

Synthesize Nano ZnO-ZrO₂ Composite by Combustion Method and Studying their Dielectric Properties

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ABSTRACT

Combustion method had been used to prepare a composite material from doping ZnO by 10 mol% ZrO₂. XRD showed a good crystalline powder comparing with ASTM cards. Dielectric properties such dielectric strength, dielectric constant, dielectric loss and tangent loss have been measured. All the dielectric properties have decreased as the frequency increasing.

The particle size has great effect on the dielectric properties of the composite which decreased as the particle size increased.

Keywords : ZnO , ZrO₂ dielectric constant, dielectric loss and tangent loss .

تحضير متراكب نانوي من اوكسيد الخارصين – الزركونيا بطريقة الانفجار ودراسة خواصها العزلية

الخلاصة

أستخدمت طريقة الانفجار ، لتحضير مادة متراكبة بأضافة 10مول % من اوكسيد الزركونيوم الى اوكسيد الزنك. اكدت حيود الاشعة السينية للنماذج المحضرة بأنها متبلورة طبقاً الى المواصفات الاصلية . تمت دراسة الخواص العزلية للمترابك والتي تمثلت بجهد او متانة الانهيار ، ثابت العزل ، معامل فقدان العزل وظل زاوية الفقدان . جميع الخواص العزلية قلت عند زيادة التردد . كان للحجم الحبيبي تأثير واضح على جميع الخواص العزلية حيث تقل هذه الخواص مع زيادة الحجم الحبيبي للمادة المترابكة .

الكلمات المرشدة : اوكسيد الخارصين ، اوكسيد الزركونيوم ، ثابت العزل ، الفقدان العزلي ، فقدان ظل الزاوية .

INTRODUCTION

Zinc oxide has been produced commercially for considerably more than century , originally for use as a pigment in paints and also for rubber , glass, porcelain enamels and pharmaceuticals . More recently zinc oxide has found new applications in semiconductors, luminescence and photoconductivity besides the Varistor device ^[1].

Many investigations on the synthesis of ZnO in the nanoscale with additive were studied in relation to sintering temperature and time, additive contents and different properties by using different synthesis method such as soft chemical method, sol gel, coprecipitation , ion exchange or hydrolysis^[2] .

Hoon and Knowles [2000]^[3] have studied microstructure and nonlinear properties of multicomponent vanadium – doped zinc oxide varistor. They found that varistor performance can be improved by increasing V₂O₅ content to 0.5wt.% in zinc oxide varistor.

Hynes et al [2002]^[4] showed that the nanocrystalline, single phase undoped ZnO was sintered to more than 95% of theoretical density at up to 700 °C, using pressureless isothermal sintering.

Lu et al [2004]^[5] have studied the effect of pore and grain size on the fracture strength of ZnO. They found that the fracture strength of ZnO influenced by the ratio of pore and grain sizes or pore/ grain size interaction which increases the fracture probability of small pores and decreases the fracture probability of large pores. This fact yields a homogenization of the critical flaw sizes.

Ibrahim and Osama [2004]^[6] have studied preparation of ZnO varistors with CeO₂. The microstructure of ceramic revealed the presence of a liquid phase which enhanced the preferential grain growth of the ZnO.

Han et al [2005]^[7] studied the intermediate stage sintering kinetics of undoped ZnO and ZnO doped with different contents of Mn. It was found that the densification in the initial and intermediate stages is affected by surface diffusion in both samples. This contribution increases with the increasing in the Mn content.

Bottger [2005]^[8] mentioned that the particle size has a strong effect on the permittivity (dielectric constant) specially for the fine powder (i.e below 10 μm). The increase of permittivity could be caused by internal stresses because each particle is clamped by its surrounding neighbours or by the increase of the number of domain walls contributing to the dielectric constant.

Ramirez et al [2008]^[9] have study the mechanical properties and dimensional effect of ZnO doped by different percentages of SnO₂ using mixing oxide route and pressing uniaxially to obtain rectangular shapes.

