Morphologic and luminescent characteristics of the zinc aluminate nanopowders doped with terbium

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Abstract: Zinc aluminate (ZnAl₂O₄) is a ceramic material with spinel structure and is used as catalysis for reduction of NOx and SOx, and also as electronic ceramic. Zinc aluminate when doped with rare earth ions, such as Tb³⁺ ion, the matrix of ZnAl₂O₄:Tb acquires luminescent properties. This material has been produced in laboratory scale by different methods of chemical synthesis, such as, spray pyrolysis, hydrothermal synthesis, co-precipitation and Pechini method. Among this method, the combustion reaction is an alternative, simple, fast and safe method, used to prepare ceramic powder with high purity, chemical homogeneity and nanosize particles. So, the aim of this work is to evaluate the influence of the Tb³⁺ ion in the morphologic characteristics and luminescent properties of the zinc aluminate powder. The resulting powders from the combustion were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM) and excitation and emission spectroscopy. The XRD results showed the formation of ZnAl₂O₄: Tb³⁺ as main phase and TbAlO₃ as a secondary phase. The powder presented morphology constituted of the agglomerates of fine particles (<100nm) and green luminescence, characteristic of the Tb³⁺ ion.

Introduction

Bhagrava and Galagher [1] reported that nanoparticles semiconductors doped with ions lanthanides introduce significant radioactive transitions. From of this discovery several researches has been developed aiming prepared material monocrystalline doped with rare earths ions with particles size lower than 100 nm. These materials can be used as Converting Molecular Devices of Luz (DMCL), absorbing radiation in the ultraviolet one and emitting in visible [2]. The studies spectroscopic rare earth ions have increased in the last decades due to the photoluminescent properties favorable to many types of applications. Luminescence is the name given to the phenomenon related to the capacity that some substances present in converting certain types of energies into emission of electromagnetic radiation, with an excess of thermal radiation. It has some types of luminescence, that they differ between itself, for the energy used for excitement. The photoluminescence is a result of the fotons absorption, using an electromagnetic radiation with an excess of thermal
radiation. The photoluminescence includes the fluorescence in such a way as phosphorescence. The fluorescence differs from the phosphorescence, in the fact of that the responsible transitions of electronic energy for the fluorescence do not involve the electronic change of spin [3, 4].

In contrast, an electronic change of spin, follows the phosphorescent emissions which make the radiation to be able to last for an easily detectable time after finish it of the irradiation, frequently some seconds or more. The luminescence in the majority of inorganic solids involves structural impurities or defects that are called activators. The electronic states had to the impurities, involved in the luminescence are related with bands structure of the solid. Solid semiconductors are characterized by a valence band and a conduction band separated by one energy gap. The luminescence occurs for the electron excitation for the conduction band empty, leaving holes in the valence band completely filled. The emission occurs for the recombination of the pair electron-hole. This recombination if gives due to proximity or to the presence of defects in the crystal structure [3, 4]. Ion terbium (III) has attractive a special one for biological applications that involve fluorimetric techniques. The luminescent properties of the made up of Tb$^{3+}$ include wide Stokes displacements, emission specters presenting fine bands, wavelength of emission and time of long life fluorescent [5].

Zinc aluminate (ZnAl$_2$O$_4$) is oxides with typical structure of spinel normal AB$_2$O$_4$ that consists of a close-packed arrangement of oxygen atoms, two small site crystallographically not equivalents tetrahedral (A) and octahedral (B), where A and B are bivalent and trivalent ions, respectively [6, 7]. This material is world-wide used as material high temperature, catalytic, catalytic supports [8, 9], optic layers [11, 12] and as a lattice hostess in the pigments manufacture [10, 11, 12]. It is a semiconductor that presents one gap of energy around 3,8 eV [17], what it indicates its transparency for light with superior wavelength 320nm. This characteristic becomes it sufficiently attractive as lattice hostess for ions capable to generate luminescence, such as, ions of metals transistion and rare earth ions. Currently, some authors have reported the obtaining of rare earth ions doped zinc aluminate for use as phosphor of high efficiency in displays type FED (Field Emission Display) and PDP (Plasma Display Panels) [18, 19]. Lluminescent materials the base of oxides are preferable in relation to the materials to the base of sulfur, as for example transition metals or rare earth doped ZnS, due to the oxides be chemically inert [19].

