersL single crystals, which leads to a continuous refractive index, leading to transparency. However, even though some recent studies have been gathering success in this area <sup>70–72</sup>, the production of optimized PersL single crystals is not a trivial task *e.g.*, it depends highly on synthesis optimization, and the formation of structural defects is lowered, thus might reduce the emission quantum yield, and the final product must be further tailored to match certain shapes to be used as functionalizer. Another approach is the production of hybrid films and thin-films. Hybrid PersL films consist of an organic polymer used as the matrix for the PersL particle. This approach is very similar to the production of PersL paintings or plastic composites. Still, it differentiates from the mainstream composites due to its controlled thickness and facilitated adherence to substrates.

Nowadays, there is a great appeal to using abundant materials and resources for the development of new devices, concerning not only ecological issues but also the further applicability and commercialization of this novel product <sup>73</sup>. With this in mind, the selection of an organic matrix to form a composite with PersL materials (SMSO, ZGO and YOS) was based both its chemical and physical properties, and on its availability. It is known that cellulose is an abundant material, of "almost inexhaustible quantity" and recently there are a lot of efforts on producing cellulose-based composites for application

on interdisciplinary sectors, such as electronics, optical, biomedical, and engineering <sup>74,75</sup>. Nevertheless, cellulose-based composites are known for producing flexible and transparent films (on visible range), and some types of cellulose are water soluble, which allows the use of H<sub>2</sub>O as the main solvent for the films casting process, such as Hydroxypropyl Methylcellulose (HPMC) <sup>76</sup>. This investigation will make use of HPMC as the organic matrix to produce a HPMC/PersL composite (PersL = SMSO, ZGO, and YOS), aiming the obtention of a flexible and transparent composite based on an abundant material. Nevertheless, the production of a novel cellulose-based composite featuring persistent Luminescence could take advantage of the physical properties of cellulose, such as its transparency and flexibility, combined with the photonics properties of persistent luminescence particles.

#### 1.4 Possible Applications for Persistent and Transparent Composites

The novelty of a method that allows the obtention of transparent composites does not limit itself on its obtention and characterization. It also brings new perspectives and applications to the research area. Following is a list of possible applications and area that this novelty could impact:

• **Counterfeiting component:** Transparent materials could be used as counterfeiting components without compromising the design and/or layout of commercial materials, such as a watermark component. As example, it could be used as counterfeiting component of packages, labels, electronic devices, bills, and on personal identification components, such as ID or passport.

- **Bioreactors or greenhouses:** transparent films featuring persistent luminescence could be used to develop a bioreactor that can allows the sunlight comes inside and emits its own light during period of shadow. Films with blue or red emission would be the most suitable for this application due to the natural absorption from chlorophyll.
- Ornamental windows: a possible application that holds a strong commercialization appeal is the use of transparent persistent luminescent composites on ornamental windows. The windows would provide light for the room during the nighttime, but without compromising the view through it during daytime.
- **Methodology expansion:** the methodology developed for obtaining transparent persistent luminescent composites could be further applied to produce other transparent materials with different photonic properties, such as upconversion, down conversion, or a combination of properties.

# **Chapter 2: Objectives**

#### 2.1 General Objectives

This Ph.D. thesis focuses on developing a novel material featuring PersL and transparency. For this, the PersL compound will be synthesized through different synthesis methods – in the function of the type of material -, and then inserted in an organic matrix to produce a transparent film.



Figure 3: Schematic Representation of Films to be Prepared.

#### **2.2 Specific Goals**

1. Synthesis and characterization of a (A) blue-emitting, (B) green-emitting, and (C) red-emitting PersL material. In this case, the focus is the production of a compound with optimized afterglow (bright and enduring emission, in the scale of hours) with sharp size distribution.

- 2. To cast the obtained PersL compound into an organic matrix, aiming to obtain a flexible, transparent, and persistent film.
- 3. Verify the influence of the concentration of PersL compounds on the films' transparency and afterglow properties. In this case, it is expected that increasing the amount of persistent inorganic material will increase the apparent emission of the film but decrease the transparency. Therefore, the relationship between nanoparticle concentration versus transparency and luminescence will be studied.

We reiterate that the production of a transparent persistent luminescence composite would expand the applicability of PersL materials, providing a new path for application in development and even partially, or completely, solve the challenges of more complex and advanced applications, such as light harvesting for biorecators or greenhouses.

# Chapter 3: Characterization Techniques

#### **3.1 Characterization Techniques**

• X-ray Powder Diffraction (XRD): X-ray Diffraction (XRD) patterns of obtained solid materials (SMSO, ZGO, and YOS) were carried out in a Bragg-Brentano XRD (Brucker D2 PHASER) using Cu K $\alpha$  radiation ( $\lambda = 1.5406 \text{ Å}$ ), with the integration of 1 s for each 0.5° 2 $\theta$ . XRD is used to identify the crystalline phase of the obtained crystals, also to access if there are impurities obtained with the main material. It is the first characterization process used to verify the materials obtained after each synthesis.

• Scanning Electron Microscopy (SEM): SEM images of obtained solid materials (SMSO, ZGO, and YOS) were captured by a JEOL JSM-740 1F Field Emission Scanning Electron Microscope using a carbon stub. Samples were prepared using isopropanol to suspend the materials prior to the analysis. SEM technique is used to identify the shape, size, and morphology of the crystals obtained.

• **Transmission electron microscopy (TEM):** TEM analyses were performed using the MET JEOL JEM 20110. Samples were prepared using isopropanol to suspend the materials prior to the analysis. In this work, TEM characterization has a similar goal as the SEM technique, with a difference that TEM allows the obtention of images with higher resolution, and therefore, more quality images of small crystals.

• X-Ray Fluorescence (XRF): XRF mapping of HPMC/SMSO films was performed on Sirius - Synchrotron facility at Carnauba beamline (Campinas, São Paulo -Brazil, project #20210013, using a Vortex SDD, 4 elements Hitachi. The analysis was performed at room temperature and ambient pressure. The film samples were placed over an aluminum frame for the measurement. The excitation energy of 9.656 keV was used for the measurements. The mapping was applied to access the distribution of PersL particles within the film matrix, and also to verify if the signals of the elements are consistent, i.e., if they match regarding the positional of each other within the film extension.

• Scanning Transmission X-Ray Microscopy (STXM): STXM of HPMC/SMSO films was performed on Sirius - Synchrotron facility at Carnauba beamline (Campinas, São Paulo - Brazil, project #20210013), using a Photodiode AS04-105A Alibava. The analysis was performed at room temperature and ambient pressure. The film samples were placed over an aluminum frame for the measurement. STXM mapping was applied to verify the dispersion of particles withing the matrix, and access if the particle is well-dispersed.

• Photoluminescence spectroscopy (PL) and Persistent Luminescence (PersL) decay curve and emission spectra: PL and PersL characterization of the films and their respective solid materials was performed using a (1) spectrophotometer Edinburgh FLS 980 equipped with both continuous and pulsed 450W Xenon lamps as the excitation source or a (2) Horiba-Fluorog-3 spectrofluorometer, equipped with a Xe-lamp 450 W, equipped with a Charge-Coupled Device (CCD) and a photomultiplier (PMT). PL and PersL measurements are required to characterize the spectroscopical properties of the particles and the films produced. These techniques are crucial to identify if the PersL of the composites differs from the pure particles.

• **Transmittance Spectra (T):** Transmittance of the films was measured to quantify the transparency of the materials. Transmittance spectra of the films were carried out in a Shimadzu UV-16019C, measuring from 200 to 800 nm at room temperature and ambient pressure. The transmittance spectra will be used to quantify and evaluate the transparency of the composites. Hence the goal is to identify a visual transparency, the main transmittance at the visual range will be acquired from the obtained data.

