SYNTHESIS OF ZnO / (Al_2O_3-Bi_2O_3-CoO-Cr_2O_3-MnO-NiO-Sb_2O_3) COMPOUND NANO POWDER BY GEL COMBUSTION METHOD

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In this research first, ZnO nano powder plus different additives of Al_2O_3-Bi_2O_3-CoO-Cr_2O_3-MnO-NiO-Sb_2O_3 was synthesized by sol-gel combustion method. Nitric salts of above compounds and citric acid as a fuel was used. Various ratios of fuel to salt, different primary pH, and different calcination temperatures of 400-600 ^oC were used as variable parameters. The results showed that the ratio of fuel to raw material 0.5, basic pH (10), and calcinations temperature of 400 ^oC were the optimum conditions to prepare ZnO/(Al_2O_3-Bi_2O_3-CoO-Cr_2O_3-MnO-NiO-Sb_2O_3) compound nano powder of about 25 nm crystallite size and 42.3 m^2/g surface area.

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1. Introduction

ZnO powders are very important materials due to its so many interesting inherent properties such as dielectric, semiconducting, optical, photo electrochemical, and electrical properties [1-6]. Moreover, ZnO ceramics containing several metal oxides, such as Al_2O_3, Bi_2O_3, CoO, Cr_2O_3, MnO, NiO, and Sb_2O_3 show highly nonlinear current-voltage characteristics in varistors, which enables them to be used as protection devices against voltage surges and voltage transients [1-3].

The characteristics of ZnO powder depend on its size and methods of preparation. It has been reported that Nano-size ZnO powder has been prepared by different methods such as solution evaporation and suspensions, evaporative solution decomposition, solid state reaction, wet chemical synthesis, aerosol, ultrasonic, micro-emulsion, sol–gel, and conventional ceramic fabrication [3]. However, sol gel combustion (or gel combustion) is one of the new methods for synthesis of nano metal oxide powder.

Nano-scale particles possess different physical and chemical properties compared to bulk materials. Better sinterability, higher homogeneously, and other unusual properties may be expected because of their nano-sized crystallite, large surface area, and different surface properties [7,8].

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The combustion technique which employs in the area of propellants and explosives, involves a mixture of reagents that transform to the oxide easily (such as nitrates) and a fuel (such as glycine, urea, and citric acid) that acts as a reagent reducer. The method is actually self-sustainable after the reaction has initiated and, owing to the exothermic characteristic of the reaction, high temperatures guarantee the crystallization and formation of oxides in a short period of time. This normally prevents the hard agglomeration of particles being formed instantaneously [6]. The method also offers the advantage of high chemical homogeneity since the initial reagents are mixed in the form of an aqueous solution and, as a result, favor the production of phases or multi component ceramics [6].

In comparison to the conventional oxide mixtures and the sophisticated techniques in industrial scale, gel combustion process is promising powder production for varistor applications with more practical method due to the lower costs involved. Moreover, because the method of combustion reaction quickly converts a liquid solution into a solid, segregation of ions can be avoided, resulting in improved chemical homogeneity [6-9].

Several works were reported in the field of ZnO powder preparation by gel combustion method. Sousa et al. [10] used metallic nitrate plus urea and make ZnO nano powder with about 400-500 nm for varistor application. Hwang et al. [11] worked on ZnO nano powder by combustion method. They used glycine as fuel and metallic nitrates with stoichiometric ratio. However, in this research, for the first time, ZnO / (Al_2O_3-Bi_2O_3-CoO-Cr_2O_3-MnO-NiO-Sb_2O_3) compound were synthesized in one step by citric acid as a fuel in gel combustion method.

2. Experimental procedures

The raw materials were nitrate of zinc, aluminum, bismuth, cobalt, chrome, nickel, manganese, antimony citrate, and citric acid reagent grades[1]. ZnO/additives compound powders were synthesized by an amount of 25 g per batch according to the flow chart shown in Figure 1.

The mixture of salts and fuel (citric acid) were dissolved in ionized water, then homogenized and heated on a hot plate up to 300 ^{o}C. Initially, the solution underwent boiling and dehydration, followed by decay and accompanied by the release of large amounts of gases. A huge combustion occurs when heating continued and the mixtures took a more viscous appearance,

The molar ratio of fuel to metallic nitrates (fuel to salts, F/S) was selected as 0.5, 1, and 2. The materials were weighed, dissolved in ionized water, and homogenized by a magnetic stirrer.

