Effect of Fe$^{3+}$ Doping in the Photocatalytic Properties of BaSnO$_3$ Perovskite

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In the last ten years, stannates with perovskite structure have been tested as photocatalysts. In spite of the ability of perovskite materials to accommodate different cations in its structure, evaluation of doped stannates is not a common task in the photocatalysis area. In this work, Fe$^{3+}$ doped BaSnO$_3$ was synthesized by the modified Pechini method, with calcination between 300 and 800°C/4 h. The powder precursor was characterized by thermogravimetry after partial elimination of carbon. Characterization after the second calcination step was done by X-ray diffraction, Raman spectroscopy and UV-visible spectroscopy. Materials were tested in the photocatalytic discoloration of the Remazol Golden Yellow azo dye under UVC irradiation. Higher photocatalytic efficiency was observed under acid media. As no meaningful adsorption was observed at this condition we believe that an indirect mechanism prevails. Fe$^{3+}$ doping decreased the band gap and favored the photocatalytic reaction, which may be assigned to the formation of intermediate levels inside the band gap.

Keywords: Perovskite, Fe-doped, polymeric precursor method, photocatalysis, RNL.

1. Introduction

Alkaline earth stannates (MSnO$_3$, M = Ba, Sr, Ca) with perovskite structure have become alternative materials to the technological sector due to its applications as dielectric components. Its use as photocatalyst has also been reported, especially for water splitting$^{1-3}$ and for the photodegradation of organic dyes, with emphasis in the SrSnO$_3$.$^{4,5}$ Previous results of our research group indicated that BaSnO$_3$ has a higher photocatalytic activity than SrSnO$_3$, for the degradation of an azo-dye, the golden yellow remazol (RNL)$^6$.

BaSnO$_3$ has been studied in various applications in recent years but it is not widely explored as photocatalyst. In spite of its band gap of 3.1 eV, a small activity is usually reported, being assigned to a high electron-hole recombination rate$^7$. This drawback may be overcome by the use of nanostructured materials, as reported by Moshtaghi et al.$^{5,9}$, who attained a high activity in the photodegradation of organic dyes. A high activity may also be attained, using the perovskite ability to form solid solutions resulting in defects, which can therefore improve its photocatalytic properties$^{10,12}$. For instance, the solid solution BaSn$_{0.2}$Pb$_{0.8}$O$_3$ has been evaluated by Borse et al. showing a high activity for the photo-oxidation of water$^{10}$. Literature also reports the use of La$_{1-x}$Ni$_x$O$_3$, Fe$_{1-x}$Z$_x$O$_3$, Cu$_{1-x}$Co$_x$O$_3$ as dopant into oxides as TiO$_2$, ZnTiO$_2$, ZnO$^{13-17}$. Fe$^{3+}$ has been used as TiO$_2$ dopant in several studies$^{18-23}$, behaving as electron scavenger which suppress electron-hole recombination improving the photocatalytic efficiency. Fe$^{3+}$ has also been used as BaSnO$_3$ dopant and leads to formation of multi energy levels below the conduction band edge. Charge balance is obtained by formation of oxygen vacancies, besides oxidation or reduction of Fe$^{3+}$, which contribute to the perovskite stabilization$^{24-26}$. The magnetic properties of this Fe-doped perovskite have been studied, but, up to our knowledge, its use as photocatalyst has not been reported yet. The heterogeneous catalysis offers technical and environmental advantages over homogeneous catalysis, allows the recycling of the solid catalyst over its useful life and minimizes the generation of effluents. Several solids have been proposed as potential catalysts for photodegradation of textile dyes. The performance of these materials as catalysts is naturally related to the nature of the acid or basic sites found in these materials.

In the present work, Fe-doped BaSnO$_3$ was synthesized by the modified Pechini method and applied in the photoactivity degradation of RNL azo-dye.