Aiming at to the attainment of zinc aluminate with raised superficial area, some methods of chemical synthesis come being used in laboratory scale. A variety of techniques, such as the hydrothermal method [21], sol-gel [21, 22] and Pechini method. The synthesis for combustion reaction enters the chemical methods is distinguished as one simple and promising technique for the preparation of ZnAl$_2$O$_4$:Tb$^{3+}$ nanometrics powders. In this context, the present work has as objective the preparation and characterization of ZnAl$_2$O$_4$:Tb$^{3+}$ powders obtained by combustion reaction.

**Experimental**

The process of synthesis for combustion reaction involved a mixture contends ions metallic desired, used as reacting oxidantes and a fuel (urea) as reducing agent. For this mixture redox had been used zinc nitrate - Zn(NO$_3$)$_2$.6H$_2$O, aluminum nitrate - Al(NO$_3$)$_3$.9H$_2$O, oxide of terbium Tb$_2$O$_3$ and urea - CO(NH$_2$)$_2$. The combinations between these reagents had been carried through in order to define the compositions in function of its respective molar amounts. Samples with the ZnAl$_{2-x}$Tb$_x$O$_4$ compositions
had been prepared where \( x = 0.010 \) and \( 0.025 \) \( x = \) mol of the Tb, specified for Tb01 and Tb02, respectively. The proportion of each reagent and the fuel had been calculated on the basis of the concepts of the propellants chemistry [25]. Carbon, hydrogen, aluminum, zinc and terbium had been considered as reducing elements, with respective valences of +4, +1, +3, +2, +3. The oxygen was considered as oxidant agent, having -2 as valence. The valence considered for nitrogen was zero. The solutions were mixed in a vitreous silica basin and heated directly on a hot plate at 480°C until self-ignition occurred. The phases of the powder samples were identified using an X-ray diffractometer (XRD-6000 Shimadzu, Cu K\( \alpha \) radiation, 40 KV and 30 mA). The scanning speed was 0.02° per step and 1 s per step in the 2\( \theta \) range of 10 to 80°. The morphologic characteristics of the powders obtained by combustion reaction were analyzed by scanning electron microscopy (Philips / XL30 – FEG) – SEM. Photoluminescence emission (PL) and excitation (PLE) measurements were taken with a K2 Multifrequency Phase Fluorimeter. The detention of the rays-X emitted for the sample were carried by the measure X-ray dispersion specter (EDS).

Results and discussion

Figure 1 presents the X-ray diffraction patterns for the compositions Tb01 and Tb02 obtained by combustion reaction and corresponding the phases ZnAl\(_{1.990}\)Tb\(_{0.010}\)O\(_4\) and ZnAl\(_{1.975}\)Tb\(_{0.025}\)O\(_4\), respectively. We can observe that both the samples had presented characteristic peaks of the crystalline main phase ZnAl\(_2\)O\(_4\):Tb\(^{3+}\) and traces of the characteristic peaks of the TbAlO\(_3\) secondary phase. The formation of secondary phase in larger proportion and intensity was observed in the Tb02 sample in consequence of solubility low of the Tb\(^{3+}\) ions (ionic radius = 1Å) in the ZnAl\(_2\)O\(_4\) structure. The Tb\(^{3+}\) ions substitutes the Al\(^{3+}\) ions (ionic radius = 0.54Å) have same valence, but ionic radius smaller size. This difference of size between ions makes it difficult the substitution thus reducing the solubility limit. As we can observe for the Tb01 composition the characteristic peaks of the secondary phase had been discrete. This sample that the solubility limit of ions Tb\(^{3+}\) substituting ions of Al\(^{3+}\) is very low. The crystalline size,\( D \), was calculated for both the samples using the Scherrer’s equation [26] through the width of half height of the peak of larger intensity of the main phase. The samples Tb01 and Tb02 had presented crystallite size of the 24 and 18 nm, respectively, indicates the nanometrics characteristic of the obtained powders.

Figure 1 - X-ray patterns of the compositions Tb01 and Tb02 (\( x = 0.010 \) and \( x = 0.025 \)).

