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Dielectric properties of $ZnO/ZnNb_2O_6$ composite for energy storage applications

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Graphical Abstract

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Abstract.
In this paper, the dielectric properties of synthesized $ZnO/ZnNb_2O_6$ composite were investigated. The solid-state synthesis method was used. Then the elaborated composite was characterized using X-ray diffraction and impedance spectroscopy. The XRD patterns confirm the co-existence of a hexagonal ZnO and an orthorhombic $ZnNb_2O_6$ phases. Then, the dielectric properties were investigated at room temperature (RT) in a wide range of frequencies (from 20 Hz to 1MHz). The composite Nyquist curve revealed the grain and grain-boundaries contributions. Indeed, theoretical fit evidenced high resistance, and low dielectric losses simultaneously with capacitive behavior of the composite. So this composite is promising to be used in super capacitor for energy storage applications.

Introduction

Energy storage will be more important in the future than at any time in the past. Thus, lithium batteries are one of the most useful materiel in this domain [1]. But this material had many inconvenient: pollutant, high cost. So we have to search new sources that are more efficient and more secure. In this topic, we are interested to the $ZnO/ZnNb_2O_6$ composite that can be used in this application thanks to the interesting properties of the ZnO and $ZnNb_2O_6$. In fact, the columbite ($ZnNb_2O_6$) has interesting properties: low cost [1], good dielectric properties [2] and its suitability to numerous applications such as microwave dielectric ceramics [3], gas sensing [4], photocatalytic applications [5]. This work is focused on $ZnO/ZnNb_2O_6$ composite prepared using solid state method. XRD data are analysed to identify the crystal phases. Then, Dielectric spectroscopy was used to investigate the dielectric properties of the composite. Theoretical models were used to fit the experimental data.

Materials and Methods

The powder of ZnO/ $ZnNb_2O_6$ composite was prepared by a solid state method. 1 mol.% Nb_2O_5 was added to 99mol.% ZnO powder. ZnO and Nb_2O_5 powders were provided by Sigma Aldrich. Then, the mixture was milled then calcinated (400 °C, 4 hours). After that, the mixed powder was milled for a second time then pressed into pellets (1 mm thickness, 8 mm diameter). Then, the pellets were sintered (900°C, 24 hours). Finally, the pellets were milled for a last time to obtain the $ZnO/ZnNb_2O_6$ composite powder. The structural data were investigated by an X-ray diffractometer (Panalytical X Pert PRO MPD) with $Cu_{k\alpha}$ radiation (λ = 1.5406 Å), 2θ varying from 20° to 80°. Dielectric measurements were carried out using dielectric spectroscopy (Hewlett Packard 4284A LCR meter) from 20 Hz to 1MHz at room temperature (RT).

Results and Discussion

The XRD patterns (fig.1) evidenced the presence of two phases; ZnO and $ZnNb_2O_6$ with hexagonal (P63mc) and orthorhombic (Pbcn) structures, according to JCPDS files:(96-210-7060) and (31-5041) respectively. The sharpness of diffraction peaks proves the good crystalline quality of the prepared powder. Fig.2 shows experimental and theoretical adjustment of the Nyquist plots of ZnO and $ZnO/ZnNb_2O_6$ composite, according to equations (2) and (3). It displays non-Debye type relaxation shape. Indeed, as noticed, the experimental data of composite

were well modeled by an equivalent circuit composed by two parallel composition of resistances (Rg, Rgb) and fractal capacitances (CPE_g, CPE_{gb}) related to the presence of grain and grain boundaries effects. Whereas, those of ZnO were modeled by an equivalent circuit formed by one parallel composition of resistance Rg and fractal capacitance CPE_g.

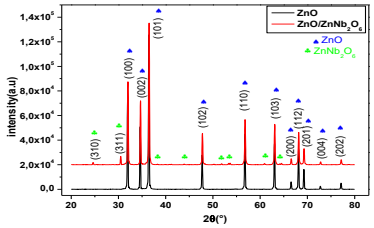

Fig.1: Powder X-ray diffraction pattern for ZnO and $ZnO/ZnNb_2O_6$ samples.