2. Experimental

2.1 Synthesis of photocatalysts

Fe$^{3+}$-doped BaSnO$_3$ (0; 0.05 and 0.1 in mol) was synthesized by the modified Pechini method, similarly to the methodology described Lucena et al.$^{27}$. After tin dissolution in a 0.1 mol.L$^{-1}$ nitric acid aqueous solution cooled with an ice bath, citric acid (C$_3$H$_4$O$_7$H$_2$O, Cargill - 99.5 %) was added into the solution. The pH of the solution was adjusted to 3 by adding ammonium hydroxide (NH$_4$OH, Vetec - 28-30 %). Solutions of iron citrate or barium citrate were prepared from the respective nitrates, Ba(NO$_3$)$_2$ (Vetec - 99
%, Fe(NO₃)₃·9H₂O (Vetec - 99.5 %), and added into the tin citrate solution under a slow agitation at 25°C for 12 h. A molar ratio citric acid:metal of 3:1 was used for all of the citrates. Ethylene glycol (Vetec - 99.5 %) was added into the solution at 90°C to promote its polymerization. The mass ratio of citric acid to ethylene glycol was 60:40.

The polymeric resins were calcined at 250°C/2 h, deagglomerated, dry milled in a Spex mill, and sieved (100 mesh) to obtain the powder precursors. A heat treatment under an oxygen atmosphere (O₂) was performed at a temperature of 300°C /6 h at a heating rate of 1°C min⁻¹ under a flow of 1000 cm³ min⁻¹ to partially eliminate the organic material. The materials were calcined from 300 to 800°C/4 h under stagnated air atmosphere at a rate of 10°C min⁻¹.

The precursors obtained after heat treatment under oxygen atmosphere were characterized by thermogravimetry (TG) and its derivative curve (DTG) using a SDT-2960 thermobalance (TA Instruments) with a heating rate of 10°C min⁻¹ up to 1000°C under synthetic air with a flow of 100 mL min⁻¹ using alumina crucibles. The samples calcined at 300-800°C were characterized by X-ray diffraction (XRD) using an XRD-6000 Shimadzu diffractometer with Cu Kα radiation between 10° and 80°, using a step size of 0.02° 2θ values was observed after doping indicating that Fe⁺⁺ got into BaSnO₃ lattice. The lattice parameters, a, of BaSnO₃ were calculated and indicated that a small lattice decrease took place, which is assigned to the smaller ionic radius of Fe³⁺ (0.64 Å) compared to Sn⁴⁺ (0.69 Å)³⁴.

The X-ray diffraction (XRD) patterns of the materials obtained after heating between 300 and 800 °C are shown in Figure 2.

The planes were indexed according to ICDD 01-074-1300 (BaSnO₃), 00-041-1445 (SnO₂), 00-045-1471 (BaCO₃), 00-024-0053 [Ba(NO₃)₂] and 00-010891 (Sn). For the precursor’s heat treated at 300 °C, peaks assigned to tetragonal SnO₂, Ba(NO₃)₂, Sn and BaCO₃ were observed. After heat treatment at 400 °C, higher intensity peaks were observed for Ba(NO₃)₂, while the intensities of these peaks decrease at 500 °C. The formation of the cubic BaSnO₃ (Pm3m) was observed at 600°C besides a small amount of SnO₂ and BaCO₃, which is in agreement with the TG/DTG analysis shown in figure 1. This crystallization temperature below 600°C is quite low compared with other synthesis methods as solid state reaction³⁰-³³. No significant change was observed with temperature increase from 600 to 800 °C.

The XRD patterns of Fe-doped BaSnO₃ are shown in Figure 3. Highly crystalline cubic BaSnO₃ was observed while no peaks assigned to Fe₂O₃ (ICDD 03-065-3107) were found. A slight shift in the diffraction peaks towards higher 2θ values was observed after doping indicating that Fe³⁺ got into BaSnO₃ lattice. The lattice parameters, a, of BaSnO₃ were calculated and indicated that a small lattice decrease took place, which is assigned to the smaller ionic radius of Fe³⁺ (0.64 Å) compared to Sn⁴⁺ (0.69 Å)³⁴.

