SYNTHESIS OF ZnO NANOPARTICLES BY SOL-GEL PROCESSING

Bruna Martinello Savi, Larissa Rodrigues, Adriano Michael Bernardin

Ceramic and Glass Materials Group, Santa Catarina Extreme South University, Av. Universitária 1105, 88.806-000, Criciúma, SC, Brazil

amb@unesc.net

ABSTRACT

The aim of this study was to obtain and characterize ZnO nanoparticles by sol-gel technique. $ZnCl_2$, $Zn(NO_3)_2$, NaOH were used as precursors for the synthesis. NaOH was dissolved in distilled water at a concentration of 1.0 M with agitation to the desired reaction temperature (50°C and 90°C). 0.5 M $ZnCl_2$ and 0.5 M $Zn(NO_3)_2$ were added by dripping (60 and 30 min). The powder was characterized by XRD (Cu Kα), UV-Vis, and HR-TEM. Nano ZnO particles were obtained with crystallite size between 20 and 40 nm (HR-TEM and XRD). The results of UV-Vis spectrometry show that the band gap energy, given by the absorbance at 300 nm depends on the precursor used.

1. INTRODUCTION

Zinc oxide is a chemical compound found naturally in the mineral called zincite and has attracted much attention in recent times due to its low cost and because it can be obtained by simple techniques (1). ZnO crystallizes in the typical wurtzite hexagonal structure where oxygen and zinc atoms are spatially arranged in a way that O atoms are arranged in a closed hexagonal structure, while the Zn atoms occupy the centre of the distorted tetrahedron structure (2). Moreover, it is a semiconductor material of the II-VI group with a large energy gap around E_g = 3.2 eV, a large range of excitation energy and controlled electrical conductivity (3), and when doped with transition metals exhibits the ferromagnetic phenomenon at room temperature, and because of that it has attracted much interest due to their potential applications in "spintronics" (4).

Nanocrystalline powders – due to their average particle size (below 100 nm) – may show different behaviours resulting from a higher surface energy due to the large surface area and the wider gap between the valence band and conduction band, effects characteristic of sizes close to the atoms. These phenomena may increase the potential use of the material, including optical, chemical, electromagnetic, among other properties. Therefore, because of its exceptional physical and chemical characteristics (5), the nano zinc oxide (ZnO) is an important raw material for many applications as the design of varistors, gas sensors, luminescent oxides (6), rubber, paints, ceramics, and others (7).

The ZnO is insoluble in water and ethanol but is soluble in dilute mineral acids and is a fine powder, white or slightly yellow. In large quantities and high purity it is recommended for use in the pharmaceutical, food and cosmetic industries (8). Zinc oxide is a transition metal and semi-metal that can react with both acids and bases providing water and salt. Because ZnO presents intermediate properties between acid and basic oxides it can behave as both acid and basic oxide (9). It is an intrinsic n-type semiconductor material that crystallizes in the hexagonal crystal system; it is relatively inexpensive, presents low toxicity, and is very effective in protecting against UV rays. ZnO is an excellent material for the manufacture of sunscreen, because it absorbs ultraviolet (UV) rays and combat the potential problems associated with sun exposure.

The search for nanostructured ceramic materials that result in high-performance materials has led to the development of several chemical methods on a laboratory scale. Among the various methods of chemical synthesis there are the sol-gel method (10), spray pyrolysis (11), liquid combustion reaction (12), hydrothermal synthesis (13), spray drying (14) and the Pechini method (15), highlighting the combustion reaction method, which makes use of redox reactions between the decomposition products of nitrate and a fuel, such as urea. An alternative method is the solochemical process, a sol-gel method that produces nanometric powders used initially to produce ZnO (16), where an initial solution containing a zinc complex is decomposed to form nanometric powder zinc oxide. Another name for this

method is two-stage solochemical (TSSC) method. The method can also be used to produce other oxides such as NiO and Mn_2O_3. The mixture of a pure chemical compound (containing the zinc complex) in a second chemical causes the formation of a nanometric powder.

The nano powder formed by the solochemical process can then be doped with other oxides, and the product can be a nanocomposite. Composite nanoparticles are commonly used as varistors with nanostructured morphology. Results of more recent works show the synthesis of ZnO nanopowders from the two-stage solochemical reaction (16-17):

$$(NH_4)_2ZnO_2 + H_2O \rightarrow ZnO + 2NH_4OH$$

Therefore, this paper proposes the use of sol-gel synthesis (two stages solochemical process) for the production of nanostructured zinc oxide powders in function of the type of precursor, temperature of synthesis, and dripping time, in order to evaluate the influences of these conditions on the structure and morphology of the powders obtained. The main objective is the synthesis of nanoparticles to be deposited on the surface of ceramic tiles in order to obtain functional ceramics.