Noori et al [2008]^[10] reported the synthesis of zinc oxide by the gel combustion method, where the as prepared powder was amorphous in nature and a calcinations temperature of 500 °C changed the amorphous to crystalline phase.

Zhang and Hea [2008]^[11] prepared fine powders by a solvothermal synthesis method in dimethylformamide (DMP) solvent. The size of the powder synthesized at 180 °C for 48 h is about 35 μm.

Kumar et al [2011]^[12] showed that the nanocrystalline ZnO has been successfully synthesized through combustion route, without any calcinations step. Nano particles of ZnO obtained by the combustion

method were sintered to 97% of the theoretical density at 1200 °C for 4 hrs.

The objective of this work is to synthesis nano composite material and studying their dielectric properties against particle size.

THEORITICAL PART

ZnO crystal could posses a dielectric behavior when the energy barrier is large and its diffusion coefficient is low. Besides, the most important of ZnO is that it has built in polarization. Thus, it is important to know the basic of dielectric in term of polarization and electric field. In dielectric all charges are attached in specific atoms or molecules and all they can move a bit within it. Their

microscopic displacement affects the characteristics behavior of dielectric materials. In any substance, including ZnO crystal, the atom is electrically neutral because there is a positively charged core "nucleus" and a negatively charged electron cloud surrounding it. These two rejoin of charge within the atom are influenced by the electric field. The nucleus is pushed in the direction of the field and the electrons are pushed in the opposite way. The two opposing forces, electric field, pull in the electrons and nucleus apart which their mutual attraction drawing them together reach a balance, leaving the atom polarized, i.e. dielectric polarization arises due to the existence of atomic and molecular forces, appears whenever charges in a material are displaced with respect to one another under the influence of an electric field [13].

The dielectric properties such dielectric constant ϵ_r , can be calculated from the measurement of capacitance value which can be obtained from the measurements using the following equation.

$$\epsilon_r = (t \times C_p) / (A \times \epsilon_0) \quad \dots\dots\dots (1)$$

where

t = thickness of the pellet

C_p = Equivalent parallel capacitance which obtain from the data of measurement by LCR device.

ϵ_0 = permittivity of vacuum = 8.854×10^{-12} (F/M)

d = Diameter of guard electrodes

A = Gross- Section area = $\lambda (d/2)^2$

$\tan \delta$ is directly obtain from data of measurements

where dielectric loss factor obtained from equation (2)

$$\tan \delta = \epsilon_i / \epsilon_r \quad \dots\dots\dots (2)$$

EXPERIMENTAL PROCEDURE

materials used

The starting materials for sol-gel preparation of the composite material were zinc nitrate ($Zr(NO_3)_2 \cdot 6 H_2O$) (Himedia laboratories pvt . Ltd. India), zirconium oxychloride ($ZrOCl_2 \cdot 8 H_2O$) (ammonia , citric acid and distilled water).

Preparation of powder

10 mole % of 1M zirconium oxychloride solution mixed with 90 mol% of 1M zinc nitrate solution, good mixing by magnetic stirrer for 30 min .The addition of citric acid as a fuel combustion about 15%.Then, the solution was mixed and homogenized with heating up to 60 °C . Drops of ammonia are slowly added to the stirred solution and monitoring the PH.

The gel formation start at PH about 5 . After raising the temperature to 80 °C many beats are heard notifying the combustion of the citric acid that help in reducing the particle size of PH produced zinc and zirconium oxide. The gel is filtered many time to remove the excess chlorine ions or nitrate ions .

The gel has been dried at 60 °C for 24 hrs and then calcined to 500°C for half hour .

Compaction

The powder was pressed with compaction pressure of 81 MPa via tool steel die. (10mm × 10mm) cylindrical compacts dimensions used. The pellet were sintered to 1400 °C for one hour .

3-4 Characterizations

Using LCR machine to measure the dielectric properties, i.e , dielectric constant, dielectric loss factor , tangent loss were measured using equation 1 and 2. The dielectric strength measured by subjected the sample to high voltage and the breakdown (dielectric strength) equal the voltage divided by the thickness of the samples .