The impedance of the fractal capacitance is giving by: $Z_{CPE} = \frac{1}{Q(i\omega)^{\alpha}}$ **(1)**, Where Q is the CPE capacitance, ω is the angular frequency (ω = 2πf, f is the frequency), i is the imaginary unit (i^2 = -1) and α is the fractal exponent: (as α → 0, Z_{CPE}→ 1/Q involving a pure resistance, and as α → 1, Z_{CPE} →1/iQω involving a pure capacitance[6]. Accordingly, the real and imaginary parts of the complex impedance were expressed as:

$$Z' = \frac{R_g + R_g^2 Q_g \omega^{\alpha g} \cos(\alpha_g \frac{\pi}{2})}{(1 + R_g Q_g \omega^{\alpha g} \cos(\alpha_g \frac{\pi}{2}))^2 + (R_g Q_g \omega^{\alpha g} \sin(\alpha_g \frac{\pi}{2}))^2} + \frac{R_{gb} + R_{gb}^2 Q_{gb} \omega^{\alpha gb} \cos(\alpha_{gb} \frac{\pi}{2})}{(1 + R_{gb} Q_{gb} \omega^{\alpha gb} \cos(\alpha_{gb} \frac{\pi}{2}))^2 + (R_{gb} Q_{gb} \omega^{\alpha gb} \sin(\alpha_{gb} \frac{\pi}{2}))^2} \quad \textbf{(2)}$$

$$-Z'' = \frac{R_g^2 Q_g \omega^{\alpha g} \sin(\alpha_g \frac{\pi}{2})}{(1 + R_g Q_g \omega^{\alpha g} \cos(\alpha_g \frac{\pi}{2}))^2 + (R_g Q_g \omega^{\alpha g} \sin(\alpha_g \frac{\pi}{2}))^2} + \frac{R_{gb}^2 Q_{gb} \omega^{\alpha gb} \sin(\alpha_{gb} \frac{\pi}{2})}{(1 + R_{gb} Q_{gb} \omega^{\alpha gb} \cos(\alpha_{gb} \frac{\pi}{2}))^2 + (R_{gb} Q_{gb} \omega^{\alpha gb} \sin(\alpha_{gb} \frac{\pi}{2}))^2} \quad (3)$$

The electric parameters extracted from the fit of experimental data were given in table 1. This table shows that the composite is more resistive compared to ZnO. In addition, α value is found to be near the unity and is higher than that of ZnO, indicating that $ZnO/ZnNb_2O_6$ composite has a capacitive behavior. Moreover, Fig.3 shows the frequency dependence of dielectric loss factor, according to equation (4) [7]. In fact, the prepared composite exhibited a lower loss factor compared to ZnO, this makes it useful for energy storage applications [8]. $tg\delta = \frac{\varepsilon''}{\varepsilon'}$ **(4).** Where $C_0 = \frac{\varepsilon_0 . S}{e}$; is the vacuum capacity, e is the sample thickness and S is the electrode area.

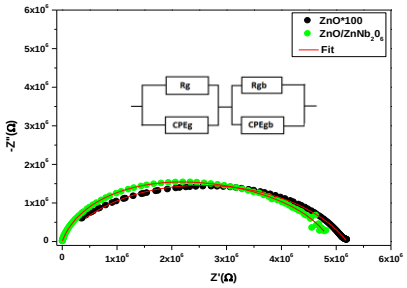

Fig.2: Nyquist diagram for ZnO and $ZnO/ZnNb_2O_6$ composite at RT: experiments and theoretical fit

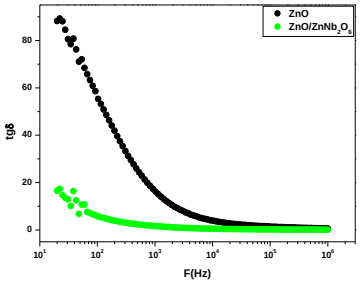

Fig.3: The frequency dependence of the loss factor of ZnO and $ZnO/ZnNb_2O_6$ composite.

Conclusions

In this paper we elaborated a polycrystalline $ZnO/ZnNb_2O_6$ composite using solid state method. This composite exhibits several interesting properties such as higher resistivity, noticeable capacitive behavior, and lower dielectric losses compared to ZnO powder. Thanks to these characteristics the $ZnO/ZnNb_2O_6$ composite is a good candidate to be used in super capacitors for energy storage applications.

Table.1: Adjustment parameters of equivalent circuit for ZnO and $ZnO/ZnNb_2O_6$ composite.

Sample	Rg (Ω)	Qg(F)	αg	Rgb (Ω)	Qgb(F)	αgb
ZnO	5.257 E4	1.726 E-8	0.642	-		
$ZnO/ZnNb_2O_6$	2.578 E6	5.176 E-10	0.863	2.319 E6	4.839 E-9	0.761

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