# Chapter4:SynthesisandCharacterizationofSr2MgSi2O7:Eu2+,Dy3+ (SMSO)

#### 4.1.1 Co-Precipitation Synthesis for SMSO obtention

Co-precipitation synthesis (CPC) consists of a wet-chemical reaction in which ions of precursors are mixed with a precipitant agent to obtain a solid product. This type of procedure can be controlled in order to obtain size-homogeneous solids during the precipitation process. In general, the factors that contribute the most to the dimension of the solid during a CPC are temperature, agitation, and concentration of metals/precipitants <sup>57,77,78</sup>. The Diagram 1 below shows a schematic representation of the synthesis procedure



Diagram 1: Schematic representation of CPC synthesis for SMSO obtention

#### 4.1.2 Materials

Sr(NO<sub>3</sub>)<sub>2</sub> (Sigma Aldrich 99.99%), Eu<sub>2</sub>O<sub>3</sub> (99.999% Quingdao Xinguanya Mining Industry Co.), Dy<sub>2</sub>O<sub>3</sub> (99.999% Quingdao Xinguanya Mining Industry Co.), MgCl<sub>2</sub> (Sigma Aldrich 99.99%), and Na<sub>2</sub>SiO<sub>3</sub> (99.99% Merck).

#### 4.1.3 Procedure

Nitrates of Eu and Dy were obtained by adding stoichiometric amounts of HNO<sub>3</sub> to Eu<sub>2</sub>O<sub>3</sub> and Dy<sub>2</sub>O<sub>3</sub>, the solution of the nitrate was dried, and Eu(NO<sub>3</sub>)·6H<sub>2</sub>O and Dy(NO<sub>3</sub>)·6H<sub>2</sub>O were obtained. This solution was prepared by mixing 0.3333 g of Sr(NO<sub>3</sub>)<sub>2</sub>, 0.7490 g of MgCl<sub>2</sub>, 0.0078 g of Eu<sub>2</sub>(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O, and 0.0321 g of Dy<sub>3</sub>(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O, in order to obtain a final material of the type Sr<sub>1.95</sub>Eu<sub>0.01</sub>Dy<sub>0.4</sub>MgSi<sub>2</sub>O<sub>7</sub>. The metal solution was dropwise added into the precipitant solution of Na<sub>2</sub>SiO<sub>3</sub> (0.1 mol/L). The precipitated solids were centrifuged four times for 5 min under 9000 rpm and washed with EtOH/H<sub>2</sub>O solution to remove excess ions on the solid. The supernatant was tested for the presence of chlorides ions (with Ag<sup>+</sup>) between each washing process, and between the third and fourth time, no qualitative amounts of chlorides ions were observed. Further, the solids were dried for 2 hours at 100°C and then heated using a microwave oven. The time and power of MW was varied to study their influence from 10 to 40 min and 700 to 1000 W, respectively. Activated carbon was used as a susceptor to generate heat to the precursors. The system for the reaction creates a semi-closed environment in which carbon undergoes an incomplete combustion process, producing significant amounts of CO<sub>(g)</sub>, which is necessary to produce a reducing atmosphere required to obtain  $Eu^{2+}$  from the precursors containing  $Eu^{3+}$ .

#### 4.2 Results

#### 4.2.1 Synthesis Optimization

The variation of microwave potency in Watts (W) and the heating process time, in minutes (min), were varied to find the optimized condition to obtain a pure SMSO solid. Table 4.1 below shows the observation for each synthesis process. The first eliminatory analysis for the process was the visual presence of blue afterglow after UVlight irradiation and XRD diffractogram analysis.

Time (min)	Potency (W)	Afterglow	XRD	Observation
10	700 800 900 1000	No	No SMSO phase observed	-
20	700 800 900	No	No SMSO phase observed	-
20	1000	No	Pure SMSO phase	-
30	700 800 900	No	Pure SMSO phase	
30	1000	Yes	Pure SMSO phase	-
40	1000	Yes	_	Solid Vitrified on Crucible

**Table 4.1:** Study of Variables Time and Potency on MW Assisted Annealing Synthesis

 for SMSO Obtention

Regarding the synthesis optimization, one might notice that for a time less than 20 min with potency less than 900 W, no blue emission is observed, and no SMSO phase is observed on XRD diffractograms. For parameters of 20 min and 1000 W, no afterglow was seen, although a pure phase of SMSO was observed on XRD analysis. Finally, the synthesis with 30 min of MW radiation exposure at 1000 W, a strong blue-emission of the material was seen after UV-light excitation (Figure 4.1). For time above 30 min at 1000 W, the solid was vitrified on the crucible, and it was not possible to isolate the material for further analysis.



Figure 4.1: Photo of SMSO under UV-Light (ca. 365 nm)

#### 4.2.2 Structural and Morphological Characterization

The XRD characterization for SMSO powder shows a diffractogram with a pattern similar to the reference of  $Sr_2MgSi_2O_7$  crystals (JCPDS 15-0016). Therefore, the presence of the rare-earth dopants did not show any phase segregation on the SMSO inorganic matrix (Figure 4.2).



Figure 4.2: SMSO diffractogram pattern (black) and reference pattern for comparison (blue)

Scanning Electron Microscopy (SEM) images for the obtained SMSO shows aggregates and agglomerates with a dimension of approximately 300 nm (Figure 4.3a-b). Statistical treatment using Image-J software indicates that the average particle size and standard deviation is  $204 \pm 70$  nm for the precursors, and  $245 \pm 84$  nm for the SMSO (Figure 4.3c-d).


Figure 4.3:(a) SEM of precursor, (B) SEM images of SMSO, (C) Histogram of particle size, obtained using Image-J software of (c) precursor and (d) SMSO.

# 4.2.3 Spectroscopic Characterization

The excitation and emission spectra for SMSO particles are shown in Figure 4.4. Excitation spectra show a broad band with a maximum at ca. 350 nm that arises from  $Eu^{2+} 4f^7 ({}^8S_{7/2}) \rightarrow {}^65d^1 ({}^2D)$  transition . Emission spectra show characteristic broad emission, centered at 475 nm, from  $Eu^{2+} 4f^65d^1({}^2D) \rightarrow 4f^7 ({}^8S_{7/2})$  transition. The persistent luminescence decay time shows an afterglow longer than 3 hours for the synthesized SMSO nanoparticles (Figure 4.5). A representation of the mechanism is found in Figure 4.6,  $Eu^{2+}$  acts as the emission center, while  $Dy^{3+}$  acts as traps/defects to hold electrons, which are further release with thermal energy. The steps of the mechanism are (1) excitation of  $Eu^{2+} 4f^7 ({}^8S_{7/2}) \rightarrow {}^65d^1$ ; (2) trapping the electrons on  $Dy^{3+}$  defects; (3) the electros are thermally released, recombined with the conduction band; (4) the radiative decay of  $Eu^{2+} 4f^65d^1({}^2D) \rightarrow 4f^7 ({}^8S_{7/2})$  transition takes place, leading to a blue afterglow. In comparison to other synthesis methodologies for SMSO nanoparticles production (pechini, sol-gel, and complexation), reported by Merizio et al. (2018)<sup>60</sup>, nanoparticles ranging from 200 to 300 nm with an afterglow enduring for up to 3 hours. Therefore, the afterglow results for CPC method synthesis are similar to those obtained, indicating that the synthesis is well optimized regarding its PL properties.



Figure 4.4: (left) Excitation spectrum of SMSO, fixed excitation scan at 475 nm. (right) Emission spectrum of SMSO, performed at room temperature, fixed excitation at 350 nm.