2. EXPERIMENTAL PROCEDURE

Zinc chloride ($ZnCl_2$), zinc nitrate ($Zn(NO_3)_2$) and sodium hydroxide (NaOH), all of analytical grade were used as precursors for the synthesis. The production unit of ZnO nanocrystals (nano-ZnO) consisted basically of a reactor with heating. The NaOH was dissolved in distilled water at a concentration of 1.0 M. The resulting solution was heated under constant stirring at the desired reaction temperature (50°C and 90°C).

After obtaining the desired temperature, a solution of $ZnCl_2$ 0.5 M and another of $Zn(NO_3)_2$ 0.5 M were slowly added (dripping for 26 min and 52 min) into the reactor. This procedure was performed under constant stirring and the reaction temperature was maintained at the desired value. The dripping of the $ZnCl_2$ and $Zn(NO_3)_2$ solutions in an aqueous alkaline solution results in immediate precipitation of ZnO, and the colour of the suspension changes from transparent to white. After completing dripping, each solution – according to an experimental design – remained agitated for a period of two hours, maintaining the desired temperature.

The material formed in the reactor was filtered, washed several times with deionized water and dried in a vacuum oven at a maximum temperature of 70°C for several hours. The experimental design for obtaining ZnO from 0.5 M $ZnCl_2$ and 0.5 M $Zn(NO_3)_2$ using 1.0 M NaOH at constant agitation at 50°C and 90°C is shown in Table 1.

Run	Precursor	Temp. (°C)	Drip (min)	Crystallite size (101) (Å)
1	Chloride	50	26	261.1
2	Nitrate	50	26	241.0
3	Chloride	90	26	210.1
4	Nitrate	90	26	261.4
5	Chloride	50	52	247.1
6	Nitrate	50	52	255.6
7	Chloride	90	52	217.3
8	Nitrate	90	52	258.8

Table 1. 2^3 full factorial design for the synthesis of nano-ZnO

Each run corresponds to a precursor and a condition of temperature and drip. After each synthesis the powder sample was analysed by XRD (Cu K_α (λ = 1.5418 Å), 40 kV and 30 mA, 2θ from 0 to 80°, 0.05° step and 1 s time). The crystallite size was calculated using the FWHM method. The diffraction pattern of ZnO was provided by the ICSD database (card number 57450). The high-resolution images were obtained by TEM (200 kV, HRTEM). The UV-Vis analysis was performed with dilution of newly synthesized samples in deionized water (50 vol.% / 50 vol.%), with readings between 200 and 800 nm in a double beam spectrometer in quartz sample holder (4 ml), and the absorbance of the solutions was read.

3. RESULTS AND DISCUSSION

Figure 1 shows the XRD patterns for runs 1 to 8 of the experimental design, noting that the runs 2, 4, 6 and 8 are in duplicate. In all diffractograms the plane (101) – peak 3 in Figure 1 – is more intense than others. This characteristic indicates the direction of crystal growth, which in the case of ZnO is along the c axis (direction [0001]) of the wurtzite structure.