RESULTS AND DISCUSSION

Fig.(1) shows the X-ray diffraction (XRD) pattern of ZnO nanoparticles after calcinations . It is clear that all the peaks were matched well with the hexagonal structure of ZnO corresponding to JCPDS card No. 36-1451 % No peak from any other phases of ZnO were observed, having high peak intensities and clean profiles, indicating that the obtained ZnO nanoparticles have high crystallinity .

Fig.(2) shows XRD pattern of ZnO doped with 10% of ZrO₂ . Also it is clear that all the peaks were matched well with the hexagonal structure of ZnO but with a small peak very low intensity at $2\theta = 31^\circ$ which may be for ZrO₂ .

It also clear the addition of ZrO₂ to ZnO powders increased the intensities of all the peaks with clean profile .

Fig .(3) represents the effect of frequency on the dielectric constant of the composite at different particle size .At increasing the frequency, dielectric constant decreased sharply [14] where the highest value of the dielectric constant for all the particle size was at 25 KHz and the lowest value at 5 MHz .To polt a relation between the particle size and the dielectric constant of the composite, we chose the values at 1 MHz as shown in fig.(4)which is a clear dramatic decrease in the dielectric constant at increasing the particle size of the composite material .

Fig .(5) shows the effect of particle size of the materials on the dielectric loss factor at 1 MHz . Again the same behavior of dielectric constant which as the particle size increased the loss factor decreased .

The behavior of the tangent loss of the composite was slightly decreased and that is true because tangent loss calculated from the division of ϵ_i to ϵ_r .

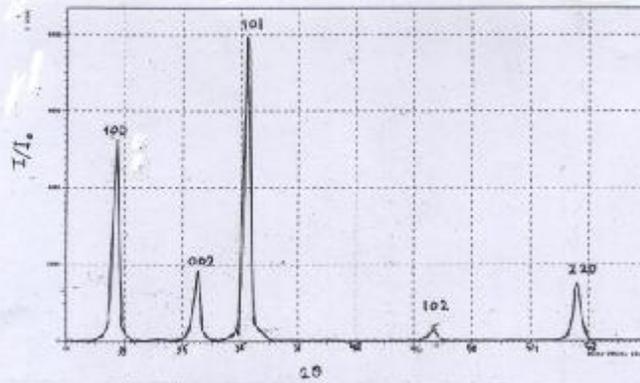
Fig .(7) represents the dielectric strength in KV / mm of the composite at different particle size, where, the nanosized has the highest breakdown voltage and that decreased at increasing the particle size .

The dielectric behavior may be due to many reasons even the reducing in particle size which decreased the porosity of the sample which enhanced the dielectric properties.

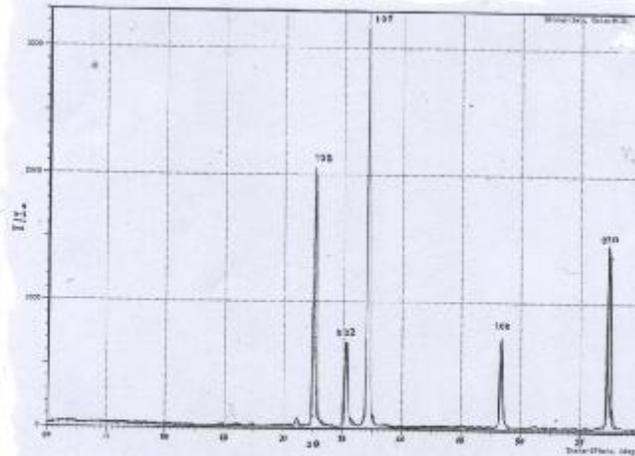
Introducing the ZrO₂ particles through ZnO may be filled most the pores in the samples besides that ZnO has large energy barrier which built in polarization which make the atoms or molecule to move in a microscopic displacement which affect the dielectric behavior^[15].

The decreasing in dielectric properties may due to the absorption of electric field energy by dipoles to overcome the viscous media which covered then through

their revelation. This absorbed energy reduced the charge carriers between the capacitor ends at increasing the frequency^[16].



