Synthesis and structural properties of Fe-doped ZnO nanoparticles

Síntese e propriedades estruturais de nanopartículas de ZnO dopadas com Fe

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ABSTRACT
There is a wide variety of methods to synthesize ZnO nanoparticles, among them the polymeric precursors method is attractive because of its high reproducibility. In this work, attention is paid to the changes that the ZnO matrix can present when Fe is introduced to substitute Zn ions. Iron ions can stabilize in two

oxidation states (Fe2+ and Fe3+), with different ionic radii, which can affect the resulting magnetic properties of the Fe doped ZnO nanoparticles.

Keywords: Fe-doped ZnO.

RESUMO
Há uma grande variedade de métodos para sintetizar nanopartículas de ZnO, entre os quais o método dos precursores poliméricos é atraente devido à sua alta reprodutibilidade. Neste trabalho, a atenção está voltada para as mudanças que a matriz de ZnO pode apresentar quando o Fe é introduzido para substituir os íons de Zn. Os íons de ferro podem se estabilizar em dois estados de oxidação (Fe2+ e Fe3+), com diferentes raios iônicos, o que pode afetar as propriedades magnéticas resultantes das nanopartículas de ZnO dopadas com Fe.

Palavras-chave: ZnO dopadas com Fe.

1 INTRODUCTION

There is a wide variety of methods to synthesize ZnO nanoparticles, among them the polymeric precursors method is attractive because of its high reproducibility. In this work, attention is paid to the changes that the ZnO matrix can present when Fe is introduced to substitute Zn ions. Iron ions can stabilize in two oxidation states (Fe^{2+} and Fe^{3+}), with different ionic radii, which can affect the resulting magnetic properties of the Fe doped ZnO nanoparticles.

2 METHODOLOGY

The synthesis procedure was carried out by dissolving zinc nitrate hexahydrate and citric acid in ethylene glycol at 70°C with permanent magnetic stirring, and then the temperature was raised to 120°C. Iron nitrate nonahydrate was added to the obtained resin in a molar ratio and then pyrolyzed at 400°C for 4h. Subsequently, it was thermally treated at 500°C for 6 hours, obtaining a homogeneous and thermally stable powder product.

3 RESULTS AND DISCUSSION

In Figure 1(a) the XRD patterns for each nanoparticle obtained are shown. A progressive peaks broadening is observed as the Fe content is increased, which suggests a decreasing trend of the crystallite size. The (101) peak intensity indicates a good crystallinity of the wurtzite phase. Any evidence of a second phase was determined. The lattice constants of the undoped ZnO NPs are a = b = 3.2493 Å and c = 5.2070 Å and the unit cell volume is V = 47.611 $Å^3$. This is in line with values reported in the literature [1]. However, for the Fe-doped ZnO NPs, the unit cell volume (V) shows an increasing trend as the Fe content increases up to x = 0.075, Figure 2(a), followed by a downward trend above that Fe content. There are 2 possible scenarios here:

i) In the low Fe content region, the Fe^{2+} ions (0.63 Å) substitute Zn ions (0. … Å) in the tetrahedral sites (coordination number 4), therefore, increasing its volume, due to the difference in ionic radii. For x > 0.075, Fe^{3+} ions (0.49 Å) [2] would enter, which would lead to a decrease in volume and segregation of Fe ions on the surface of the nanoparticle.

ii) Fe dopants occupy octahedral sites (coordination number 6), as Fe^{3+} ions (0.65 Å) up to x = 0.075, although it was energetically unlikely and Fe^{3+}/Fe^{2+} would coexist in the surface region for higher Fe concentrations. [3]

TEM micrographs (Figure 3(a) and (b)) confirm results obtained from XRD and show that crystallite size is related to Fe content, suggesting that the incorporation of Fe ions prevents the growth of ZnO NPs. In (Figure 3(c) and (d)), the histograms evaluate the mean physical sizes for the undoped and 10% Fe-doped ZnO.

Figure 1 - (a) XRD of the $Zn_{1-x}Fe_xO$ NP, with x ranging from 0.000 to 0.200.