Figure 4.5: Persistent Luminescence Decay time for SMSO particles, fixed exaction at 350 nm and fixed emission at 475 nm



Figure 4.6: Persistent Luminescence mechanism for SMSO materials. BC stands for conduction band, and BV stands for valence band.

# 4.3 Conclusion

A novel synthesis process for SMSO obtention was optimized here. The obtained material presented nanoparticulate size (ca. 245 nm), as well as bright and enduring afterglow, compared to the SMSO obtained by other routes, previously reported in the literature <sup>59</sup>. As will be seen in chapter 7, these materials will be further used to produce composites based on ether cellulose matrix to obtain flexible and transparent materials featuring persistent blue Luminescence.

# Chapter5:SynthesisandCharacterizationofZnGa2O4:Mn2+(ZGO)

#### 5.1.1 Hydrothermal Synthesis for ZGO obtention

To obtain  $Zn_{0.995}Ga_2O_4$ :Mn<sub>0.005</sub> nanoparticles, a biphasic hydrothermal system was used, following the procedure described by Srivastava *et al.* – in which the authors described the obtention of Cr-doped ZGO. Therefore, the synthesis was adapted for the obtention of Mn-doped ZGO materials, as described below <sup>63</sup>. Diagram 2 below shows a schematic representation of the synthesis procedure.



Diagram 2: Schematic representation of hydrothermal synthesis for ZGO obtention.

### 5.1.2 Materials

ZnO (Sigma Aldrich 99,0%);  $Ga_2O_3$  (Sigma Aldrich 99,99%);  $Mn(NO_3)_2$  (Sigma Aldrich > 97,0%); HNO<sub>3</sub> concentrated (Sigma Aldrich); Toluene (Sigma Aldrich,99,8%); Oleic acid (Sigma Aldrich technical degree); NaOH (Sigma Aldrich 97,0%).

#### 5.1.3 Procedure

First,  $Ga(NO_3)_3$  and  $Zn(NO_3)_2$  were prepared from corresponding oxides. 2 mmol of  $Ga(NO_3)_3$ , 0.9995 mmol of  $Zn(NO_3)_2$  and 0.0005 mmol of  $Mn(NO_3)_2$  were mixed into 15 mL of H<sub>2</sub>O. The pH of the solution was adjusted to 10, using NaOH 1M solution. Then, 30 mL of toluene and 3 mL of oleic acid were added to the system. The reactional medium was transferred to a Teflon-lined stainless autoclaved and heated at 160 °C for

24 h. After colling, the ZGO nanoparticles were separated from the biphasic liquid medium using a centrifuge (5 min at 9000 rpm). Then, the solids were taken to the microwave-assisted annealing process and heated at 1150 °C for 30 minutes, using an synthesis microwave (PYRO). The final product is a white powder that presents an intense green afterglow after UV irradiation (Figure 5.1)



Figure 5.1: Pictures of ZGO under room light (left) and dark (right)

# **5.2 Results**

# 5.2.1 Structural and Morphological Characterization

The ZGO diffractogram pattern matches the reference JCPDS 38-1240, indicating that a pure material was obtained, with no phase segregation due to the presence of  $Mn^{2+}$ 

ions as dopants (Figure 5.2). Therefore, the procedure allowed the obtention of a pure ZGO phase



Figure 5.2: ZGO diffractogram pattern (black) and reference pattern for comparison (green).

Both SEM and TEM images of ZGO reveal the obtention of particles with an average size equal to *ca*. 62 nm, as shown on the ZGO-size histogram (Figure 5.3). The SEM images reveal the formation of sharp-distributed particles, with a cubical shape, like the ZGO spinel cubic unit cell geometry. Only a few agglomerates are present, but still it is possible to distinguish the nanoparticle forming the clusters, as it can be seen in higher resolution on TEM images.



Figure 5.3: (a) SEM and (b) TEM images of ZGO obtained from hydrothermal synthesis; (c) ZGO size histogram

### 5.4.2 Spectroscopic Characterization

The excitation spectrum exhibits a broad band centered at ca. 300 nm, which is an energy above the ZGO band gap energy (ca. 4.6 eV) <sup>79</sup> (Figure 5.4a). The emission spectra of Mn-doped ZGO show a band centered at 505 nm, characterized as  $Mn^{2+4}T_1 \rightarrow {}^{6}A_1$  spin-forbidden emission (Figure 5.4b). After 5 min charging at 300 nm, the ZGO presents an afterglow for up to 2 hours, emitting at 505 nm (Figure 5.5), which is appreciable in comparison to the previously reported works on ZGO afterglow,

showing persistence of 15 to 60 min  ${}^{61,80}$ . The mechanism for the persistent luminescence phenomenon on ZGO shows the (1) exciton excitation within band-gap energy, (2) energy transfer for defects, (3) thermal released of trapped energy on defects, (4) energy transfer from exciton emission center, and (5) radiative decay characterized as  $Mn^{2+4}T_1 \rightarrow {}^{6}A_1$  transition.



Figure 5.4: (a) Excitation spectra of ZGO, emission monitored at 505 nm; (b) emission spectra of ZGO, excitation monitored at 300 nm. Measurements were performed at room temperature.



Figure 5.5: Persistent Luminescence decay time of ZGO particles after 5 min charging at 300 nm, monitored at 505 nm.



Figure 5.6: Persistent Luminescence mechanism for ZGO materials

# 5.5 Conclusion

In this section of the investigation, nanoparticles of ZGO were obtained with a sharp distribution of approximately 60 nm. The ZGO nanoparticles also feature an enduring and bright afterglow in the green region, assigned as the  $Mn^{2+}$  transition. In comparison to previous works reported in the literature, one might conclude that the persistent luminescent properties of the obtained ZGO are well optimized, with an emission longer than 2 hours. These materials will be further discussed in Chapter 7, where it will be described the use of ZGO to produce transparent green-persistent films.

# Chapter6:SynthesisandCharacterizationofY2O2S:Eu3+,Ti,Mg (YOS)

#### 6.1.1 Microwave-Assisted Synthesis for YOS obtention

The red-emitter Y<sub>2</sub>OS<sub>2</sub>: Eu<sup>3+</sup>,Ti, Mg (5 mol-% of Eu<sup>3+</sup>, 1.5 mol-% of Ti and 4.5 mol-% of Mg<sup>2+</sup> in relation to Y) (YOS) material was obtained via collaboration with the PhD candidate Karina Torres, from Laboratório de Materiais Fotônicos (LMF) under the supervision of Prof. Dr. Lucas C. V. Rodrigues. Karina kindly agreed to participate in this current project by providing synthesized YOS produced by microwave-assisted solid-state synthesis. The methodology for YOS production was similar to the one reported by Carvalho *et al.*<sup>81</sup>, and presents the advantage of being an energy-saving and fast synthesis for complex inorganic materials achieving purity of phase within a few minutes of annealing. The Diagram 3 below shows a schematic representation for YOS obtention.



Diagram 3: Schematic representation of hydrothermal synthesis for ZGO obtention

#### 6.1.2 Materials

 $Y_2O_3$  (CSTARM, 99.99%), Eu<sub>2</sub>O<sub>3</sub> (CSTARM, 99.99%), S (Sigma-Aldrich, 99.5%), TiO<sub>2</sub> (Sigma-Aldrich, 99.5%) and MgCO<sub>3</sub> (Sigma-Aldrich, 99.5%), Na<sub>2</sub>CO<sub>3</sub> (Vetec, 99.5%) used as flux, in a  $Y_2O_3$ :Na<sub>2</sub>CO<sub>3</sub> mole proportion of 4:1. Excess of Sulfur was added to starting materials so that Y:S final proportion was 1:3.