Figure 4 shows the Raman spectra of the Fe³⁺-doped BaSnO₃ (0; 0.05 and 0.1 in mol). The group theory predicts the absence of active modes in the Raman spectra for a perfect Pm3m perovskite structure. In spite of this, Cerda et. al.³⁵ reported bands at 238, 408, 543 and 724 cm⁻¹, attributed to distortions of the cubic structure of BaSnO₃ due to defects, which modify the internal symmetry of the perovskite phase, leading to unexpected modes in Raman spectra. These modes were assigned to the six fundamental vibrations of SnO₆ with O₃ symmetry. Similar studies on various perovskite compounds show that distortions of these materials are due to the presence of defects (ν₁''O₆, ν₄''O₆, ν₃'Sn²⁺)³⁶-³⁸.

Balamuragan et al.³⁹,⁴⁰ evaluated the optical and electromagnetic properties of Fe-doped BaSnO₃. According to the authors, when iron is added into the perovskite lattice, a center of extrinsic defects is formed with the formation of oxygen vacancies for charge compensation, as showed in Equation (1).

\[
Fe_{2}O_{3} + 3O_{0}^{-} + 3O_{0}^{X} \rightarrow 2Fe^{2+}_{Sn} + 2Fe^{3+}_{Sn} + 2Fe^{+}_{Sn} + 3O_{0}^{X}
\] (1)
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In the present work, the mode at 150 cm$^{-1}$ was attributed to the vibration of carbonate groups. Undoped BaSnO$_3$ showed bands at similar regions to those reported by Cerda et al. indicating that distortions are present in the structure. After doping, dislocation of the bands to 252, 413, 535 and 663 cm$^{-1}$ took place. A higher definition was observed for the bands at 252 and 413 cm$^{-1}$, which may be correlated to the oxygen vacancies, which change the symmetry.

Figure 1. a) TG and b) DTG curve of the precursor after heat treatment in the O$_2$ atmosphere at 300°C.

Figure 2. XRD patterns of the BaSnO$_3$ heat treated at different temperatures.

Figure 5 shows the absorption spectra of Fe$^{3+}$-doped BaSnO$_3$, with a strong absorption in the visible region. The optical absorption edge of BaSnO$_3$ was observed around 477 nm, with a red shift as doping concentration increases. The band gap values of the as-synthesized samples were estimated from diffuse reflectance spectra using the Wood-Tauc method. Incorporation of Fe$^{3+}$ into the lattice resulted in a band gap decrease, indicating that intermediate levels were formed inside the band gap.

3.2 Photocatalytic properties

The photocatalytic decomposition of RNL by Fe-doped BaSnO$_3$ is presented in Figure 6. The highest degradation efficiency occurred at pH = 3 and the lowest degradation occurred at pH = 6 (aqueous solution of the dye). Photocatalysis may occur by two different mechanisms: direct or indirect one. For the direct mechanism, dye is adsorbed on the photocatalyst surface and electron transfer takes place without the formation of intermediate compounds. During the indirect mechanism, hydroxyl radicals are formed due to electron/hole transfer between the surface and compounds as O$_2$, H$_2$O and OH$^-$. Then, hydroxyl radicals in solution react with the substrate.

The possibility of a discoloration by a direct mechanism was evaluated by the adsorption analysis, as adsorption of
Figure 3. XRD patterns of the BaSn$_{1-x}$Fe$_x$O$_3$ (0; 0.05 and 0.1 in mol) samples. Detail of the (110) peak in the XRD patterns as a function of the iron concentration.

Figure 4. Raman spectra of BaSn$_{1-x}$Fe$_x$O$_3$ (0; 0.05 and 0.1 in mol) samples.

Figure 5. UV-Vis spectra of samples BaSn$_{1-x}$Fe$_x$O$_3$ (0; 0.05 and 0.1 in mol).

the dye on the material surface is a requested prerequisite step for direct charge transfer\textsuperscript{42}. Results displayed in Figure 7 indicate that the maximum discoloration due to adsorption process was 7\% for the BaSn$_{0.9}$Fe$_{0.1}$O$_3$ sample, much smaller than the discoloration percentage under UVC irradiation (93 \%). This small adsorption indicates that the indirect mechanism prevails for this system.