After mixing and homogenizing metallic nitrates with fuel, while heating the solution, the gel combustion process was carried out and ZnO / additives compound nano powder was prepared. The prepared nano powders were calcinated at 400-600 ^{O}C, then XRD, SEM, and TEM tests were carried out and the results were analyzed.

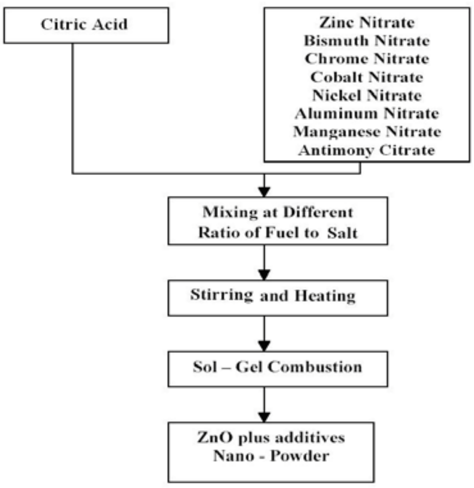


Fig. 1. Flow chart for synthesis of ZnO/additives compound by gel combustion methot

[1]Supplied by Merck company

3. Results and discussion

XRD pattern of powder synthesis with different ratio of fuel/salt (F/S) have been shown in Figure 2. Then, the average crystallite size was estimated using the Scherer and Warren equation:

$$D_{SW} = \frac{0.9\lambda}{(B^2 - b^2)^{1/2}\cos\theta} \quad (1)$$

Where, λ is the wavelength of the radiation, θ the Bragg's angle, while B and b are full width at half maximum for the sample and a standard silicon sample, respectively. The size of all crystallites and their surface areas were measured and the obtained results were collected in Table 1.

Figure 3 shows the particle size distribution by zeta sizer analysis in different F/S.

From XRD patterns, surface area, and zeta sizer diagrams of synthesized nano powders, it is possible to find out that citric acid to raw material ratios (F/S) of 1 to 2, gave better result.

Also, using citric acid fuel with fuel to raw material ratio of 0.5, three primary solutions with three types of pH (acidic, basic, and neutral) were prepared and sol-gel combustion process was repeated. According to the XRD pattern and zeta sizer diagram (Figures 4&5) and Table 2, it will be concluded that using medium basic pH in gel combustion method, can be demonstrated a finer powders.

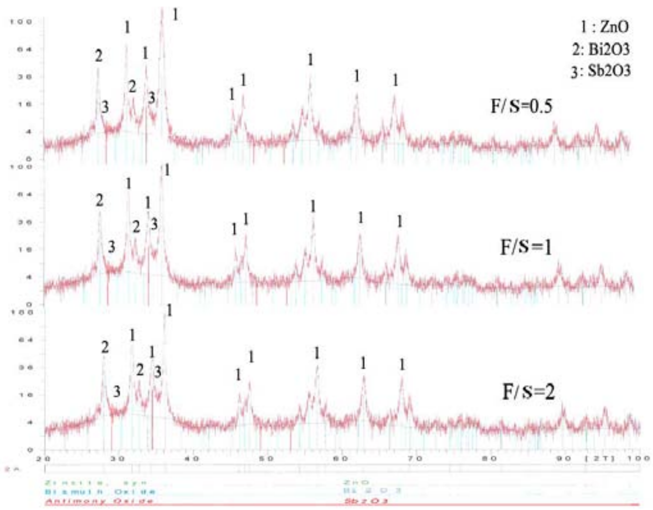


Fig. 2. XRD pattern of powder synthesis in different F/S

Table 1 Crystallite size of powder synthesis in different F/S.

F/S ratio	Crystallite size (nm)	Surface area (m^2/g)
0.5	25	42.3
1	32	33.2
2	39	27.1

