INTRODUCTION

Zinc oxide is a type \( n \) semiconductor with excess of interstitial ions \( \text{Zn}^{2+} \) that shows a hexagonal crystalline structure of the wurtzite (ZnS) and spatial \( P6_3mc \) group. The candidates to Simulation Model are a zinc atom tetrahedrally coordinated by four adjacent oxygens \( (\text{ZnO}_4^-) \) or an atom oxygen in the center and four atoms of zinc \( (\text{ZnO}_6^{6+}) \) like your neighbors \([1]\). It is a wide band gap \( (E_g = 3.3 \text{ eV}) \) metal oxide semiconductor with interesting piezoelectricity in thin polycrystalline layers with preferential orientation around axis \( c \) of the structure besides wide power to technological application such as UV protection, photocatalysis, field emission displays, varistors, functional devices, thermoelectric materials, sensors and acoustic transducers \([2–6]\). The structure of zinc oxide consists of tetrahedral sites oriented in just one direction with occupied layers by oxygen atoms. Figure 1 shows the structure and the distribution of the zinc and oxygen atoms.

Because of the difference of radius oxygen and zinc atoms, the structure becomes relatively open, making possible the lodging of strange atoms, diffusion of the atoms by crystalline lattice or formation of solid solution leading to the formation of groups like \( \text{Zn}_3\text{MnO}_{6+} \), \( \text{Zn}_3\text{CoO}_{6+} \), and \( \text{Zn}_3\text{CuO}_{6+} \). When small quantities of others metallic oxides are added to zinc oxide, the mixture becomes to exhibition an inconstancy in the stress current because of the reactions between zinc oxide and other oxides that leads to the formation of different phases and compounds of high complexity during the process of sinterization occurring the formation of varistors based in zinc \([8]\).

Thin and homogeneous ceramic powders are important compounds to attainment of ceramic materials more sophisticated principally to applications that require high performance and technology that assure purity, controlled and reproductive chemical composition, atomic homogeneity, and rigorously controlled and consisting size of particles.

Ceramic materials can be obtained through methods of reactions in solid state of mixture of powders, fusion, crystallization and chemical synthesis (precipitation), and other methods more sophisticated like sol–gel, reactions in gaseous phase, “freeze drying,” hydrothermal synthesis, and the reactions in liquid phase. In comparison with other oxide preparation methods, the polymerized complex method designed by Pechini \([9]\) is a low temperature synthesis route which can produce a more uniform particle distribution \([2, 5, 10]\).

Pechini method is based in formation of a polymeric resin produced by polyeстерification between a chelated metallic complex using hydrocarboxylic acids (lake citric or maleic acids) and a polyhydroxy alcohol like ethylene glycol. The sources of metallic ions can be nitrates, oxides, carbonates, acetates, etc. The chelated was obtained of the reaction is polyesterification-hot.
(80–100°C) (polymerization by condensation or polycondensation) with ethylene or polyethylene glycol (polyalcohol). Removing of the product the excess of dissolvent remaining, a solid and transparent resin with metallic ions. This resin is submitted to a thermal decomposition and having like product a thin and amorphous powder without needing calcinations to crystallize.

In this work, zinc oxide was produced by Pechini method. The obtained powder was calcinated in different temperatures. The products of the reactions were characterized by x-ray diffraction to estimate the formation of the phase, crystallite size, crystallinity degree, and the lattice parameter. Infrared analysis was achieved to check the present functional groups.

EXPERIMENTAL

Zinc oxide was obtained by method of polymeric precursors developed by Pechini. The zinc acetate \((\text{(CH}_3\text{CO}_2\text{)Zn}_n\text{H}_2\text{O})\) supplied by Mallinckrodt, the ethylene glycol \((\text{C}_2\text{H}_6\text{O}_2)\) and citric acid \((\text{C}_9\text{H}_7\text{O}_8)\) both supplied by Carlo Erba-Analytics were utilized like precursors to the synthesis. Citric acid was dissolved in water, under constant stirring and heated to 70°C approximately. In this aqueous solution of citric acid was added the zinc acetate in same conditions of stirring and temperature. The ethylene glycol was added under constant stirring and temperature of 90°C to make possible the polymerization of mixture and occurring the reaction of polyesterification between polyalcohol and the free carboxyls of the complex salts. When the solutions reach a loss of 50% of bulk, a viscos resin has been formed. The relation [citric acid/lions] was 3.0 mol %. Ethyleneglycol was added in 40/60 (wt %) compared to citric acid. It was added nitric acid in the mixture of citric acid/ethyleneglycol to improve the solubility of the salts. The pyrolysis of the organic substance occurred in 350°C and a heating rate in 2°C/min under room temperature in furnace EDG F-1800. The precursor’s powders were milled in mortar and agate pistols and passed in a sieve 100 mesh. The material was calcinated in 500, 600, 700, 800 and 900°C/1 h on plates of sinterized alumina with heating rate 10°C/min in room temperature in furnace EDG F-1800 and characterized by x-ray diffraction. Infrared analyze was accomplished in the powders calculate in 500 and 700°C.