Figure(1) XRD of nanosized of ZnO powder



Figure(2) XRD of composite ZnO-ZrO₂ powder

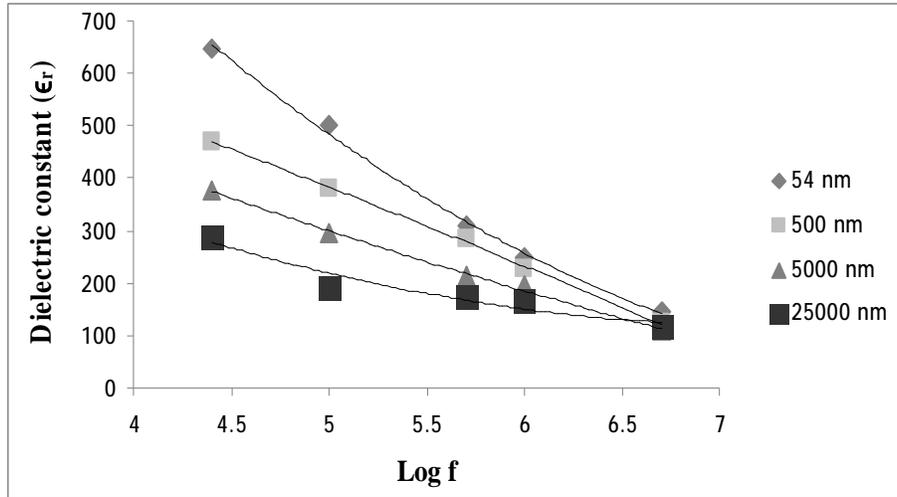


Figure (3) Dielectric constant versus frequency for the composite at different particle size.

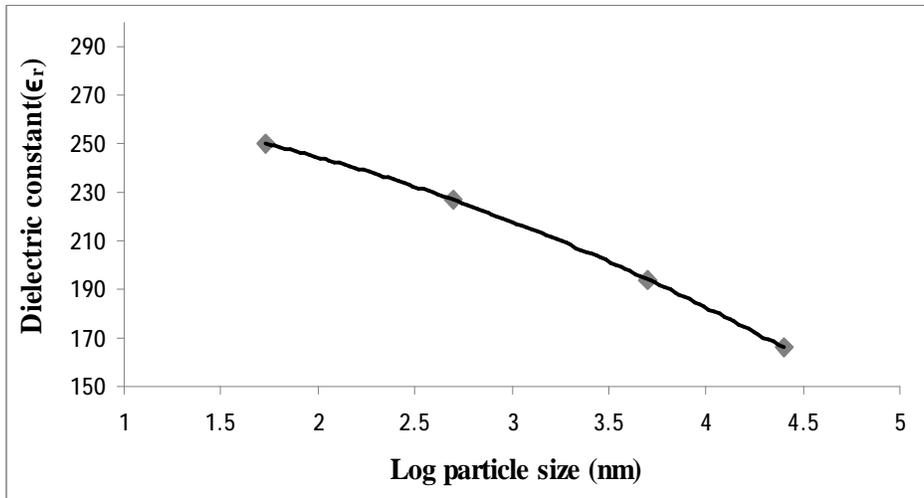


Figure (4) Dielectric constant versus particle size of the composite at 1 MHz.

