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Recent advances in lanthanide spectroscopy in Brazil

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1. Introduction

The great interest in trivalent lanthanide (Ln3+) compounds is in part due to their strong luminescence observed in a broad spectral range and to their long-lived excited states. For this reason, lanthanide compounds have been used in a variety of applications involving sol–gel, glasses, light-emitting diodes (LEDs), metal–organic frameworks (MOFs), among others. In many investigations of lanthanide-based systems, experimental measurements are interpreted with the help of theoretical models, through which properties and processes of excited and ground states are also described [1]. The development of new theoretical models and methodologies in this field has been shown to be very important in the last decades, since they nicely complement and enrich experimental investigations, as well as guide new experiments. Theoretical models addressing energy transfer processes [2,3], ligand field interactions [4], electronic transitions [5], chemical bond properties [6], geometry optimization [7], among others [1], have been extensively used due to their large applicability to this research field. Many of these theoretical models and investigations carry the name of Prof. Oscar L. Malta, who has done pioneering work in the field of lanthanide spectroscopy in Brazil for almost four decades, and whose contributions are also internationally recognized.

The aim of this review is to describe the recent advances in the field of lanthanide luminescence in Brazil and to highlight the important contributions of Prof. Malta in honor of his 60th birthday. The revised topics include glasses, sol–gel, LEDs, nanoparticles, crystals, metal–organic frameworks, coordination polymers, thin films, energy transfer, upconversion, and the development of theoretical methods. Spectroscopic treatments in general are discussed inside each topic.

2. Results and discussion

This review describes the work published in the last decade (2005–2014) on lanthanide luminescence by brazilian corresponding authors. The bibliographic search under these conditions has given up to date 235 publications. This number would be 284 if one considered publications involving brazilians without the restriction of brazilian corresponding authorship. However, discussing these additional investigations is out of the scope of this review.

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These international publications came from collaborations between Brazil and other countries, such as Germany, England, France, Canada, Finland, Switzerland, Spain, South Korea, Poland, Italy, Portugal, India, Turkey, Serbia, and China. The published work selected here is described in the frame of the research topics shown in the keywords of this paper. Before going into detail about each topic, it might be instructive to get a general picture of the distribution of the scientific production of the last decade found in the field of lanthanide luminescence (235 papers) over different states and cities of Brazil (Fig. 1). Note that the background picture is a recent photo of Prof. Oscar L. Malta, which is justified by his expressive participation in about 11% of the whole Brazilian scientific production in that period, as well as by the fact that his theoretical models and findings are cited in almost all analyzed publications.

From the distribution of published papers per state, São Paulo (SP) has the highest production, followed by Pernambuco (PE). This may be due to a very large number of universities and much larger investment in science in the former. The scientific production per city delivers a much sharper picture of where science is mostly applied in this field. The capital of Pernambuco state, Recife, is highly active, even surpassing the production of the city of

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but also by the presence of Prof. Malta there, which has been
influencing different generations of scientists and directly con-
tributing to different investigations on several topics as well.

The papers discussed in Fig. 1 can also be organized in terms of
the journals where they were published, as shown in Fig. 2. Most
investigations were published in the Journal of Luminescence,
followed by the Journal of Applied Materials.

The scientific production shown in Fig. 1 is now divided into
the topics shown below. Many publications are discussed in the
frame of two or more topics.

2.1. Energy transfer

More than 40% of the publications shown in Fig. 1 describe
experimental and/or theoretical investigations of lanthanide-

Fig. 4. Intermolecular and intramolecular energy transfer paths involving two
lanthanide complexes. (Reproduced with permission from Ref. [11].)

Fig. 5. Comparison between the (a) crystallographic and (b) Sparkle/PM3-opti-

Fig. 6. Emission spectra of $\text{Y}_2\text{O}_3\text{Er}^{3+}$(0.1%),$\text{Yb}^{3+}$(1%) and $\text{Y}_2\text{O}_3\text{Er}^3^+$(0.5%),
$\text{Yb}^{3+}$(1%) prepared from a polymeric precursor, under excitation at 980 nm
($\text{Yb}^{3+}-\text{F}_{2}^{3/2} \rightarrow \text{F}_{4}^{15/2}$ transition). (Reproduced with permission from Ref. [12].)