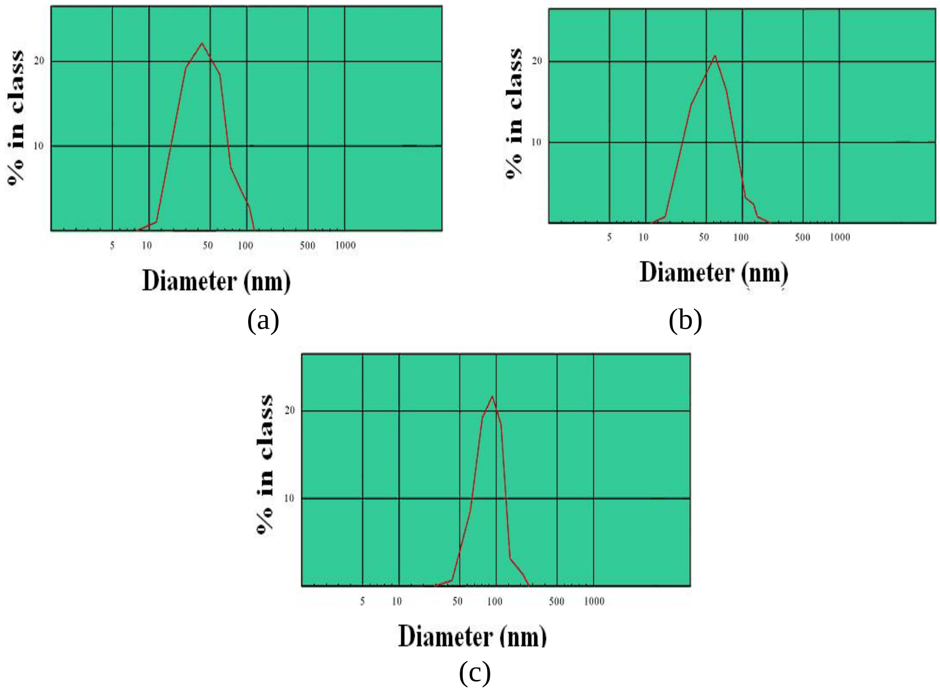


Fig. 3. Particle size distribution analysis by zeta sizer for combined ZnO/additives nano powders in different F/S (a: F/S=1/2, b: F/S=1/1, c: F/S=2/1)

According to Figures 4 & 5 and Table 2, it will be concluded that using basic pH in gel combustion method, can be demonstrated a more homogeneous and finer microstructure. When pH is increased from 2 to 10, in addition to color changing of primary solution, both combustion reaction and external gases volume will be extremely increased. This is due to this fact that the nitrate ions make an oxidant medium around metallic ions, which are useful for burning of organic part of a sol-gel, so increasing pH (adding ammonia) causes an increase in NO_3^- ion contents and thus combustion reaction rate will be increased.

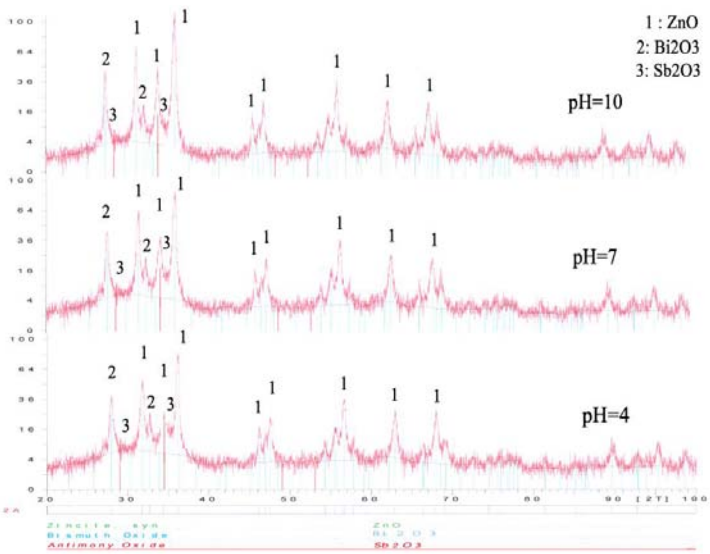
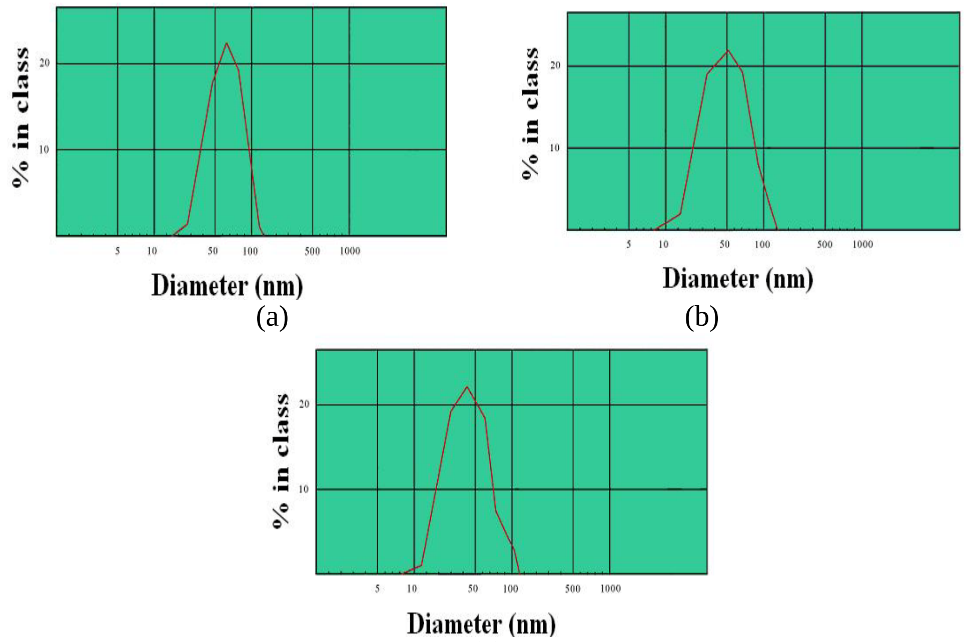