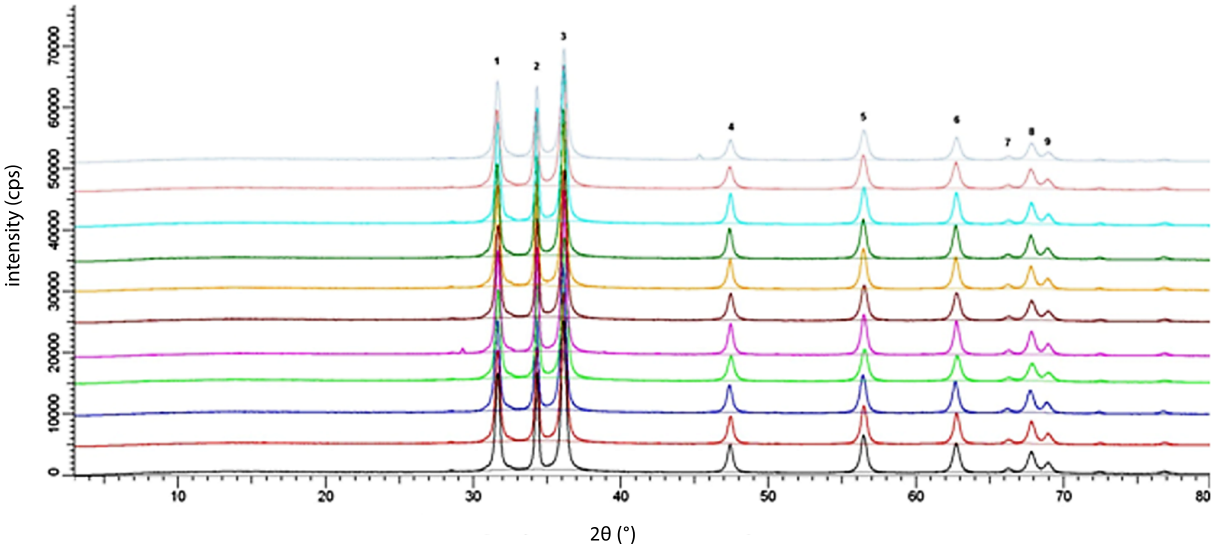

Figure 1. Diffraction patterns for the 2^3 full factorial design for the synthesis of ZnO

Table 2 shows the analysis of the results (ANOVA) for the crystallite size of the samples in function of the type of precursor, synthesis temperature and dripping time. The only factor with statistical significance that influences the crystallite size is the interaction between the type of precursor and synthesis temperature, with reliable results (α = 0.224) of 77.6%. The other factors were not statistically significant.

Factor	SQ	dF	MQ	F	p
Precursor	824.18	1	824.18	4.471	0.281
Temp. (°C)	408.98	1	408.98	2.219	0.376
Drip. (min)	3.38	1	3.38	0.018	0.914
Precursor × Temp.	1362.42	1	1362.42	7.392	0.224
Precursor × Drip	44.18	1	44,18	0.240	0.710
Temp. × Drip	2.00	1	2.00	0.011	0.934
Error	184.32	1	184.32		
Total	2829.46	7			

Where: SQ = sum of squares; dF = degrees of freedom; MQ = mean squares; F = Fischer test; p = reliability

Table 2. Analysis of variance for the crystallite size

The contour curve analysis for the interaction between the type of precursor and synthesis temperature, Figure 2, shows the strong effect of both temperature and precursor, as the crystallite size is equally affected by both factors: the lowest values for the crystallite size are obtained for the higher temperature of synthesis, using chloride as a precursor. The larger sizes can be obtained with the combination of low temperature with chloride, or nitrate at high temperature, demonstrating that the interaction curve is shaped like a saddle.

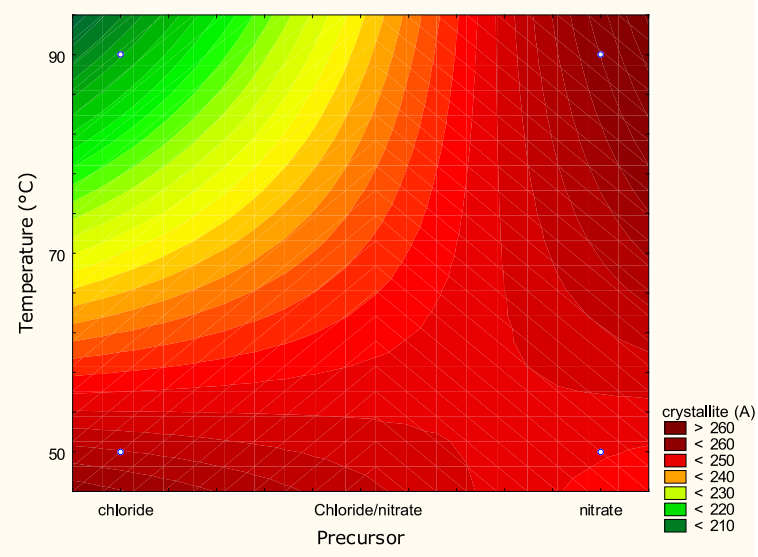

Figure 2. Contour curve for the interaction between the type of precursor and the synthesis temperature