Figure 2 shows morphological aspect of the resulting powders obtained by scanning electronic microscopy (SEM). It can be observed to the formation of hard agglomerated with irregular plate-shaped morphology. Also it is possible to observe the formation of two distinct phases, the main phase ZnAl\(_2\)O\(_4\):Tb\(^{3+}\) (particles of the dark
gray color) and the secondary phase TbAlO₃ (clearly gray color,) that it appears in the form of small particles distributed for the surface of the plates of the main phase. These results are in agreement with x-ray diffraction results, determined for both compositions.

Figure 2 - Morphologic aspects of the ZnAl₂O₄: Tb³⁺ powders obtained by combustion reaction. (a) Tb₀₁ and (b) Tb₀₂.

Figure 3 presents the micrograph of the Tb₀₁ composition and the EDS specters for the point 1 (main phase) and point 2 (secondary phase). In both the points had been identified terbium traces, indicating that this element was incorporated in the matrix. In the specter of point 2, we can observe an increase in the intensity of the referring peaks to the element zinc, proceeding from the secondary phase, proving the result of the X-ray.

Figure 3 – (a) Morphologic aspects of the Tb₀₁ composition, (b) X-ray dispersion specter (EDS) of the point 1 and (c) X-ray dispersion specter (EDS) of the point 2.

Figure 4 show the excitation spectra for the samples Tb₀₁ and Tb₀₂. The excitation was carried through scanning the specter of 200 the 350 nm. The excitement band observed for the green color (542 nm), occurs around 230nm.

Figure 4 - Excitation spectra of the powders of ZnAl₂O₄: Tb³⁺.
Due to electrons shield 4f for orbital 5s and 5p filled, the emission spectra of the lanthanides ions present fine lines. This because this shield takes to a weak coupling of electrons with the chemical neighborhood [27]. When this ions is incorporated the crystalline matrix is observed radioactive transitions $4f \rightarrow 4f$ [1, 28], these transitions can occur way forced electric doublet (FED), electric magnetic doublet (MD) or magnetic quadrupole (MQ) and is provoked by the action of the ligante field that distorts the free ion [28]. The emission spectra of the two compositions Tb01 and Tb02 to the ambient temperature when excited in 230 nm, is presented in Figure 5. In both the spectras are possible to observe the presence of the characteristic peaks of emission of the Tb$^{3+}$ centered in 488, 543, 585 and 621 nm. These peaks had been attributed by Lou and Hao [18], the transitions $^{5}D_{4} \rightarrow ^{7}F_{6}$, $^{5}D_{4} \rightarrow ^{7}F_{5}$, $^{5}D_{4} \rightarrow ^{7}F_{4}$ and $^{5}D_{4} \rightarrow ^{7}F_{3}$, respectively. The larger intensity of the peak centered in 543 nm due to transition $^{5}D_{4} \rightarrow ^{7}F_{5}$, is responsible for the luminescence of green color of these compositions.

![Emission spectra of the Tb01 and Tb02 compositions.](image)

**Figure 5 - Emission spectra of the Tb01 and Tb02 compositions.**

As observed in the spectra photoluminescence of the samples ZnAl$_{1.99}$Tb$_{0.01}$O$_4$ (Tb01) and ZnAl$_{1.975}$Tb$_{0.025}$O$_4$ (Tb02), the intensity of the luminescence increased proportionally to the addition in the concentration of Tb$^{3+}$. According to Nikl et al [29] this effect occurs for concentrations below of a critical value, determined for the distance between Tb$^{3+}$ ions, inside of the crystalline matrix. In concentrations above a limit value, the small distance between Tb$^{3+}$ ions provokes the process of crossed relaxation, that consists of the energy transference between these ions, thus diminishing the intensity of the luminescence generated for the doped sample.

**Conclusions**

On the basis of the results obtained in this work, we can conclude that: 1. The synthesis by combustion reaction was favorable in the attainment of the desired phase, terbium doped ZnAl$_2$O$_4$. 2. Both compositions had presented formation of TbAlO$_3$ second phase, in consequence of solubility low of the rare earth ions in the crystalline matrix. 3. The crystallite size calculated from the X-ray patterns had evidenced the nanosized characteristics of the powders. 4. The micrographs of the powders had shown that the particles form agglomerated of irregular format and easy desagglomerated and presence of the main and secondary phase. 5. Through the emission spectras it is possible to verify characteristic the green luminescence of Tb$^{3+}$ ions. The luminescence of the powders showed dependent of the rare earth ion concentration.
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