#### 6.1.3 Procedure

The starting materials were well mixed and inserted in a crucible system containing the precursors and the microwave susceptor (12 g of granular carbon). The system was based on a two-step process. The first step consists of 900 W irradiation for 10 min. After cooling and grounding the materials, it is taken to the second step, irradiating with 800 W for 15 min. The final product is a white powder that presents an intense red afterglow after UV irradiation (Figure 5.1).



Figure 6.1: Pictures of YOS under room light (left) and in dark (right)

# 6.2 Results

The XRD for the YOS indicates the obtention of pure material from the previously described synthesis. The diffractogram matches the reference CDDC 198147 (Figure 6.2) <sup>82</sup>. Therefore, the dopants Eu<sup>3+</sup>, Ti<sup>3+/4+</sup>, and Mg<sup>2+</sup> do not interfere with the crystalline matrix phase.

The MASS procedure for the YOS production did not follow any particle-size controlling measure regarding the particle size. Therefore, large aggregates (in the scale

of some microns) were observed on SEM images – the single particles range around 1  $\mu$ m long. However, no homogenous size distribution is presented, as observed for SMSO and ZGO (Figure 6.3).



Figure 6.2: YOS diffratogram pattern (black) and reference pattern for comparison (red).



Figure 6.3: SEM images for YOS obtained from MASS method.

The excitation spectra show a broad band absorption (300~400 nm), with a maximum at ca. 330 nm which arises from the  $O^{2-} \rightarrow Eu^{3+}$  and  $S^{2-} \rightarrow Eu^{3+}$  ligand-to-metal charge transfer (LMCT) transitions (Figure 6.4). The emission spectrum of YOS materials show characteristic  $Eu^{3+}$  red emission peaks that arise from its intraconfigurational transitions  ${}^5D_0 \rightarrow {}^7F_1$  (580~590 nm) and  ${}^5D_0 \rightarrow {}^7F_2$  (615~630 nm), with a maximum at 625 nm. After 5 min charging at 330 nm, the YOS presents an intense red afterglow for up to 1 hour, emitting at 625 nm (Figure 6.5). The mechanism for Persistent Luminescence phenomenon present on YOS is shown in Figure 6.6, step (1) shows the formation of a hole on YOS valence band (VB), then (2) the hole is trapped on defects near to VB, (3) the hole is thermally released from the trap, (4) the energy is transferred to emission center  $Eu^{3+}$ , (5) the final radiative decay, resulting in the afterglow phenomenon. Compared to previous works, the afterglow duration for the obtained YOS is considered a satisfactory achievement, as other authors produced RE-doped Y<sub>2</sub>O<sub>2</sub>S compounds with similar emission time of approx. 1 hour emission <sup>41</sup>.



Figure 6.4: (left) Excitation spectra of YOS, emission monitored at 625 nm; (right) emission spectra of YOS, excitation at 330 nm. Measurements were performed at room temperature.



Figure 6.5: Persistent Luminescence decay time of YOS particles after 5 min charging at 330 nm, monitored at 625 nm.



Figure 6.6: Persistent Luminescence Mechanism for YOS materials.

#### 6.3 Conclusion

In this section of the investigation, YOS particles were obtained through a collaboration. The particles feature an intense afterglow in the red region, characteristic of  $Eu^{3+}$  transitions. These materials will be further discussed in Chapter 7, where it will be described the use of YOS to produce transparent red-persistent films.

# Chapter 7: Transparent Thin-Films Featuring Persistent Luminescence

#### 7.1 HPMC/PersL Films Preparation

For the composite preparation, the HPMC was used as the matrix. Among the advantages of using cellulose-based composites is the high abundance of the material, with an almost inexhaustible availability. HPMC compounds are also very soluble in pure water, allowing the use of a cheap and green solvent for the process of producing and casting films, and it is by far the most common cellulose for the fabrication of water-soluble matrices <sup>83</sup>. Also, the process of thin-film based on HPMC is well described in the literature <sup>76,84–86</sup>, producing films that do not feature any relevant optical property that could quench the emission from PersL materials, being optically transparent at the UV-Vis range. The cellulose used for the films production was the HPMC F4M (Methocel ®) (Figure 7.1), which presents a low viscosity in comparison to other grades of HPMC <sup>87</sup> facilitating the production of films through casting process.



R= H, CH<sub>3</sub> or CH<sub>2</sub>CH(OH)CH<sub>3</sub> Figure 7.1: Schematic representation of HPMC chemical structure

The procedure for the production of HPMC thin-films followed the drop-casting methodology, adapted from the process reported by Marani et al. <sup>76</sup>. Briefly, the adaptation is based on the inclusion of a inorganic material within the organic cellulose matrix. First, a 10 g/L solution of HPMC was prepared - by vigorous agitation over 5 hours. Then, to 5 mL of HPMC solution, different amounts of prepared PersL materials were added and vigorously stirred for 30 min at room temperature. After mixing, the

colloidal suspension was poured onto a silicon rubber surface (3.6 cm diameter; area  $\approx$  10 cm<sup>2</sup>) and left to dry for 24 hours at 50°C. Figure 7.2 below schematizes the described procedure. The results and specificities for each HPMC/PersL (PersL: SMSO, ZGO, or YOS) are shown in the following sections of this chapter.



Figure 7.2: Schematic representation of film casting procedure. (a) PersL particle; (b) schematic of HPMC/PersL suspensions; (c) representation of the chemical structure of HPMC surrounding PersL material; (d) picture of colloidal suspensions; (e) film cast onto a vitreous substrate under room light (top picture) and under UV-light (bottom picture).

#### 7.1.1 HPMC/SMSO

For the production of HPMC/SMSO, first, SMSO particles must be treated to become water-resistant since even though SMSO is resistant to moisture, it easily undergoes hydrolysis when exposed to water. To produce water-resistant SMSO material, it can be coated with APTES, a common process well-described in literature, not only for SMSO but for other photonic materials as well<sup>88,89</sup>. The coating methodology consists in adding 400 µL of APTES to 100 mg of SMSO in 10 mL of ethanol. This mixture is then

stirred for 24 hours. The APTES creates a shell with amino groups on the SMSO surface, protecting the particles from water without quenching the PersL properties.

For the obtention of HPMC/SMSO, different amounts of SMSO@APTES were added to 5 mL of HPMC solution (0, 1, 5, 10, 50, 100 mg), and the optical properties of each material were studied. The nominal concentration of each film was normalized by the area of the substrate (10 cm<sup>2</sup>). Therefore, the HPMC/SMSO materials produced are hereinafter named 0 g/m<sup>2</sup>, 1 g/m<sup>2</sup>, 5 g/m<sup>2</sup>, 10 g/m<sup>2</sup>, 50 g/m<sup>2</sup>, 100 g/m<sup>2</sup>. The colloidal suspension for the preparation of each composite has a visual increase in its opacity; this same trend is observed in the film of each composite (Figure 7.3).



Figure 7.3: (a) Photographies of HPMC/SMSO 0, 1, 5, 10, 50 and 100 g/m<sup>2</sup> suspensions; (b) photographies of films under room-light and under UV-light irraditation (365 nm).