São Paulo. This is not only explained by the tradition of the sci-
entific community of Recife in investigating lanthanide systems,
but also by the presence of Prof. Malta there, which has been

The investigation of non-radiative ET involving lanthanide ions
has been described in Ref. [10] and has attracted much attention
since its publication. This work is better discussed in Section 2.2,
since it involves ion-to-ion ET processes, which occur during up-
conversion phenomena.

The role played by ligand-to-metal charge transfer (LMCT)
states in intramolecular ET processes taking place in lanthanide
complexes was discussed by Faustino et al. [8] and has been often
quoted by the lanthanide community. Fig. 3 shows a schematic
energy level diagram of one of the investigated systems, where $\Phi$
was analyzed as a function of the relative energy of the LMCT state in a typical Eu³⁺ compound.

Theoretical investigations calculate intensity and ligand field parameters, as well as ET rates of lanthanide compounds aiming at comparing the results with experimental data. This allows one to validate and optimize the theoretical parameters. In this context, Freire et al. [15] have done a theoretical investigation on the luminescence of Eu³⁺ cryptates with high $\Phi$ values. This work used the Judd–Ofelt theory to calculate intensity parameters and the model proposed by Malta et al. [2,3] to calculate ET rates between metal and ligand, from where $\Phi$ could be predicted and compared with the experimental one. Teotonio et al. [16] carried out a theoretical–experimental investigation of the ET process of a $\beta$-diketonate Eu³⁺ complex, also using the Judd–Ofelt theory and the calculation of ET rates to predict $\Phi$. In this work, some emphasis was given on the triboluminescence exhibited by the Eu³⁺ compound.

The work of Kai et al. [11] has received much attention in the last years and it describes ET processes and photostability of Eu³⁺ and Tb³⁺ $\beta$-diketonate complexes doped in poly(methylmethacrylate) (PMMA) films. In this study, besides the usually-observed intramolecular (ligand → ion) ET, intermolecular ET was surprisingly observed, occurring from the emitting level of a near Tb³⁺ ion belonging to one complex to the excited triplet state of the $\beta$-diketonate ligand coordinated to the Eu³⁺ ion of another complex (see Fig. 4).

Ion-to-ion energy transfer in Eu₂O₃ microspheres was recently investigated by Alves et al. [17] using theoretical methods and experimental techniques. In this work semiempirical methods based on Sparkle/X (X=AM1, PM3, PM6) were used to treat part of the solid Eu₂O₃ system comprising 600 atoms (Fig. 5). The ET rates calculated via dipole–dipole or dipole–quadrupole mechanisms were one order of magnitude smaller than those found for the quadrupole–quadrupole mechanism, indicating that the latter

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**Fig. 7.** Upconversion mechanism observed for the Eu³⁺-doped glasses investigated. Solid lines represent absorption or emission and dotted lines nonradiative decays by multiphonon emission. (Reproduced with permission from Ref. [122].)

**Fig. 8.** Upconversion mechanism of the Nd³⁺ ions. (Reproduced with permission from Ref. [123].)

**Fig. 9.** $\eta$ of Phosphate (Q-98), fluorozirconate (ZBLAN), and fluorooxalate (PGIZCa) glasses doped with Nd³⁺ as a function of [Nd³⁺] determined using the normalized-lifetime thermal lens technique. (Reproduced with permission from Ref. [148].)