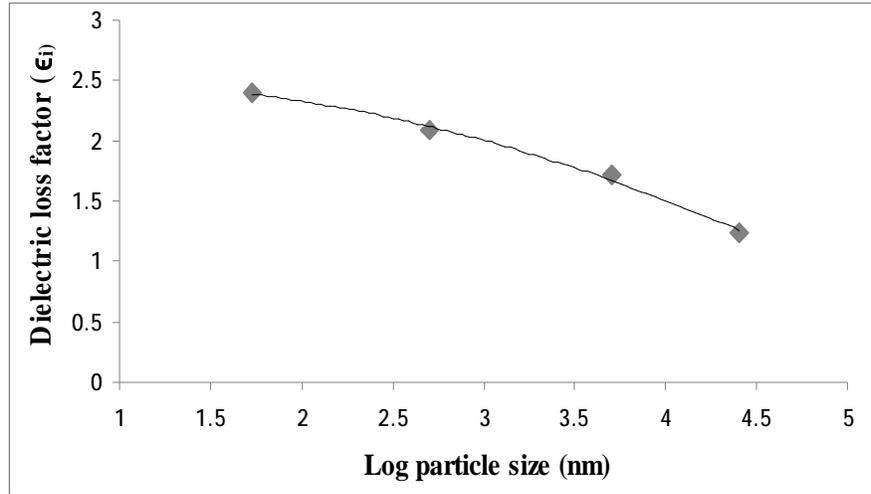


Figure (5) Dielectric loss factor against particle size of the composite at 1 MHz.

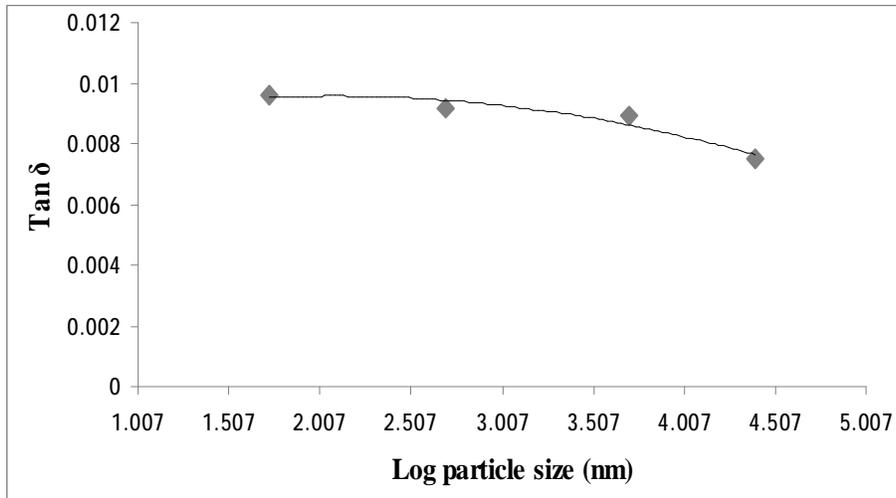


Figure (6) Tangent loss ($\tan \delta$) versus particle size of the composite at 1 MHz.

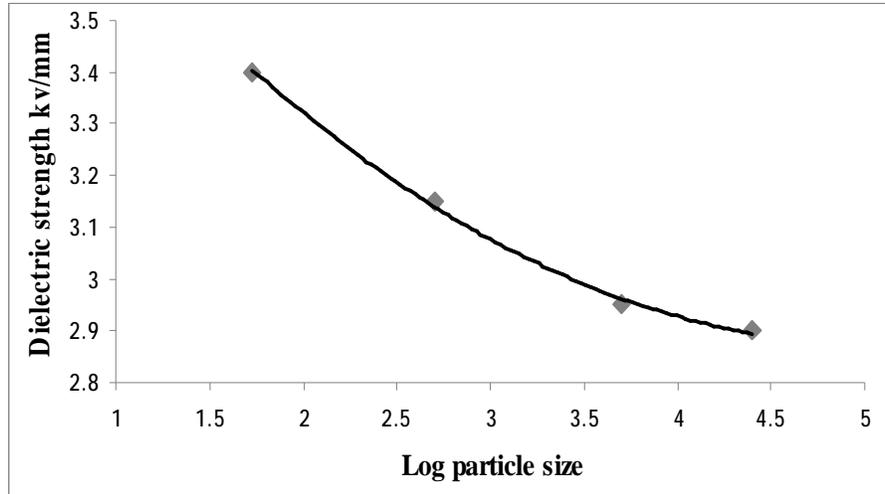


Figure (7) Dielectric strength versus particle size of the composite at 1 MHz.

CONCLUSIONS

Based on both experiment and results of the effect of particle size on the dielectric properties, the following conclusions can be drawn :

- 1- The combustion method can produce a nanosized composite material .
- 2- XRD shows a good crystalline material .
- 3- All the dielectric properties have been affected by the frequency and particle size.

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