The calcinated powders were characterized by x-ray diffraction using equipment Siemens D-5000 with CuKα radiation operating at 40 kV and 40 mA to determine formed phases, crystallite size, lattice parameters, and relative crystallinity. The calcinated powders in 500 and 700°C were characterized by infrared analysis using an AVATAR TM 360 instrument by the standard KBr disk method. It was used a wavelength range from 4000 to 400 cm\(^{-1}\).

RESULTS AND DISCUSSION

The x-ray diffraction pattern of the powders samples calcinated at 500, 600, 700, 800, and 900°C are shown in Fig. 2. The observed diffraction peaks in all the recorded XRD patterns are in agreement with those of the JCPDS card 89-7102 for hexagonal ZnO with wurtzite structure. No peaks of any other phase were detected.

The influence of the calcination temperature in diffractograms of x-ray diffraction of the samples can be observed in the variations of intensity and full-width to medium-height (FWHM) of the diffraction peaks of ZnO. These characteristics were utilized to determination of the crystallinity degree and crystallite size of the samples showed in the table. The crystallinity of the
samples was estimated with base in integral area of the diffraction peaks. The results revealed that the crystallinity degree increased with the calcination temperature. The reason for this fact is that in higher temperatures than the speed of crystallization of the solid phases increases due to the big movement of the atoms that facilitates a fast arrangement of the crystalline structure. The average crystallite size of the monophase samples was calculated from x-ray line broadening ($d_{101}$) using the Scherrer equation [11]. The results showed that the crystallite size increased with the calcination temperature. All the samples presented crystallite size less then 60 nm. The lattice parameters obtained from these patterns for hexagonal zinc oxide phase in the powders were calculated with the program PowderX [12] and are in good agreement with the reported values ($a = 3.249 \text{ Å}; c = 5.206 \text{ Å};$ JCPDS 89-7102). The obtained values not showed expressive alteration, indicating that calcination temperature not shows influence in the crystalline structure of the sample.

The results from infrared spectroscopy analysis carried out at 500 and 700°C are showed in Fig. 3. The spectra of sample calcinated at 500°C consist of four bands. One wide band located at 490 cm$^{-1}$ attributed to Zn–O stretching in the ZnO lattice, a small band located at 1044 cm$^{-1}$ probably due to vibration frequencies of the acetate group, and two small bands locating at about 2360 cm$^{-1}$ due to vibrations of the CO$_2$ molecules and OH groups. The spectra of sample calcinated at 700°C consist of two bands. One wide band in 450 cm$^{-1}$, attribute to Zn–O stretching in the ZnO lat-

<table>
<thead>
<tr>
<th>Calcination temperature, °C</th>
<th>Crystallinity degree, %</th>
<th>Crystallite size, mm</th>
<th>Lattice parameter, Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>500</td>
<td>47.7</td>
<td>24.3</td>
<td>$a = b = 3.250; c = 5.212$</td>
</tr>
<tr>
<td>600</td>
<td>54.1</td>
<td>31.9</td>
<td>$a = b = 3.255; c = 5.213$</td>
</tr>
<tr>
<td>700</td>
<td>56.1</td>
<td>44.0</td>
<td>$a = b = 3.250; c = 5.202$</td>
</tr>
<tr>
<td>800</td>
<td>68.9</td>
<td>45.3</td>
<td>$a = b = 3.251; c = 5.209$</td>
</tr>
<tr>
<td>900</td>
<td>73.0</td>
<td>55.1</td>
<td>$a = b = 3.252; c = 5.208$</td>
</tr>
</tbody>
</table>
tice and a small inflection in 1044 cm$^{-1}$ probably due to vibration frequencies of the acetate group.

**CONCLUSIONS**

The synthesis of nanocrystalline zinc oxide powders by Pechini method resulted in the formation of a monophase material with highly-crystalline particles upon calcination at 500°C. The zinc oxide nanocrystals calcinated in the temperature range 500–900°C display an increase in the crystallite size from 24 nm (500°C) to 55 nm (900°C). Calculated lattice parameters from the x-rays patterns presented values in good agreement with the data found in the literature. Studied samples presented good crystallization degree, standing out the calcination to 800 and 900°C (crystallization degree >60%). The infrared spectroscopy analysis confirmed the elimination of organic groups with the increase of the calcination temperature.

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**REFERENCES**