**Fig. 10.** CIE (Commission Internationale de l’Eclairage) chromaticity diagram of 75SiO₂:25PbF₂ doped with Eu/Tb and Sm/Tb samples excited at 395 nm. (Reproduced with permission from Ref. [149].)
Upconversion is related to sequential energy transfer processes involving different lanthanide ions, from which low-energy photons can be converted into high-energy ones [120]. Upconversion techniques can be employed to understand several non-linear optical processes observed in lanthanide-doped solids. It can take place via ion-to-ion energy transfer, although other mechanisms are also possible (e.g. excited state absorption), as discussed below. Malta [10] has given an important contribution in this field by investigating ET processes taking place in inorganic systems with lanthanide ions. In his work, fundamentals of intramolecular and ion-to-ion energy transfer through the Coulomb and exchange mechanisms have been discussed. The shielding effects produced by the filled 5s and 5p sub-shells of the lanthanide ion and the forced electric dipole intensity parameters of 4f–4f transitions were reported to play an essential role in the description of those processes [10]. In the case of ion-to-ion energy transfer, the exchange mechanism was shown to be irrelevant for ion–ion distances larger than 4 Å.

The work of Pires et al. [121] about luminescent and morphological studies with yttrium oxide compounds doped with ytterbium and erbium has received much attention since its publication in 2005. It has shown how to tune particle size and shape by appropriate choice of the oxide precursor. Energy transfer taking place from Yb\(^{3+}\) (\(^{2}S_{3/2}\) to Er\(^{3+}\) (\(^{4}I_{15/2}\)) was responsible for the appearance of a red emission assigned to the \(^{4}I_{15/2}\) transition of Er\(^{3+}\). There is an improvement of intensity for samples having smaller crystallite sizes and a higher percentage of Yb\(^{3+}\) on the other side, green emission from Er\(^{3+}\) (\(^{4}S_{3/2}\) to \(^{4}I_{15/2}\)) also generated after energy transfer from Yb\(^{3+}\) was observed to become more intense for lower percentages of Yb\(^{3+}\) (Fig. 6).

Upconversion studies involving germanate glasses in ternary...
transfer from the NP to the Er\^{3+} ion.

Several investigations on lanthanide-based upconverted luminescence discussed in the frame of different technological applications have been reported with Eu\^{3+} and Tb\^{3+} [90], Tm\^{3+}/Ho\^{3+} [87], Er\^{3+} and Er\^{3+}$/\text{Yb}^{3+}$ [108], among others [19,20,23,24,26,27,29,33–35,41–44,50,52,60,65,69,70,82–84,95,97,99,100,102,103,125–147].

2.3. Glasses, LEDs, OLEDs and crystals

Great part of the analyzed papers deal with the investigation of glasses in the frame of several subtopics, such as materials science, optics, physics, chemistry, science technology, engineering, metallurgy and metallurgical engineering, spectroscopy, crystallography, biochemistry or molecular biology [148–195]. Several of them discuss upconversion or ET phenomena. For instance, studies involving upconversion in glasses were reported by Kassab et al. [123], Barbosa et al. [19] and Jakutis et al. [24].

Jacinto et al. [148] have reported a relatively simple method to determine emission quantum efficiency ($\eta$) and thermo-optical coefficients. This method does not require a direct comparison between the luminescence properties of reference and sample and is based on the normalized-lifetime thermal lens (TL) technique. This newly developed TL-based technique explores the linear
...dependence of the TL signal with the experimental lifetimes for different samples exhibiting different lanthanide concentrations, $\eta$ values of Phosphate (Q-98), fluorozirconate (ZBLAN), and fluoriodate (PGIZCa) glasses doped with Nd$^{3+}$ as a function of [Nd$^{3+}$] were determined, as shown in Fig. 9. The authors reported a very good agreement between the $\eta$ values found for the investigated glasses with those values calculated using standard techniques (e.g. multiwavelength or reference sample).

Gouveia-Neto et al. [149] have reported the synthesis of phosphors/vitroceramic hybrid materials composed by 75SiO$_2$:25PbF$_2$ doped with Eu$^{3+}$, Tb$^{3+}$, and Sm$^{3+}$ using the sol–gel process. The lanthanide ions were doped into the low-phonon-energy PbF$_2$ nanocrystals, which were in turn dispersed in the aluminosilicate matrix. The single-doped phosphors presented typical emission spectra in the red, green, and blue regions. The appropriate combination of the dopants inside the material gave rise to the emission colors depicted in Fig. 10, which shows the CIE (Commission Internationale de l’Eclairage) chromaticity diagram for different samples. One can see that the prepared glasses are all inside the white-light boundary represented by the white ellipse (Fig. 10), revealing that they are promising materials for use in white-light LED technological applications.

