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Luminescent and gas sensor properties of the ZrO_2:Hhpa:Eu^{3+} Hybrid Compound

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A B S T R A C T

Luminescent complexes of rare earth have been extensively studied in different fields of research improving the industrial development of these materials for their utilization as electroluminescent displays, catalysts and biomaterials. The interest in rare earth compounds having aromatic ambidental ligands has increased since it was found that they can act as light collectors (antenna effect), thus bypassing the weak absorption of the lanthanides and resulting in highly efficient luminophors. In this work ZrO_2 was prepared by the hydrothermal microwave method (HMM) at 140 °C for 32 min. The hybrid materials was obtained using the previous ZrO_2 dispersed in distilled H_2O, to which was added Eu^{3+} and the 3-hydroxypicolinamide (Hhpa), and then stirred for about 3 h. The materials were analyzed by X-ray diffraction (XRD) and Transmission electron microscopy (TEM). The photoluminescent properties were investigated through their excitation and emission spectra, and gas sensor studies were also performed. It was observed the presence of completely crystalline powders for all materials, and XRD peaks were indexed to the tetragonal phase of ZrO_2 (JCPDS 50-1089). TEM micrographs reveal a spherical nanostructure pattern presenting an average diameter of 4 nm. Excitation and emission spectra revealed the characteristic peaks of the Eu^{3+} transitions. The studies of these powders as gas sensors showed a significative change in the electric resistance for the hybrid material.

1. Introduction

Rare earth luminescent complexes have been utilized in different fields in the last decade. These materials can be used in the fabrication of electroluminescent displays, fluorescent probes, catalysts, as well as biosensors and can be a promising candidate as gas sensors. The luminescent properties of Eu^{3+} complexes are very interesting due to their thin emission bands and their long lifetime. Eu^{3+} ion presents intraconfigurational *4f-4f* transitions which are Laporte forbidden and consequently presents low absorption intensity. The presence of organic ligands, however, can intensify the ability of Eu^{3+} ions emission through the ligand absorption and transfer part of this energy in an energy transfer mechanism called as antenna effect. This phenomenon resulted in various researches and different ligands were used to this purpose. These organic-inorganic hybrid materials have attracted great interest because of their potential applications in different aspects of technology like optical materials or laser systems [1–4].

Nanostructures of zirconium oxide, ZrO_2, have been explored due to their technological importance based on their high hardness, elevated refractive index, optical transparence, chemical stability, low conductivity, high coefficient of thermal expansion, and high resistance to the corrosion [5,6]. These properties provide to ZrO_2 different application in the field of optic [7], solid state electrolytes, gas sensors, and so on [8]. The application of ZrO_2 in the photonic field is already know due to their high performance in wave guide and their efficient thermoluminescent response [9,10]. The properties of ZrO_2 can be influenced by the preparation method, being possible to obtain metastable phases depending on the methodology employed. Microcrystalline ZrO_2 is obtained when prepared at atmospheric conditions and it is obtained as amorphous, monoclinic, tetragonal, and cubic polymorphic phases [11,12]. So, ZrO_2 can be present as three different crystalline structures P21/c monoclinic (bellow 1170 °C), P42/nmc (137) tetragonal (between 1170 and 2370 °C) and Fm3m (225) cubic (up to 2370 °C) [13].

The monoclinic phase (A) is less symmetric than the tetragonal one (B), and is more stable at room temperature. This phase is transformed in the tetragonal one at 1170 °C, but at 2370 °C the cubic phase (C) is formed [14]. The phases obtained at higher temperatures are unstable

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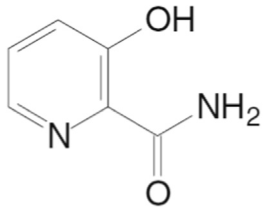

Fig. 1. Molecular structure of the 3-hydroxipicolinamide (Hhpa) ligand.

at room temperature, but these phases are more important for technological applications than the monoclinic one. So, various bivalent and trivalent cationic species like Mg^{2+}, Ca^{2+}, and Y^{3+} are incorporated to the ZrO_2 promoting the obtention of the cubic and tetragonal phases stables at room temperature [15].