The effect of pH on photocatalysis has been evaluated by different researchers, as reported in the review published by Akpan and Hameed\textsuperscript{43}. Much of them report a direct
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Figure 6. Results of the photocatalytic decomposition of RNL as a function of pH for the photocatalysts BaSn$_{1-x}$Fe$_x$O$_3$ ($x = 0, 0.05$ at $0.1$ in mol): a) pH = 6; b) pH = 3 and c) Percentage of photodegradation of the RNL.

Figure 7. Evaluation of RNL adsorption at pH = 3 after 4 h for the samples BaSn$_{1-x}$Fe$_x$O$_3$ ($x = 0, 0.05$ and $0.1$ in mol).

mechanism at low pH when TiO$_2$ is used as photocatalyst. On the other hand, according to Guo et al., hydrogen radicals also take part in the photodegradation of phenol using TiO$_2$ as photocatalyst. These H radicals may be produced from H$_2$O molecules and also from H$_3$O$^+$ ions especially in acid media, and may react with O$_2$ forming HO$_2^-$ which finally convert to 'OH. According to Texeira et. al., the RNL azo dye has three pK$_a$ values: the sulphonic group is deprotonated at pH = 3, the sulphate group is deprotonated at pH = 3.5 and the amide group is deprotonated at pH = 6, which results in a large negative charge. Therefore, an attractive force between the positive surface charge of the perovskite and the negative charge of the azo dye occurs at pH 3 favoring the dye attraction and the highest solution discoloration. At pH 6, few molecules are attracted on the BaSnO$_3$ surface due to the slight positive surface charge, leading to a small discoloration of the solution.
In the present work, the highest efficiency at acid media cannot be assigned to a direct mechanism, as only a small adsorption was detected. It seems clear that RNL photodegradation is promoted by OH radicals whose formation is favored at acidic conditions, probably due to the highest amount of H₂O² ions.

Figure 6c shows that the color was halved after 1 h of photocatalysis with BaSn₀.₉₅Fe₀.₀₅O₃ (x = 0.05 and 0.10), 2.5x higher than undoped BaSnO₃. For longer times, doped samples also presented a higher photocatalytic activity than pure one, increasing with Fe content. After 4 h, a photocatalytic efficiency of about 93% was attained for the sample BaSn₀.₉₅Fe₀.₁₅O₃.

Several papers using Fe-doped TiO₂ nanoparticles assumed that a higher photocatalytic efficiency for Fe-doped samples is possible in comparison with the undoped material, especially because Fe³⁺ can act as both hole and electron traps to enhance lifetimes of electrons and holes.

Fe-doped BaSnO₃ has been studied for magnetoelectronic applications, classified as oxide-diluted magnetic semiconductor, displaying ferromagnetism even with small doping amounts. This property is enhanced due to a F-center exchange mechanism, which enables Fe-ions to order ferromagnetically. This F-center is characterized by a Fe⁴⁺-V⁻Fe⁴⁺ configuration which is able to trap electrons⁹,⁴⁰,⁴⁷.

In the present work, XRD patterns and Raman spectra indicated that Fe³⁺ was added into the BaSnO₃ lattice leading to a shift of the absorption onset to the visible region due to the formation of intermediate levels inside the band gap. These intermediate levels may trap electrons preventing the electron-hole recombination. As a consequence, higher photocatalytic efficiency is obtained.

4. Conclusions

BaSnₓFe₁₋ₓO₃ (x = 0, 0.05 and 0.10) was successfully synthesized by the modified Pechini method, with crystallization around 600°C. XRD patterns and Raman spectra indicated that Fe³⁺ got into the perovskite lattice leading to a decrease of the band gap. The samples showed high potential for photodegradation of the RNL azo-dye at pH = 3 with prevalence of indirect mechanism. Efficiency was improved by Fe³⁺ doping probably due to the formation of intermediate levels inside the band gap, which may trap electrons avoiding electron-hole recombination.

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6. References


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