A recent investigation reported by Rivera et al. [40] discussed the best way to achieve efficient coupling between Er$^{3+}$-doped germanium–tellurite TeO$_2$–Na$_2$O–ZnO–GeO$_2$–Er$_2$O$_3$ glasses and Au NPs. The upconversion process exhibited by the Er$^{3+}$ ion inside the glass matrix was shown to be favored by the presence of NPs. The Au NPs, which were ca 1.6 nm in diameter and were grown inside the germanium–tellurite glass during thermal treatments, were responsible for enhancing the local field in the surroundings of the Er$^{3+}$ ion. Energy transfer between the NP and the lanthanide ion was also observed. Fig. 11 shows a schematic representation of all photophysical processes (absorption, energy transfer, emission) occurring in the Er$^{3+}$:Au–NP glass.

Few investigations have reported the use of lanthanides in LEDs or Organic Light-Emitting Diodes (OLEDs). Cremona et al. [150] have synthesized new quinoline-based lanthanide complexes (Ln$^{3+}$, La$^{3+}$ and Lu$^{3+}$) and determined their electro-luminescent, electrical and optical properties in OLED devices. Emissions assigned to the organic ligand in the green and yellow spectral ranges were observed for the prepared complexes. When using a β-diketonate Eu$^{3+}$ complex as the emitting layer of the OLED, the typical emission lines of Eu$^{3+}$ were observed, as shown in Fig. 12. The Eu$^{3+}$-based OLED exhibited a turn-on voltage of 15 V and the maximum luminance value of 20 cd/m$^2$ at 0.2 mA. Santos et al. [189] have reported the use of a β-diketonate Eu$^{3+}$ complex with 1,10-phenanthroline to build OLEDs. Other investigations have reported the fabrication of LED and OLED devices with lanthanides [35,97,159,168,182,190–195].

![Fig. 18. 2D view of a coordination polymer based on the 2,5-piperazinedione-1,4-diacetic acid (H$_2$FDA) with lanthanide ions. (Reproduced with permission from Ref. [200].)](image)

![Fig. 19. Sensitization of the Eu$^{3+}$ emission caused by its interaction with Au NPs. (Reproduced with permission from Ref. [177].)](image)

The luminescent properties of lanthanide-doped amorphous silicon nanocrystals (Ln$^{3+}$, Nd$^{3+}$, Eu$^{3+}$ and Tb$^{3+}$) have been reported by Tessler [151]. Other lanthanide systems based on crystals [152–155], silica [156], kaolinite [157], PMMA [158], alumina [159,160], and poly-β-hydroxybutyrate (PHB) [161] have been discussed. The preparation of glasses containing lanthanides and their luminescence properties have been discussed in the literature for several different systems and discussed in the frame of a wide range of applications [10,20,26,29,34,35,38–42,44,45,50–52,54,60,61,65,67,69,70,73,82–84,87,90,92,94,95,97–100,102,103,123–132,134,136,141–145,162–188].

2.4. Theoretical methods and methodologies

The theoretical methods used to treat lanthanide compounds are usually related to predictions of photophysical properties, description of the electronic structure, numerical calculation of emission quantum yields, estimates of ET rates, calculation of Judd–Ofelt intensity parameters, prediction of the ground state geometry using semiempirical models as well as first principles methods and description of the chemical environment around the lanthanide ion.