The FTIR spectra of the SMSO and the resulting composite are presented in the Figure 7.4. Intense bands ranging from 550  $cm^{-1}$  to 983 cm<sup>-1</sup> are assigned to Si-O vibrations: 983  $cm^{-1}$  band assigned to the Si-O-Si asymmetric stretch; 835 and 693  $cm^{-1}$ 

bands assigned to Si-O symmetric stretching. They are all present in the three spectra of SMSO, SMSO@APTES and SMSO@APTES/HPMC <sup>90</sup>. The presence of APTES forming a silica-like shell is evident by the presence of the vibrational modes related to NH<sub>2</sub> and CH<sub>2</sub> in the SMSO@APTES SMSO@APTES/HPMC spectra. The band at 3400  $cm^{-1}$  is attributed to the asymmetric stretching of NH<sub>2</sub> in amines. The bands at 2917  $cm^{-1}$  and 2837  $cm^{-1}$  are assigned to stretching modes of CH<sub>2</sub> at alkanes and the 1562 cm<sup>-1</sup> assigned to the N-H bending of the amine groups <sup>91</sup>. A more detailed analysis of the Sr<sub>2</sub>MgSi<sub>2</sub>O<sub>7</sub> was made by Salim *et al.* and, based on their work, the majority of the bands of our material is presented in table 7.1 <sup>92</sup>.



Figure 7.4: FTIR spectrum of SMSO NPs (blue), SMSO@APTES NPs (green) and Composite (red).

Attribution	Energy <i>cm</i> <sup>-1</sup>
Si-O symmetric stretching	693
Si-O symmetric stretching	835
Si-O-Si asymmetric stretching	983
Sr-O-Si bending	1460
N-H bending	1580
Mg-O-Si stretching	1640
C-H stretching alkane	2837
C-H stretching alkane	2917

Table 7.1. Attribution of the Main Vibrational Bands of SMSO, SMSO@APTES and SMSO@APTES/HPMC.

To quantify the transparency of each film, their transmittance was recorded and is shown in Figure 7.5a. One might note that the transmittance of each compound lowers as the concentration of SMSO on HPMC increases. Hence the visual aspect of transparency is the one this investigation is looking up to, the average transmittance in the visible range (400 ~ 700 nm) is considered (Figure 7.5b). The transmittance for the films 0, 1, 5, 10, 50, and 100 g/m<sup>2</sup> are (approx.) 82%, 62%, 36%, 11%, 1%, and 0.3%, respectively.



Figure 7.5: (a) Transmittance of HPMC/SMSO films ranging from 200 - 800 nm; (b) mean transmittance in the visible range (400 - 700 nm).

Regarding the luminescent properties, the excitation spectra of SMSO (Figure 7.6), SMSO@APTES, and HPMC/SMSO all feature the broad band assigned to Eu<sup>2+</sup>  $4f^7$  ( ${}^8S_{7/2}$ )  $\rightarrow 4f^65d^{1}({}^2D)$  absorption. One can observe that the bands are very similar with a small shift in the film composite. The emission spectra for all materials are also similar, exhibiting the broad band ascribed to  $4f^65d^{1}({}^2D) \rightarrow 4f^7$  ( ${}^8S_{7/2}$ ) transition have similar band shapes.. The only difference is that the emission spectra of SMSO@APTES and HPMC/SMSO present a sharper band when compared to the SMSO spectrum. The transition from the emission band ( $4f^65d^{1}({}^2D) \rightarrow 4f^7$ ) is very sensitive to vibronic effects, therefore, the particle's surface can significantly influence the emission spectra shape. The broader emission of SMSO can be explained based on this effect since SMSO particles are on the nanoscale. The APTES coating creates Si-O groups along the surface of the nanoparticles, which can lead to diminished surface energy, lowering the vibronic influence on the emission band, resulting in a sharper band.



Figure 7.6: (left) excitation spectra of SMSO, SMSO@APTES, and HPMC/SMSO, with emission monitored at 475 nm, and (right) emission spectra of SMSO, SMSO@APTES and HPMC/SMSO with excitation fixed at 350 nm.

The afterglow decay time for the films was measured at room temperature, with 5 min of charging at 350 nm (UV) and excitation monitored at 475 nm (blue) (Figure 7.7). The total decay time was determined by considering the moment in which the decay curve matches the measurement background reading. For the films 0, 1, 5, 10, 50, and 100 g/m<sup>2</sup>, the total decay times are 0 min, 5 min, 15 min, 80 min, 90 min, and 90 min.



Figure 7.7: Afterglow decay time of SMSO/HPMC thin films.

Even though the afterglow decay time is an intrinsic property of PersL materials, and therefore, usually does not change in function of the PersL mass, it has been reported that PersL composites may have a variation on its absolute photons' storage, and therefore its brightness in comparison to the pure photonic solid. Van der Heggen reported that this variation is due to two major effects: (1) the small number of absorbed and emitted photons per area, and (2) shadowing effects <sup>51</sup>. The number of photons absorbed/emitted per area are more significant on films of low SMSO concentration (*i.e.* [SMSO]  $\leq 5$  g/m<sup>2</sup>) - a low SMSO concentration on HPMC composites results in fewer photons being absorbed and emitted per area of films, and therefore fewer number of photons being

captured by the detector. This effect can also be perceived by human vision, given that low concentrated composites appear to be more dim under UV-light (see Figure 7.3). The shadowing effect is most prominent at high SMSO concentration (i.e. [SMSO]  $\geq 10$  g/m<sup>2</sup>) - as the SMSO concentration increases, the surface area of the films saturates, and the shadow cast by the particles over each other hampers the absorption of light, as well as blocks the path towards the detectors of emitted photons, given the reason the PersL decay time of composites only increased up to 90 min with increasing SMSO concentration. The particles saturation also plays a significant role in film thickness, which increases in function of SMSO concentration in the HPMC matrix. For the 0, 1, 5, 10, 50, 100 g/m<sup>2</sup> films, the thickness is 12, 23, 29, 32, 104, and 105 µm, respectively (Figure A.1).

Comparing the PersL decay time of the films with different SMSO concentrations and the mean opacity in the visible range, one might notice they follow similar trends: as the SMSO concentration increases from 1 to 100 g/m<sup>2</sup>, both the PersL decay time and the opacity increases up to saturation points (90 min for the PersL time and 99% of opacity) (Figure 7.8). The point of saturation is close to 10 g/m<sup>2</sup>, which leads to the conclusion that this could be considered an optimal point when the goal is to produce transparent HPMC/SMSO films with the maximum emission time possible (Figure 7.8). However, the other SMSO concentration should not be disregarded. The films 1g/m<sup>2</sup> and 5g/m<sup>2</sup> have the advantage of greater transparency, even though the PersL bright is dimmer when compared to other films' concentration, but are still visible (Figure 7.9a-d). For instance, low concentrated SMSO/HPMC films that could be applied to commercial products are a counterfeiting material. On the other hand, high concentrated SMSO/HPMC films lack the transparency feature, but they have a brighter PersL emission when compared to others and still remain significant flexibility (Figure 7.9g-h)



7.8: Relationship between Concentration of SMSO on HPMC/SMSO films to their opaqueness and persistent luminescence period until fading.



Figure 7.9: Photography of HPMC/SMSO composites. (a) 1 g/m<sup>2</sup> under room light and (b) showing its afterglow and transparency. (c) HPMC/SMSO 10 g/m<sup>2</sup> folded under room light and (b) showing its afterglow, transparency, and flexibility. (e) unfolded and (f) folded HPMC/SMSO 1 g/m<sup>2</sup>. (g) folded HPMC/SMSO 100 g/m<sup>2</sup> under room light and (h) under UV light.

In order to characterize the homogeneity of the particle distribution in the films, X-Ray fluorescence (XRF) mapping and Scanning Transmission X-Ray Microscopy (STXM) were performed at Carnauba beamline - Sirius Synchrotron Facility (Campinas, Brazil), in collaboration with Dr. Verônica de Carvalho Teixeira. The use of Synchrotron light in this stage of the investigation is essential to analyze, with high definition, how the nanoparticles are dispersed in the cellulose-based composites. The nanofocused-beam facility provides characterization with a resolution of 100 nm by pixel. The microscopic study of the nanomaterials dispersion in cellulose-based composites is a hard task, as stated by Oksman and Moon <sup>93</sup> due to the low contrast in TEM images, requiring staining procedures with high atomic number compounds like uranyl acetate. Besides, analyses like SEM and AFM are limited to surface characterization.