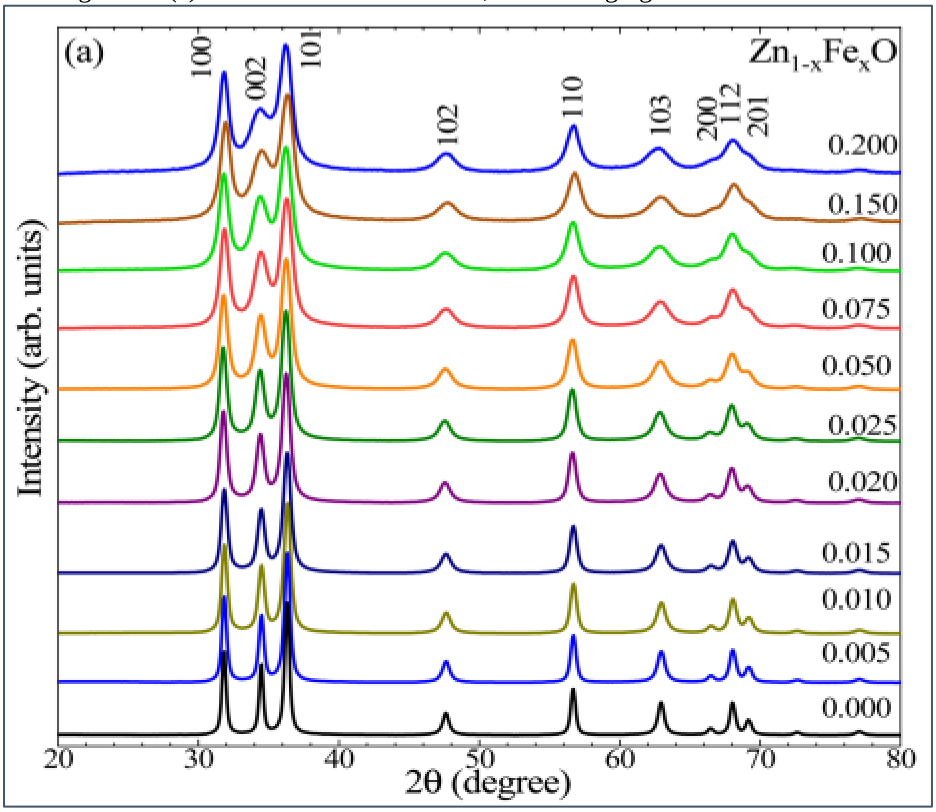

Figure 2 - (a) Cell volume unit (V). (b) Bond length (l) depending on the content of Fe (x).

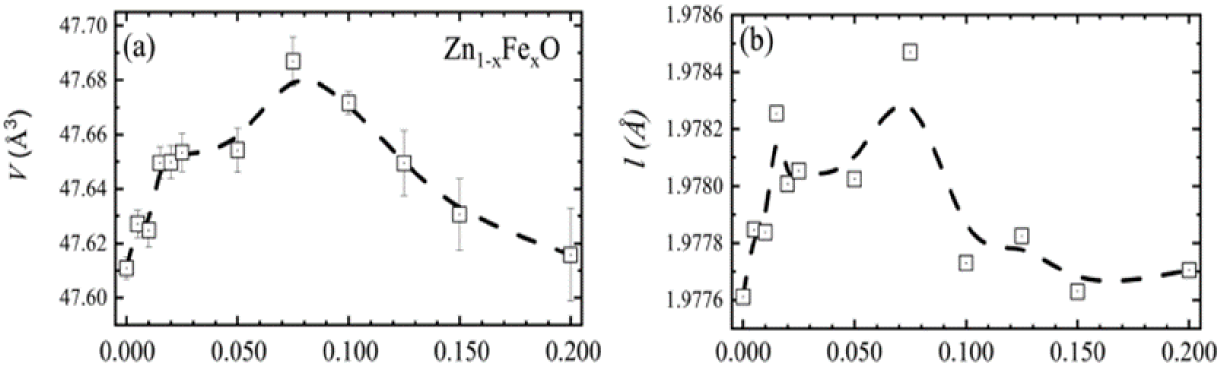

Figure 3 – (a) TEM for undoped and (b) 10% Fe-doped ZnO nanoparticles, with their particle size histograms for (c) undoped and (d) Fe-doped ZnO.