Freire et al. [37] have recently presented a detailed investigation of the photoluminescence of a Eu$^{3+}$ complex, where different theoretical tools were introduced step-by-step to predict several properties of interest. In addition, the Sparkle Model and Density Functional Theory (DFT) methods were used to predict ground
state geometries. Prediction of excited states (singlets and triplets) of the ligands is carried out by using the semiempirical INDO/S-CIS model and the Judd–Ofelt theory is used to calculate intensity parameters based on the model developed by Malta et al. [196] and φ's were predicted. Malta et al. [36] have also used such theoretical tools to make a systematic investigation of the luminescence properties of several β-diketonate Eu³⁺ complexes and could observe a linear relationship between theoretical and experimental Φ values.

The use of periodic DFT methods to predict ground state geometries, partial charges and density-of-states of perovskite doped with Sm³⁺ was reported by Figueiredo et al. [185]. In this study, the effect of the order–disorder transition of the simulated material over its photoluminescent properties was discussed. The authors have concluded that the luminescence exhibited by the Sm³⁺-doped material in its disordered state is independent of the Sm³⁺ emission. The ordered and disordered structures were associated to the Ti sites in the TiO₆ and TiO₅ clusters, respectively. The Ti-O displacements of the investigated material were reported to influence the formation of TiO₆ clusters, as revealed by the charge density contour plots (see Fig. 13).

Belian et al. [48] have investigated the luminescent properties of Eu³⁺ complexes, in which the 1,10-phenanthroline (Phen) ligand was substituted at the 4 and 7 positions by chlorine atoms. Their intensity parameters were calculated using the model...
developed by Malta et al. [196] and compared with experimental results. Molecular structures of the complexes and excited states were predicted using the Sparkle model and DFT method, and the INDO/S-CI model, respectively. Fig. 14 shows the theoretical (Sparkle/DFT) and experimental triplet state energies of the investigated Eu\(^{3+}\) systems. The energies predicted for the triplet states of the complexes followed the experimental data, where a blue shift was observed upon chlorinating the ligand.

Among the different theoretical methods developed to investigate luminescent lanthanide systems, many of them being developed by Prof. Malta, the prediction of ground state geometries plays a very important role, since the optimized atomic coordinates are always the starting point for other theoretical models. The Sparkle model [197] is often used for this purpose and it is implemented in the MOPAC program, which, until very recently, could not be run in parallel, therefore limiting its range of application. However, the Sparkle model can now be used to treat much larger lanthanide systems due to the pioneering work of Rocha et al. [198], which made possible running parallel computations to optimize lanthanide compounds using the MOPAC program.

The recent publication of Rivera et al. [82] reports the incorporation of either Ag or Au NPs into Er\(^{3+}\)–Tm\(^{3+}\)–doped tellurite glasses and makes a complete description on how the photon–plasmon interaction can help control the radiative properties of these materials. The Hamiltonian used to describe the oscillator strength or the local crystal field in the material expresses the dynamic coupling mechanism which is associated with the interaction between the NP and the lanthanide ion. The noble metal NPs enhance the emission intensity and expand the bandwidth of the luminescence spectrum of the doped glasses by both the combined emission of Er\(^{3+}\) and Tm\(^{3+}\) ions and efficient ET processes. The latter are thoroughly described in Ref. [82]. The schematic representation of these interactions is shown in Fig. 15.

Other investigations reporting the use and/or development of theoretical models or methodologies have been discussed in the literature [8,12,13,15,17,28,43,55,56,86,199–207].

2.5. Thin films, metal–organic frameworks and coordination polymers

The application of metal–organic frameworks (MOFs) with Yb\(^{3+}\) and Tb\(^{3+}\) as optical problems to detect gunshot residues has been reported [138]. These luminescent markers (Fig. 16) have allowed one to identify ammunition origins and to make caliber recognition by adding them directly to conventional gunpowder in a ratio of 10 wt% before reassembling the bullet. The luminescence associated to each marker arises from excitation of Yb\(^{3+}\) at 980 nm, where ground and excited state absorptions take place using two photons, followed by the upconverted Tb\(^{3+}\) emission in the visible spectral range.