The STXM images were registered under irradiation energy of 9.656 keV, which is above the L-edges of the Eu, Dy, and Sr, and above K-edge of Al, Si, Mg, and O. First, for  $1g/m^2$  film, the image in low magnification (pixel size: 5 µm) shows a homogeneous absorption all over the scanned area (Figure 7.10a1). The beam size is very close to the nanoparticle size. Therefore, it is only possible to have a good definition of larger structures within the film, and one might see that on higher magnifications (pixel size: 500 nm or 100 nm), small agglomerates are present with approx. size of 6 µm (Figure 7.10a2 and Figure 7.10a3). Since prior to film casting, the SEM images of SMSO did not show any presence of particles in this range of size, the presence of agglomerates in the film might have occurred during the casting process. A few water pockets may be created on the HPMC matrix, resulting in the accumulation of nanoparticles during the drying process. XRF mapping was created by integrating the XRF spectra scanned through the films (Figure A.2) regarding the dispersion of Eu (Figure 7.10b), Dy (Figure 7.10c), and Eu+Dy (Figure 7.10d), revealing that the dopants are homogeneously and equally distributed in the films, as well as they show signals on the same spots, indicating that the particles did not degrade during the drop-casting process.

For the 10 g/m<sup>2</sup> film, a similar aspect is observed. The film has a homogenous signal within the scanned area, and in higher magnification, it is possible to identify

agglomerates in the size of ca. 6  $\mu$ m. One might notice that the higher SMSO concentration in 10 g/m<sup>2</sup> results in high concentration of signals, but still, the SMSO particles are still homogeneously dispersed (Figure 7.11). On the other hand, for the 100 g/m<sup>2</sup> film, an uneven signal distribution is seen at low magnification, indicating that the high SMSO concentration led to a non-homogeneous particle distribution, and there are no empty spaces on the mapping (black space), which explain the opacity of the film (Figure 7.12).



Figure 7.10: Figure 5: (a) STXM of SMSO@APTES/HPMC 1 g·m<sup>-2</sup> film at 9.656 keV. (b-d) XRF mapping of SMSO@APTES/HPMC 1 g·m<sup>-2</sup> film at (b) Eu L $\alpha$  (5.845 *keV*); (c) Dy L $\alpha$  (6.495 *keV*); (d) Eu and Dy L $\alpha$  lines under 9.656 *keV* excitation



Figure 7.11: a) STXM of SMSO@APTES/HPMC 10 g·m<sup>-2</sup> film at 9.656 keV. (b-d) XRF mapping of SMSO@APTES/HPMC 10 g·m<sup>-2</sup> film at (b) Eu L $\alpha$  (5.845 *keV*); (c) Dy L $\alpha$  (6.495 *keV*); (d) Eu and Dy L $\alpha$  lines under 9.656 *keV* excitation



Figure 7.12: a) STXM of SMSO@APTES/HPMC 100 g·m<sup>-2</sup> film at 9.656 keV. (b-d) XRF mapping of SMSO@APTES/HPMC 100 g·m<sup>-2</sup> film at (b) Eu La (5.845 *keV*); (c) Dy La (6.495 *keV*); (d) Eu and Dy La lines under 9.656 *keV* excitation

#### 7.1.2 HPMC/ZGO

The production of HPMC/ZGO followed a similar methodology as described for the blue-emitting film - different amounts of ZGO were mixed with HPMC solution and drop-casted for film production, but in this case no APTES coating was applied. In the case of HPMC/ZGO, the concentrations 0.1 g/m<sup>2</sup>, 1 g/m<sup>2</sup>, and 10 g/m<sup>2</sup> of ZGO in HPMC films were chosen based on the in-depth study of HPMC/SMSO films. Therefore, HPMC/ZGO film production is an extension of the previously optimized method, with the main objective of obtaining a green-emitter transparent thin film. In this subsection, the nomenclatures 0.1 g/m<sup>2</sup>, 1 g/m<sup>2</sup>, and 10 g/m<sup>2</sup> refer to ZGO concentration on HPMC/ZGO films. The produced HPMC/ZGO films are white-colored under room light, green-colored under UV-light and feature a green PersL emission (Figure 7.13). Qualitatively, the films  $0.1 \text{ g/m}^2$  and  $1 \text{ g/m}^2$  are transparent, both under room light and under its own PersL emission (Figure 7.14A-B), while the 10 g/m<sup>2</sup> film has an aspect of an uneven surface, which results in a significant light scattering and, therefore, low transparency (Figure 7.14C). The transmittance spectra for the three films are all below 25%, with mean transmittance at visible range at 23.76%, 23.44% and 19.83%, respectively (Figure 7.15). The film thickness also increases as the concentration of ZGO increases. For the HPMC/ZGO films of 0.1, 1, and 10 g/m<sup>2</sup> the thickness are 18, 24, and 30 µm (Figure A.3).



Figure 7.13: Photographs of 1g/m<sup>2</sup> HPMC/ZGO composites under (a) room light, (b) UV-light, and (c) dark. Photographs of 10 g/m<sup>2</sup> HPMC/ZGO composites under (a) room light, (b) UV-light, and (c) dark.



Figure 7.14: Photographs of 0.1g/m<sup>2</sup> HPMC/ZGO composites under (A1) room light, (A2) UV-light, and (A3) dark. Photographs of 1 g/m<sup>2</sup> HPMC/ZGO composites under (B1) room light, (B2) UV-light, and (B3) dark. Photographs of 10 g/m<sup>2</sup> HPMC/ZGO composites under (B1) room light, (B2) UV-light, and (B3) dark.



Figure 7.15: Transmittance of HPMC/ZGO films ranging from 200 - 800 nm

Regarding the luminescence properties, HPMC/ZGO excitation and emission profile are similar to the one described for pure ZGO (Figure 7.16). The excitation spectrum is centered at 300 nm, above ZGO bandgap energy, however, the emission spectrum is blue-shifted, approx. 3 nm. This shift in emission spectra is probably due to the change in the surface chemical environment of ZGO, which is surrounded by HPMC molecules. Since ZGO are nanoparticles of approx. 60 nm it has a great surface area, which might explain the large effect that the energy surface might play on the ZGO electronic transition. Nonetheless, the emission maintains its green color even with this small shift.

The afterglow decay time for HPMC/ZGO, measured at room temperature, was monitored at 500 nm, which is the max emission point for the composites, after 5 min charging at 300 nm for 5 min (Figure 7.17). The total decay time was quantified by considering the moment that the decay curve matches the background signal. For the films 0.1, 1, and 10 g/m<sup>2</sup>, the total decay time is 5, 25, and 120 minutes, respectively. The

0.1 and 1 g/m<sup>2</sup> composites have a shorter PersL decay time, when compared to the pure ZGO solid, which is explained by the fewer photons absorbed and emitted by area. In the case of the 10 g/m<sup>2</sup> film, its decay time is closer to the pure ZGO - this similarity is unexpected, having in mind the shadowing effects roles in PersL composites. However, this unexpected result might rely on the ZGO particle size (60 nm), which is small enough to avoid one nanoparticle's shadow over others.



Figure 7.16: (a) excitation spectra of ZGO and HPMC/ZGO, with emission monitored at 505 nm. (b) emission spectra of ZGO and HPMC/ZGO with excitation fixed at 300 nm



Time (hour) Figure 7.17: Afterglow decay time of SMSO/ZGO thin films.