Some works reported the doping of ZrO_2 with different rare earths like Er^{3+}, Eu^{3+}, and Sm^{3+} [16–18]. However, few of them focused on the photoluminescent properties of ZrO_2 doped with Eu^{3+} [19–21]. The spectroscopic and magnetic properties of the rare earth ions are responsible for innumerous researches based on these elements. The luminescent spectra of the Eu^{3+} present narrow lines of excitation and emission, due to the electronic transitions inside the unfilled *4f* shell. Also because of the unfilled shell, the ion presents a great number of energy levels, given rise to emission lines that appears in the luminescence spectra from ultraviolet to the infrared, and depends on the kind of matrix they are incorporated. The *4f* orbitals are protected from the environment by *5s* and *5p* ones, so there are weak effects from the ligands field. The f-f transitions are forbidden by Laporte and spin rules, but these rules are broken when the symmetry around this ion is low [22]. The Eu^{3+} is the most studied from the rare earth ions due to it special characteristics. In general, the Eu^{3+} ion presents a more intense luminescence [23]. The characteristic red emission of Eu^{3+} is due to the transitions from the excited $^5D_0$ level to the fundamental ones ^7F_J ($J = 0–6$) of its $4f^6$ configuration. These characteristics make this ion very useful in illuminations, TV color screen, and displays to diode productions.

The recent interest in study the organic-inorganic hybrid materials is motivated by the presence of their extraordinaire properties which

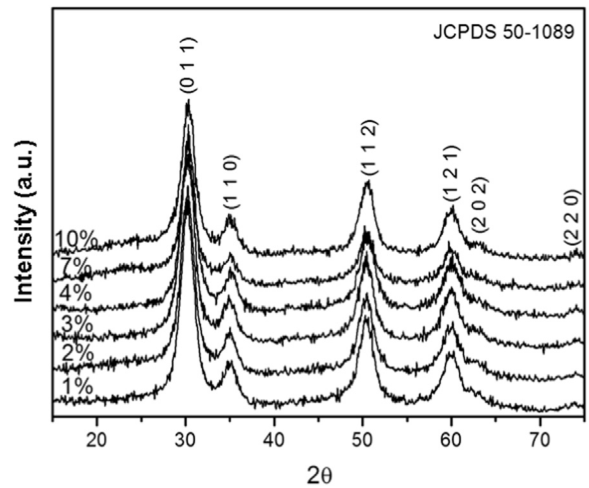

Fig. 3. Powder X-ray diffractograms of the ZrO_2:Hhpa:Eu^{3+} presenting different Eu^{3+} concentration: 1.0%, 2.0%, 3.0%, 4.0%, 7.0%, and 10.0%.

promote their applicability in different field, since this material combine the mutual vantages from the organic and inorganic material [1,24]. Hybrid materials formed with Eu^{3+} and one organic ligand are used to fabricate red luminophors for the obtention of white light emitter diodes (LEDs), since the emission of the white light can be obtained by the incorporation of blue, green, and red luminophors. The organic ligands act as antenna, which increase the luminescent intensity due to the presence of chromophores groups [1,25–29].

The organic compound 3-hydroxipicolinamide (Hhpa), Fig. 1, is an aromatic ligand considered as a model compound that is a component of the virginiamycine S (VS), an hexapeptide which act as an antibiotic that promotes the blocking of the protein synthesis into the bacterial ribosome. The 3-hydroxipicolinil residue absorbs the light and is also responsible for the complexant properties and to the phenomenon of the transference of the protons to the peptide VS. It is believed that the complexation of the species hpa (deprotonated ligand) with the rare

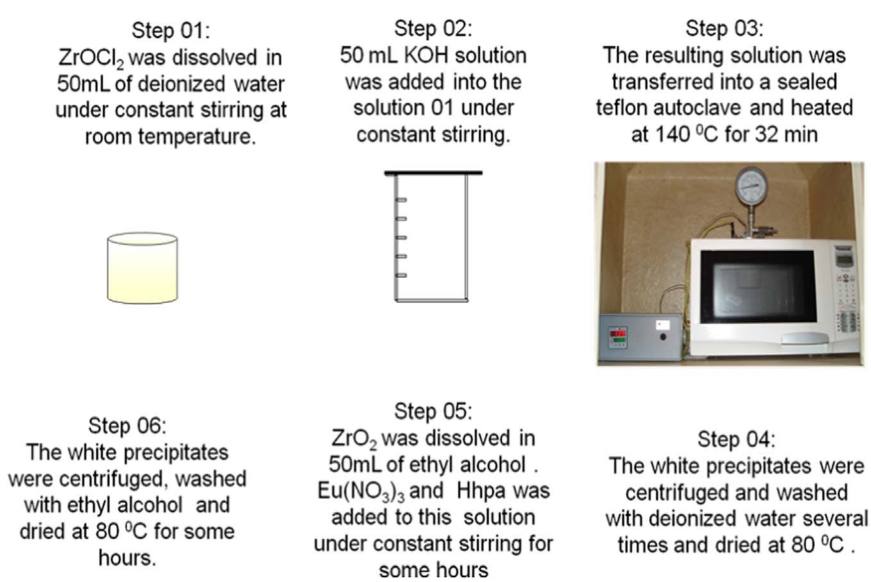

Fig. 2. Experimental procedure for preparation of the samples ZrO_2, ZrO_2:Hhpa:Eu, as well ZrO_2:Bipy:Eu.