Rodrigues et al. [20] have carried out an experimental and theoretical investigation of a Ln-based MOF (Ln=Eu\(^{3+}\) and Tb\(^{3+}\)), where ion-to-ion (Tb\(^{3+}\)–Eu\(^{3+}\)) ET takes place. In this system (Fig. 17), the Tb\(^{3+}\) emission (D\(_{0}\)→F\(_{2}\)) is strongly quenched concomitantly with the appearance of an intense red emission from Eu\(^{3+}\) (D\(_{0}\)→F\(_{2}\)). The model developed by Malta et al. [2,10] was used to predict that the dipole–dipole and dipole–quadrupole ET mechanisms were the dominant ones to describe the Tb\(^{3+}\)→Eu\(^{3+}\) ET process.

Alves et al. [200] have synthesized 3D coordination polymers based on the 2.5-piperazinedione-1,4-diacetic acid (H\(_2\)PADA) and Eu\(^{3+}\) and Gd\(^{3+}\) ions. These materials were shown to be crystalline with chemical formula [Ln(PDA)\(_{1.5}(H_2O)\)] and presented the characteristic red emission from the transition D\(_{0}\)→F\(_{2}\) in the case of the Eu\(^{3+}\)-based polymer. The energy transfer (ligand-to-metal) in this material was also described using the model developed by Malta et al. [2,3], and Judd–Ofelt intensity parameters were obtained for the prepared material. The 2D view of this coordination polymer is shown in Fig. 18.

The work of Kai et al. [11], discussed on a previous section is an example of a lanthanide-based thin film material, where PMMA was used as a matrix and Eu\(^{3+}\) and Tb\(^{3+}\) complexes as luminescent species. The PMMA promotes the close interaction between those complexes, from where intermolecular ET could be observed, as well as it enhances the overall luminescence intensity since it acts as a co-sensitizer. The materials have exhibited emission with green, red, and intermediate colors, which were fine-tuned by optimizing composition and excitation wavelength.

Other investigations involving thin films, MOFs and coordination polymers have been reported in the literature [18,63,73,78,88,94,133,141,169,178,182,185,201,208–228].

2.6. Nanoparticles, nanorods and sol–gel process

The work of Pires et al. [121] is related to morphological and luminescent studies on nanosized yttrium oxide NPs doped with Yb\(^{3+}\) and Er\(^{3+}\). Luminescent NPs as small as 12 nm have been reported, but depending on the synthetic protocol used, 90 nm-diameter NPs could also be made. The Ln-doped NPs reported in Ref. [121] were shown to be excellent candidates for use in immunoassays involving analytes of nanometer size, greatly contributing to the development of the upconversion phosphor technology.

Au and Ag NPs with 10 nm in diameter were used by Kassab et al. [177] to enhance the photoluminescence of germanate glasses doped with Eu\(^{3+}\) for wavelengths overlapping with the surface plasmon band of the NPs. The presence of noble-metal NPs has shown to influence the forced electric-dipole and magnetic-dipole transitions starting from the D\(_{0}\) level of Eu\(^{3+}\), strongly increasing the luminescence intensity from F–F transitions (Fig. 19).

This effect was attributed to ET from the NPs to the Eu\(^{3+}\) ion and to the confined electromagnetic field near the NPs.

Nanorods of 50–100 nm in length with composition of MPO\(_3\)

Ln\(^{3+}\) (M=La, Y, Gd, or Yb; Ln=Eu, Tm, or Er) were prepared by Serra et al. [139] using a synthetic route based on the reverse microemulsion method (Fig. 20). The Eu\(^{3+}\)-doped nanorods have exhibited the characteristic red emission mainly due to the D\(_{0}\)→F\(_{2}\) transition and the large number of Stark levels have revealed that the Eu\(^{3+}\) ion occupied low-symmetry sites. The LaPO\(_3\)

Tm\(^{3+}\) and YPO\(_3\)Tm\(^{3+}\) nanorods have exhibited a blue emission with high color purity, while the one with composition YbPO\(_3\)

Er\(^{3+}\) showed an upconverted red emission upon excitation at 980 nm. The authors have reported that these new materials can be designed to exhibit desired properties for a broad range of applications.