#### 7.1.3 HPMC/YOS

The production of HPMC/YOS followed the same methodology as described for HPMC/ZGO films. Also, the red-emitting film preparation extends the previously optimized study, aiming to obtain a red-emitter transparent thin film. Similar to HPMC/ZGO, the YOS concentrations studied are 0.1 g/m<sup>2</sup>, 1 g/m<sup>2</sup>, and 10 g/m<sup>2</sup>. Hereinafter, in this subsection, the nomenclatures 0.1 g/m<sup>2</sup>, 1 g/m<sup>2</sup>, and 10 g/m<sup>2</sup>. Under room light, HOMC/YOS films are white-colored, emitting a red light under UV irradiation, and feature a red afterglow in the dark (Figure 7.18).



Figure 7.18: Pictures of HPMC/YOS 10g/m<sup>2</sup> under room light, UV-light, and dark.

Qualitatively, the produced HPMC/YOS films have an even surface aspect and significant transparency. It is noticeable that the film's transparency is present even when the only light available in the room is its red persistence luminescence emission (Figure 7.19). Quantitatively, the transmittance spectra for HPMC/YOS composites have a total transmittance ranging above 20% for the 0.1 g/m<sup>2</sup> film, 12% for the 1 g/m<sup>2</sup> film, and 9% for the 10 g/m<sup>2</sup> film – and with a mean transmittance on the visible range (400 – 700 nm) equals 25.7%, 18.3%, and 9.4%, respectively (Figure 7.20). The HPMC/YOS films 0.1, 1, and 10 g/m<sup>2</sup> features a thickness equal to 26, 32, 43  $\mu$ m (Figure A.4)


Figure 7.19: Pictures of HPMC/YOS  $10g/m^2$  under room light, UV-light, and dark.



Figure 7.20: Transmittance of HPMC/YOS films ranging from 200 - 800 nm

Regarding the luminescence and persistent luminescence properties of HPMC/YOS, one might notice that the excitation and emission profile are similar to the one presented for the pure YOS. The excitation spectrum has a maximum at 330 nm, described by the  $O^{2--} \rightarrow Eu^{3+}$  transition, while emission spectra show  ${}^{5}D_{0} \rightarrow {}^{7}F_{1}$  and  ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$  transition (Figure 7.21).



Figure 7.21: (a) excitation spectra of YOS and HPMC/YOS, with emission monitored at 625 nm. (b) emission spectra of YOS and HPMC/YOS with excitation fixed at 330 nm

Differently from the other two films produced, HPMC/SMSO and HPMC/ZGO, no shift or sharpening in the emission spectra was observed. This is due to the fact that Eu<sup>3+</sup> 4f<sup>N</sup> are shielded from the chemical environment by the 5s<sup>2</sup> and 5p<sup>6</sup> orbitals. This orbital protection hampers 4f orbitals with the ligand field and with the surface effects, leading to Eu<sup>3+</sup> transitions in an inorganic matrix to be very similar to its ionic properties <sup>94</sup>. However, one might observe the excitation band is lowered in the region below 300 nm, which is due to the absorption of HPMC at the same UV region, lowering the number of photons available to be absorbed by the YOS dispersed the HPMC matrix.

The persistent luminescence decay time for HPMC/YOS composites is shorter than the PersL decay time of pure YOS. Just as with the HPMC/SMSO and HPMC/ZGO

films, the reduction in the PersL decay time in films with low YOS concentration is due to a decrease in photons absorbed and emitted by the luminescent material within the film. This time increases as the concentration of YOS increases accordingly, being ca. 10 min, 15 min, and 20 min for the 0.1 g/m<sup>2</sup>, 1g/m<sup>2</sup>, and 10 g/m<sup>2</sup> films, respectively (Figure 7.22). Furthermore, the shadowing effect is expected to be very significant due to the particle size of YOS, which is not in the nanoscale, and therefore, it is more likely for one particle to cast a shadow over others, hampering the absorption of photons during the irradiation and the path to the detector during the emission.



Figure 7.22: Afterglow decay time of SMSO/YOS thin films.

The table below summarizes the results of the optical properties of the films.

Table 8.1: Results Summary of Transparent Persistent Luminescent Films based on HPMC         Matrix and PersL Materials.				
PersL material (approx. max emission wavelength)	Concentration on film (g/m²)	Thickness (µm)	Mean Transmittance on Visible Range	PersL Total Decay Time (min)
	Pure solid	-	-	180
	1	23	82%	5
Sr <sub>2</sub> MgSi <sub>2</sub> O <sub>7</sub> :Eu <sup>2+</sup> ,Dy <sup>3+</sup>	5	29	62%	15
(ca. 475 nm)	10	32	36%	80
	50	104	1%	90
	100	105	0.3%	90
	Pure solid	-	-	120
ZnGa <sub>2</sub> O <sub>4</sub> :Mn <sup>2+</sup>	0.1	18	23.7%	5
(ca. 505 nm)	1	24	23.4%	25
	10	30	19.8%	120
	Pure solid	-	-	60
Y2O2S:Eu <sup>3+</sup> ,Ti <sup>2+</sup> ,Mg <sup>2+</sup>	0.1	26	25.7%	10
(ca. 625 nm)	1	32	18.3%	15
	10	43	9.4%	20

# **Chapter 8: Conclusions**

# 8.1 Conclusion

As aforementioned, the state-of-the-art of persistent luminescence materials are currently aiming the production of materials or composites for advanced applications. This thesis meets this research trend, as it shows the obtention of a novel material featuring transparency and persistent luminescence. A transparent and flexible materials featuring persistent luminescence, as the set of materials prepared and characterized in this thesis, improve the possible applications of regular PersL compounds. The relationship of transparency versus concentration of particle per meter square of film allows further research on applicability for each scenario. For instance, high transparency might be required (such as bioreactors or counterfeiting applications) even if it compromises the emission, in the another hand, high emission is required, even if the transparency is compromise (such as in the use on sensors).

Overall, with the achievement of all proposed goals for this thesis, it was possible to obtain a state-of-art methodology to produce transparent films featuring persistent luminescence. The study of particle concentration within an organic matrix was crucial to understand the relationship of the optical luminescent phenomenon on transparent hybrid materials. The results presented here are promising to unravel new applications that would take advantage of the transparency and the photonic property of the materials. HPMC is one of the best candidates for film production, regarding not only its chemical and physical properties, but also considering environmental causes, as it is an abundant material, easily degradable, and non-toxic to humans. Certainly, novel projects and researchers will emerge from the novelty presented here.

In more details, three novel transparent persistent luminescent thin films were successfully obtained based on the dropping-casting procedure, having HPMC as the matrix of the composite and different concentrations of each PersL material. First, the method was optimized for the HPMC/SMSO composites, and then the methodology was expanded to the other two photonic compounds,  $Sr_2MgSi_2O_7$ :Eu<sup>2+</sup>,  $Dy^{3+}$ ,  $ZnGa_2O_4$ :Mn<sup>2+</sup>,  $Y_2O_2S:Eu^{3+},Ti,Mg$  (Figure 8.1). The persistent luminescent material and Sr<sub>2</sub>MgSi<sub>2</sub>O<sub>7</sub>:Eu<sup>2+</sup>,Dy<sup>3+</sup> was successfully obtained through a novel optimized coprecipitation route combined with a microwave-assisted annealing system. The obtained SMSO materials feature a sharp and homogenous size distribution with a mean size 245 nm. The solid features a bright emission at the blue region, with a persistent luminescence enduring for up t0 3 hours after charging with UV-light. The persistent luminescent material ZnGa<sub>2</sub>O<sub>4</sub>:Mn<sup>2+</sup> was successfully obtained by an adapted biphasic hydrothermal route. The obtained ZGO materials have a homogenous size distribution centered at 62 nm. ZGO features a persistent band emission in the green region, enduring for up to two hours. Lastly, the red-emitter Y<sub>2</sub>O<sub>2</sub>S:Eu<sup>3+</sup>,Ti,Mg were prepared through a microwave-assisted annealing route. YOS materials feature an enduring red emission lasting up to 60 minutes.