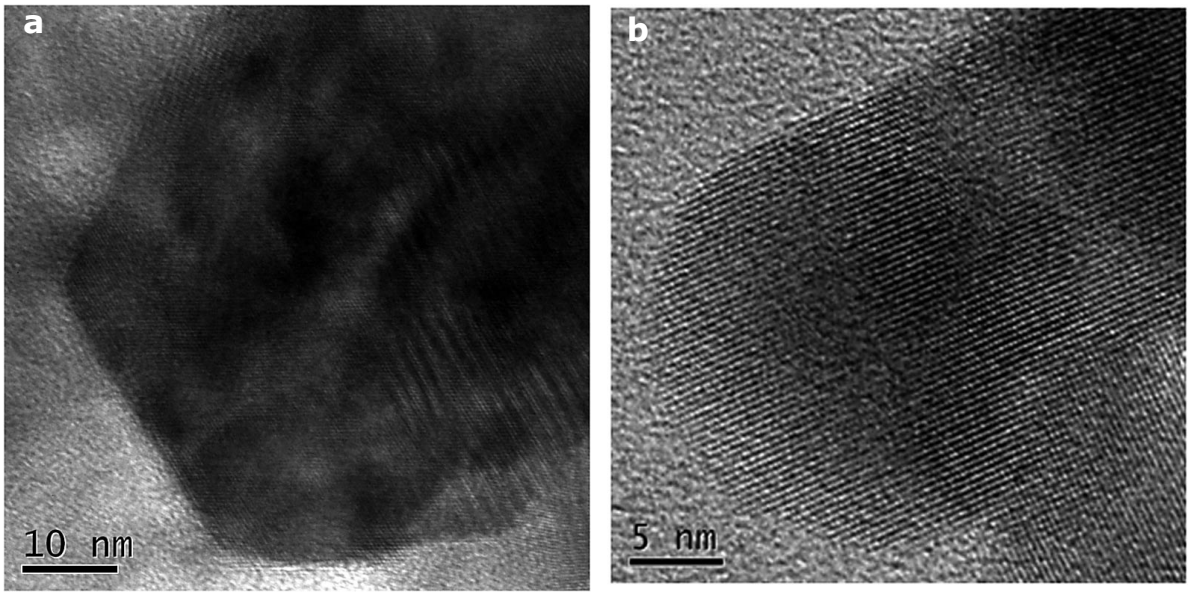

Figure 3. (a) high resolution TEM image of the (101) plane of the wurtzite structure for the condition $Zn(NO_3)_2$, 90°C and 52 min drip (b) detail

Figure 3 shows a high resolution TEM image – and detail at higher magnification – using zinc nitrate as a precursor with synthesis temperature of 90°C and dripping time of 52 min. The image shows the basal plane (101) of the wurtzite structure, which has a higher growth rate. Finally, Figure 4 shows the UV-Vis spectrum for the synthesis condition using zinc nitrate as precursor, synthesis temperature of 90°C and dripping time of 26 min. It is possible to see a strong absorbance at ~ 300 nm, showing that the synthesis resulted in photosensitive samples in the UV region.

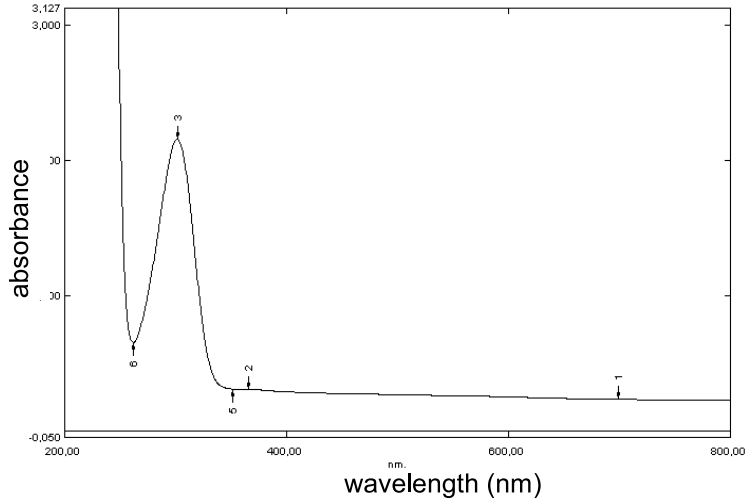

Figure 4. UV-Vis spectrum for the condition of synthesis: $Zn(NO_3)_2$, 90°C and 26 min dripping

4. CONCLUSION

ZnO nanoparticles with wurtzite structure were obtained from a sol-gel route quickly and easily, using zinc chloride and nitrate as precursors. The results of the crystallite size calculations by the FWHM method from the XRD spectra showed that for the (101) plane the crystallite size is a function of the type of precursor ($ZnCl_2$ or $Zn(NO_3)_2$) and the synthesis temperature (50 to 90°C). The smallest crystallite size is obtained using chloride as a precursor in the highest synthesis temperature, 90°C.