Sigoli et al. [229] have shown how to tune the size of luminescent Gd\(_2\)O\(_3\):Eu\(^{3+}\) NPs prepared using a modified homogeneous precipitation method. The NP size can be controlled to have diameters in the range 30–90 nm (Fig. 21) by means of appropriate selection of the counter anion types (nitrate versus chloride), chemical nature of the alcohol (high versus low viscosity) and dielectric constant of the reaction medium. The synthesized materials have exhibited a strong red luminescence due to the D\(_{0}\)→F\(_{2}\) transition of Eu\(^{3+}\). The results indicate that the strong interaction between nitrate anions and Gd\(^{3+}\) is a key to promote the stabilization of small NPs.

The article of Ferrari et al. [141] reports the preparation, structural analyses and optical properties of Er\(^{3+}\)-doped SiO\(_2\)

Ta\(_2\)O\(_5\) nanocomposite films obtained by the sol–gel process. The Er\(^{3+}\)-doped nanocomposite annealed at 900 °C consisted of Ta\(_2\)O\(_5\) NPs with average diameter around 2.4 nm and a very small size
distribution, dispersed in the SiO₂ amorphous matrix. It was observed a broad band emission (Fig. 22) peaked at around 1532 nm and assigned to the 4i3/2 → 4i15/2 transition of Eu³⁺. The photoluminescence lifetime measured for this band was 5.4 ms. The optical structural and optical properties found for this material suggest it may be used in active planar waveguides.

Pereira et al. [230] have presented a non-hydrolytic sol–gel route to prepare Y₂Al₂O₇ (YAG) phosphors doped with Eu³⁺, Tb³⁺, and Tm³⁺ in order to generate white light. The typical luminescence bands of Eu³⁺ (4D₂ → 7F₄), Tb³⁺ (4D₂ → 7F₄) and Tm³⁺ (3D₂ → 3H₄) corresponding to red, green and blue emissions, respectively, were observed in the prepared material. The green emission was more intense and narrow in relation to the red and blue emissions, which was reported to be due to differences in the size of the three incorporated ions. The results have reinforced the importance of the non-hydrolytic sol–gel route to efficiently prepare red–green–blue phosphors for applications in display technology and white light generation.

Ribeiro et al. [53] have reported the synthesis of europium sodium–phosphate–tungstate colloidal systems in which the Eu³⁺ ions occupy cage-like sites composed of phosphate groups from the metaphosphate chains. The tungstate addition has led to the formation of W-rich nanoparticles (5–10 nm in diameter) and removal of water molecules from the first coordination sphere of Eu³⁺. The authors also report an efficient energy transfer from the O–W charge-transfer states to Eu³⁺ at room temperature and in aqueous systems. The strong ligand field around the lanthanide ion, together with the absence of water in its first coordination sphere was shown to be responsible for a very high emission quantum efficiency value of 80%. A similar strategy was used by De Camargo et al. [74], where complete removal of water molecules from the first coordination sphere of a nine-coordinated Eu³⁺ complex gave rise to Φ = 85% in solution. Fig. 23 shows the emission spectra of the luminescent Eu³⁺-containing polyphosphate–tungstate aqueous colloidal systems.

Investigations of luminescent lanthanide complexes in solution bearing different applications were also reported in the literature [231–234]. Other investigations on the luminescence properties of lanthanide-based systems with NPs, nanorods or systems assembled using sol–gel techniques have been reported in the literature [17,22,27,33,34,38,40,43,45,49,50,60,61,67,73,78,82,88,93,107,127–129,133,136,140,142,143,149,163,169–171,176,178,201,211,212,214,235–246].

3. Conclusions

The overview of the representative research carried out in Brazil in the last decade in the field of luminescent lanthanide systems was presented, being discussed in the frame of several subtopics. Recent publications involving glasses, upconversion subtopics. Recent publications involving glasses, upconversion technol-
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