Figure 8.1: Persistent Luminescence Emission HPMC/SMSO, HPMC/YOS, and HPMC/ZGO films

**Chapter 9: References** 

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# Appendix: Supplementary Information



Figure A.1: HPMC/SMSO thickness in function of SMSO concentration



Figure A.2: XRF spectra for HPMC/SMSO (a)  $1g/m^2;$  (b)  $10\ g/m^2;$  and  $100\ g/m^2$ 



Figure A.3: HPMC/ZGO thickness in function of SMSO concentration



# **Academic Curriculum Vitae**

# PERSONAL INFORMATION

Name: Douglas Lourenço Fritzen Researcher unique identifier: <u>000-0003-3385-0506</u> Date of birth: August 13, 1996 Nationality: Brazilian

# • EDUCATION

02/08/2022 Successful PhD Defence ("viva") PdD Thesis Title: Transparent Films Featuring Persistent Luminescence Institute of Chemistry, University of São Paulo, Brazil Supervisor: Prof. Dr. Lucas Carvalho Veloso Rodrigues

# • **PREVIOUS POSITIONS**

11/08/2022 – 11/09/2022 Visiting Researcher Department of Chemistry, University of Turku (UTU), Finland

08/12/2015 – 15/02/2016 Visiting Research Student Department of Chemistry, University of Victoria (UVIC), Canada

01/02/2014 – 08/02/2019 Undergraduate Student Ranked in the top 3 among 63 students. Institute of Chemistry, University of São Paulo (USP), Brazil

# • FELLOWSHIPS AND AWARDS

11/08/2022 – 11/09/2022 Visiting Researcher Funder: University of Turku (UTU)

01/07/2019 – 02/08/2022 Ph.D. Funding Funder: Sao Paulo State Research Support Foundation (FAPESP)

01/08/2016 – 31/07/2017 Undergraduate Researcher Scholarship Funder: Sao Paulo State Research Support Foundation (FAPESP)

08/12/2015 – 15/02/2016 Award: Academic Merit Scholarship Funder: Institute of Chemistry, University of Sao Paulo

01/08/2015 – 31/09/2016 Undergraduate Researcher Scholarship Funder: Brazilian Council for Scientific and Technological Development

#### • INSTITUTIONAL RESPONSIBILITIES

- 01/06/2021 01/12/2021 Supervisor: Scientific Initiation of Undergraduate Researcher Title of the project: "Obtention and characterization of SrS:Eu<sup>2+</sup> nanophosphors"
- 01/02/2020 01/07/2020 Supervisor: Scientific Initiation of Undergraduate Researcher Title of the project: "Synthesis optimization and optical properties of persistent luminescence  $Mn^{2+}$ -doped ZnGa<sub>2</sub>O<sub>4</sub> nanophosphors"
- 01/06/2019 01/12/2019 Supervisor: Scientific Initiation of Undergraduate Researcher Title of the project: "Size-controlling synthesis of SrAl<sub>2</sub>O<sub>4</sub>: Eu<sup>2+</sup>, Dy<sup>3+</sup> phosphors"
- 01/07/2019 30/11/2019 Teacher Assistant Teaching Improvement Program Teaching Unit Inorganic Chemistry I Institute of Chemistry, Fundamental Chemistry Department, USP, Brazil
- 01/03/2019 30/06/2019 Teacher Assistant Teaching Improvement Program Teaching Unit Fundamentals of Experimental Chemistry Institute of Chemistry, Fundamental Chemistry Department, USP, Brazil

# • ORGANISATION OF INTERNATIONAL CONFERENCES

- 11/10/2014Member of the organization team of "Virada Cientifica".Brazilian event with 24 hours of scientific shows for general audience
- PRESENTATIONS AND PARTICIPATION ON INTERNATIONAL CONFERENCES

29/08/2022 – 02/09/2022 Poster presentation, entitled "Transparent Films Featuring Persistent

*Luminescence*", in the 6<sup>th</sup> International Conference on the Physics of Optical Materials and Devices

04/04/2020 – 07/04/2020 Poster presentation, entitled "Synthesis optimization and optical properties of persistent luminescence  $Mn^{2+}$ -doped  $ZnGa_2O_4$  nanophosphors", in the 2<sup>th</sup> Pan-American Nanotechnology Conference.

07/07/2017 – 14/07/2017 Poster presentation, entitled "Synthesis of Trivalent Rare Earths Co-Doped LaAlO<sub>3</sub>: Cr<sup>3+</sup> Nanoparticles with Infrared Persistent Luminescence", in the 46th World Chemistry Congress and IUPAC 49th General Assembly.

07/08/2014 – 10/08/2014 Participation on "VIII Encontro de Teatro e Divulgação Científica Ciência em Cena", a science communication conference, aiming to assemble theatre groups of Brazilian and European universities for exchanging ideas and experiences.

# • COMMUNICATION ACTIVITIES AND SOCIAL IMPACT

28/05/2021 Production of a popular science short video for USP, available on YouTube. The video has the purpose of reaching the general audience and to explain, in a simplified language, the PhD research of the Dr. Douglas Fritzen. Available at: https://youtu.be/bYyViwWoqJE

01/03/2014 - 01/12/2018 Member of the Science Theater Group, *Química em Ação*, from the Institute of Chemistry of the University of São Paulo, organizing and performing popular science shows for high school students.

# • PUBLICATIONS IN PEER-REVIEWED SCIENTIFIC JOURNALS

# (1) "Flexible Translucent Persistent Luminescent Films Based on Sr2MgSi2O7:Eu2+,Dy3+ Cellulose Ether Composites" Journal: Dalton Transactions

**Date of publication:** May 25, 2022 **DOI:** 10.1039/D2DT00770C

**Qualitative Assessment:** article representing the most-recent development on translucent persistent luminescent films, developed during my Ph.D. research. This article report advances on the applications and perspectives of persistent luminescent material applications, especially regarding the novel feature, translucency, which can be further used on light-harvesting (charging with sunlight), light conversion (absorption of UV light and emission of blue light), and on mechanisms/systems that requires a continuous light source (*e.g.*, greenhouse, catalytic process).

# (2) "Opportunities for Persistent Luminescent Nanoparticles in Luminescence Imaging of Biological Systems and Photodynamic Therapy"

Journal: *Nanomaterials* Date of publication: October 13, 2020

**DOI:** 10.3390/nano10102015

**Qualitative Assessment:** This review highlights the current developments on persistent luminescence materials, focusing on its novel applications on biological systems and photodynamic therapy. This review represents the interdisciplinary approach provided by the solid-state materials and the properties of the persistent luminescence compounds.

# • PUBLICATIONS AS A BOOK CHAPTER

(3) "Light Storage Perovskites: Synthesis, Mechanisms, and Applications" Publisher: Elsevier, 2022
To be published: November 10, 2022
ISBN: 9780323905862

**Qualitative Assessment:** This publication refers to a chapter written to compose the book "Perovskite Ceramics: Recent Advances and Emerging Applications". The chapter consists of a review of the state-of-art on research topic of light storage perovskites, presenting the recent advances on its synthesis, mechanism, as well as current and prospective applications.