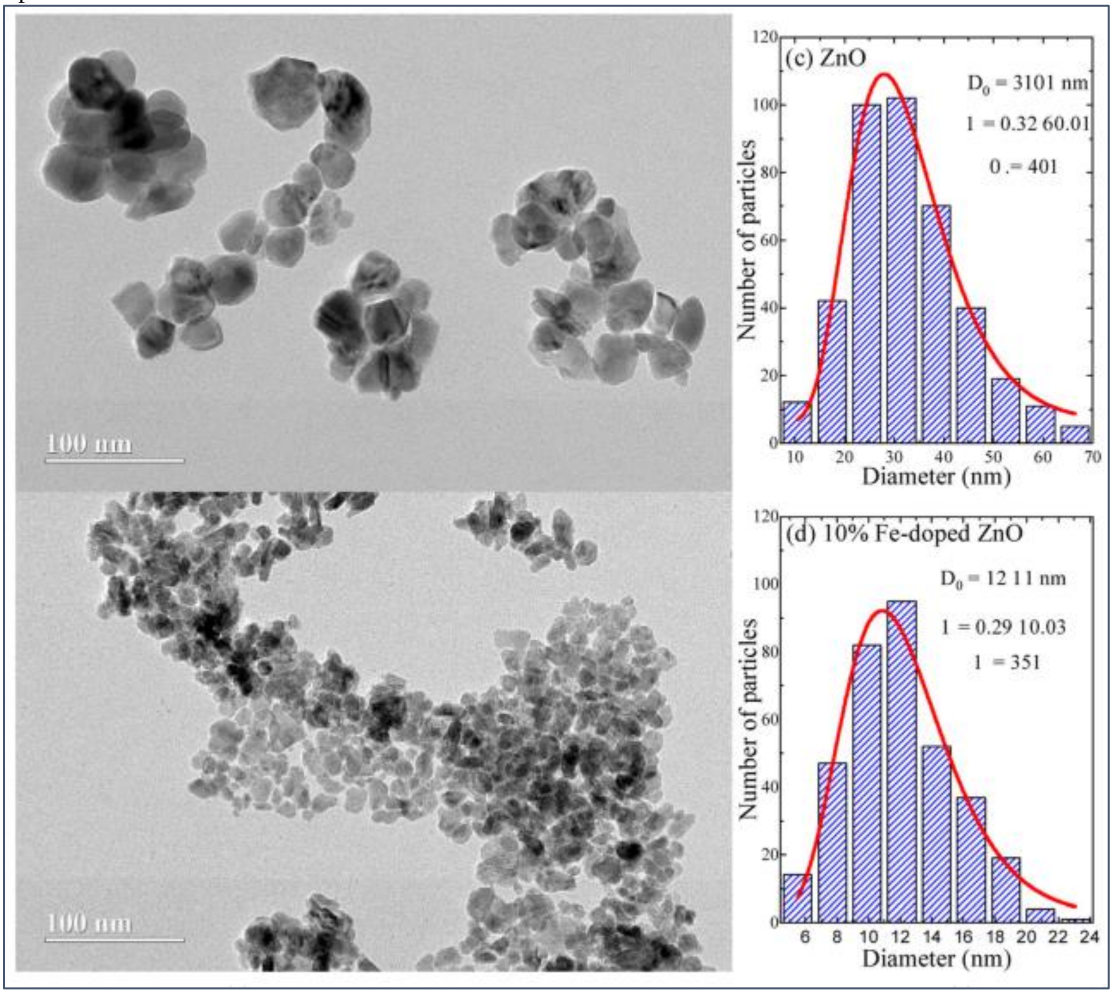

Figure 4 - FTIR spectra of undoped and Fe-doped ZnO NPs.