Images of high resolution transmission electron microscopy (HRTEM) show that zinc oxide nanoparticles were obtained with sizes close to 30 nm (300 Å) for the basal plane (101). HRTEM analysis is still being performed for all samples. Finally, partial results of the UV-Vis spectroscopy shows a strong absorbance in the UV (300 nm) region for samples synthesized from chloride.

From the results, the most appropriate route to obtain nano ZnO with increased sensitivity to UV radiation will be used for the synthesis of nanoparticles to be deposited on the surface of ceramic tiles in order to obtain functional ceramics.

REFERENCES

[1] KOUDELKA, L.; HORÁK, J.; JARIABKA, P. Morphology of polycrystalline ZnO and its physical properties. Journal Materials Science, v.29, n.6, p.1497-1500, 2004.

[2] MARTINS, J.B.L.; SAMBRANO, J.R.; VASCONCELLOS, L.A.S.; LONGO, E.; TAFT, C.A. Análise teórica da interação de CO, CO_2 e NH_3 com ZnO. Química Nova, v.27, n.1, p.10-16, 2004.

[3] LOOK, D.C.; REYNOLDS, D.C.; JONES, R.L.; LITTON, C.W.; CANTWELL, G.; EASON, D.B. Characterization of homoepitaxial p-type ZnO grown by molecular beam epitaxy. Applied Physics Letters, v.81, n.10, p.1830-1832, 2002.

[4] PRELLIER, W.; FOUCHET, A.; MERCEY, B. Oxide-diluted magnetic semiconductors: A review of the experimental status. Journal of Physics Condensed Matter, v.15, R1583, 2003.

[5] KWON, Y.J.; KIM, H.K.; LIM, C.S.; SHIM, K.B. Characterization of ZnO nanopowders synthesized by the polymerized complex method via an organochemical route. Journal of Ceramic Processing Research, v.3, n.3, p.146-149, 2002.

[6] RAVI, V.; PASRICHA, R.; DHAGE, S.R. Synthesis of fine particles of ZnO at 100°C. Materials Letters, v.59, p.779-781, 2004.

[7] PEREZ-LOPES, O.W.; FARIA, A.C.; MARCILIO, N.R.; BUENO, J.M.C. The catalytic behavior of zinc oxide prepared from various precursors and by different methods. Materials Reserch Bulletin, 2005.

[8] RAMALHO, M.A.F. Avaliação da proporção de ácido cítrico/metal no tamanho da partícula de ZnO preparados pelo método de Pechini. In: Congresso Brasileiro de Ciência e Engenharia de Materiais, 2004.

[9] HORAK, J.; KOULDELKA, L. J Mater Sci., v.29, p.1497, 1994.

[10] SILVA, R.F. Filmes de óxido de zinco dopado com alumínio ou európio: Preparação e caracterização. Tese (Doutorado), Faculdade de Filosofia, Ciências e Letras de Ribeirão Preto, 2001.

[11] ABRAROV, S.M.; YULDASHEV, Sh.U.; LEE, S.B.; KANG, T.W. Suppression of the green photoluminescence band in ZnO embedded into porous opal by spray pyrolysis. Journal of Luminescence, v.109, p.25-29, 2004.

[12] SOUSA, V.C. *et al*. Combustion synthesized ZnO powders for varistor ceramics. International Journal of Inorganic Materials, v.1, p.235-241, 1999.

[13] WANG, J.; GAO, L. Hydrothermal synthesis and photoluminescence properties of ZnO nanowires. Solid State Communications, v.132, p.269-271, 2004.

[14] MACHADO, F; COSTA, A.C.F.M.; KIMINAMI, R.H.G.A. Cinética de sinterização de ZnO preparado pelo método de freeze-dried. En: 46° Congresso Brasileiro de Cerâmica, São Paulo, p.1352-1362, 2002.

[15] LIMA, S.A.M.; SIGOLI, F.A.; DAVOLOS, M.R.; JAFELICCI Jr, M. Europium(III)-containing zinc oxide from Pechini method. Journal of Alloys and Compounds, v.344, p.280-284, 2002.

[16] VAEZI, M.R.; SADRNEZHAAD, S.K. Nanopowder synthesis of zinc oxide via solochemical processing. Mater. Des., v.28, p.515-519, 2007.

[17] WU, C.; QIAO, X.; CHEN, J.; WANG, H.; TAN, F.; LI, S. A novel chemical route to prepare ZnO nanoparticles. Mater. Lett., v.60, p.1828-1832, 2006.