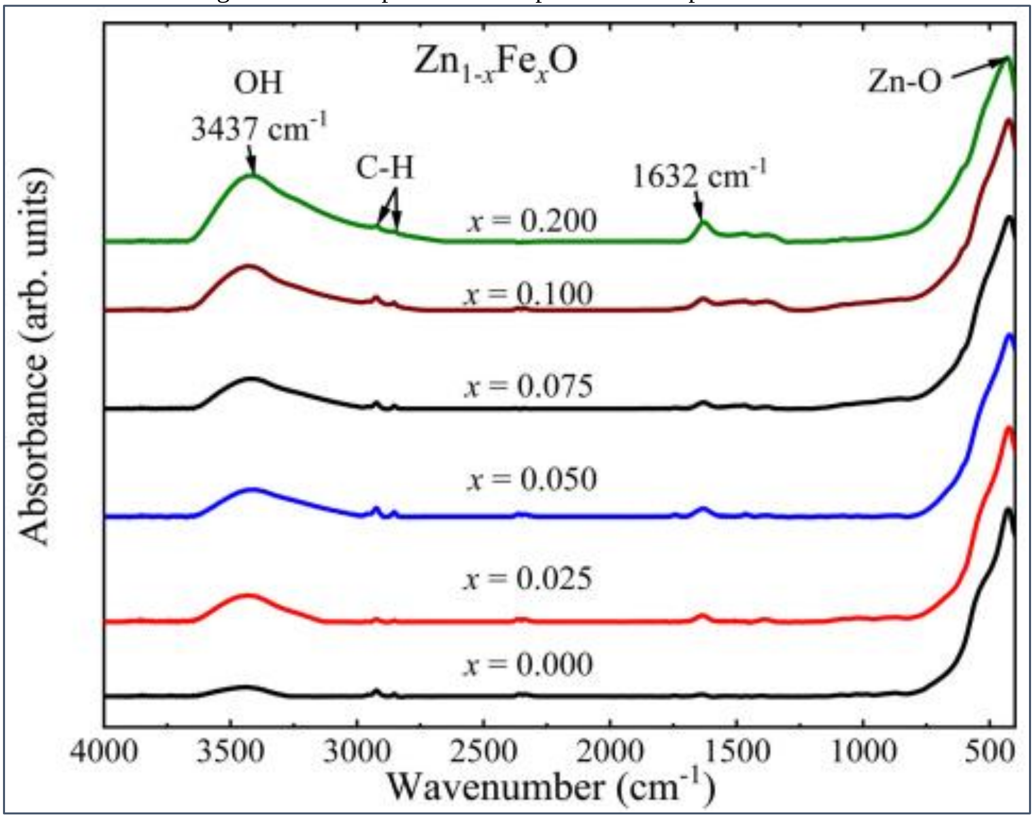

Figure 4 presents the FTIR spectra of the undoped and Fe-doped ZnO NPs. The bands corresponding to the OH and C-H vibrations are properly indicated in Figure 4. The inorganic vibrational frequency of Zn-O is found at 423 cm^{-1} for undoped ZnO NPs [5], slightly below the value (431 cm^{-1}) reported in literature. No additional vibrational modes associated with iron oxide secondary phases were observed. The main mode (inorganic mode below 430 cm^{-1}) shows a clear downward trend with the Fe content up to 7.5%, after that a gradual blueshift is determined as the Fe content is increased. This finding may be related to the possibility that iron ions enter the wurtzite crystalline structure in two different oxidation states, Fe^{2+} for lower Fe doping content and Fe^{3+} for higher doping content, which is in agreement with the XRD data analysis.

4 CONCLUSION

Undoped and Fe-doped ZnO NPs showing a single-phase were successfully synthesized. XRD data analysis reveals significant structural changes related to the presence of Fe ions in the ZnO matrix. A decreasing trend of the crystallite size with the Fe content is determined. Also, FTIR data analysis proved to be a valuable tool to determine the structural properties of Fe-doped ZnO, which is consistent with what is determined by XRD data analysis.

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