Fig. 4. XRD pattern of combined ZnO/additives nano powders with different pH

Table 2: Crystallite size of combined ZnO/additives nano powders with different pH

pH	Crystallite size (nm)	Surface area (m^2/g)
3	40	26.4
7	34	31.2
10	25	42.3



(c)

Fig. 5. Particle size distribution analysis by zeta sizer for combined ZnO/additives nano powders in different pH (a: pH=2-4, b: pH=6-8, c: pH=9-12)

The reactions, which occur during ionization of citric acid in different pH, is as follows:

$$H_3Cit \leftrightarrow H_2Cit^- + H^+ \quad pH < 3$$
$$H_2Cit^- \leftrightarrow HCit^{2-} + 2H^+ \quad 3 < pH < 7$$
$$HCit^{2-} \leftrightarrow Cit^{3-} + 3H^+ \quad pH > 7$$

These reactions show when pH is acidic, citric ionization is very low, so the role of complexation of citric acid becomes weak. Also, when pH is increased up to 7 (basic), citric anions are as cit^{3-}, so the role of complexation of citric acid is the highest at pH=7 because the number of bandings between anion citrates and metallic cations are increased. Therefore, a more homogenized sol-gel will be prepared.

Also XRD pattern (Figure 6), zeta sizer diagram (Figure 7), and Table 3, show that between three temperatures of 400, 500, and 600 ^{o}C for calcinations, the best condition is 400 ^{o}C which gives a homogenized nano size ZnO powder in the range of 20-30 nm (Table 3). In higher temperatures the particles were grown and were not taken into account as nano size powders.

Also, microstructure of powders with F/S=0.5, pH=10, and 400 ^{o}C calcination temperature has been shown in Figure 8.

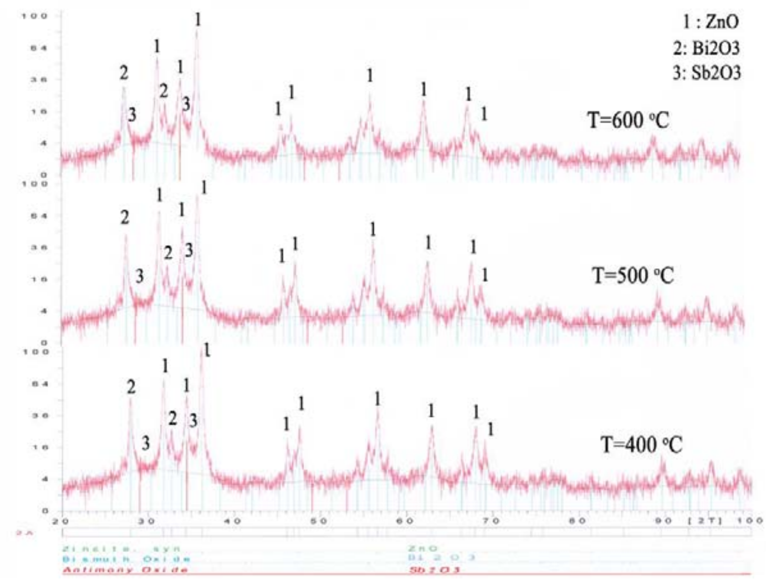


Fig. 6. XRD pattern of combined ZnO/additives nano powders with different calcination temperatures

Table 3: Crystallite size of combined ZnO/additives nano powders with different calcination temperatures

T (°C)	Crystallite size (nm)	Surface area (m^2/g)
400	25	42.3
500	36	29.5
600	41	26.1

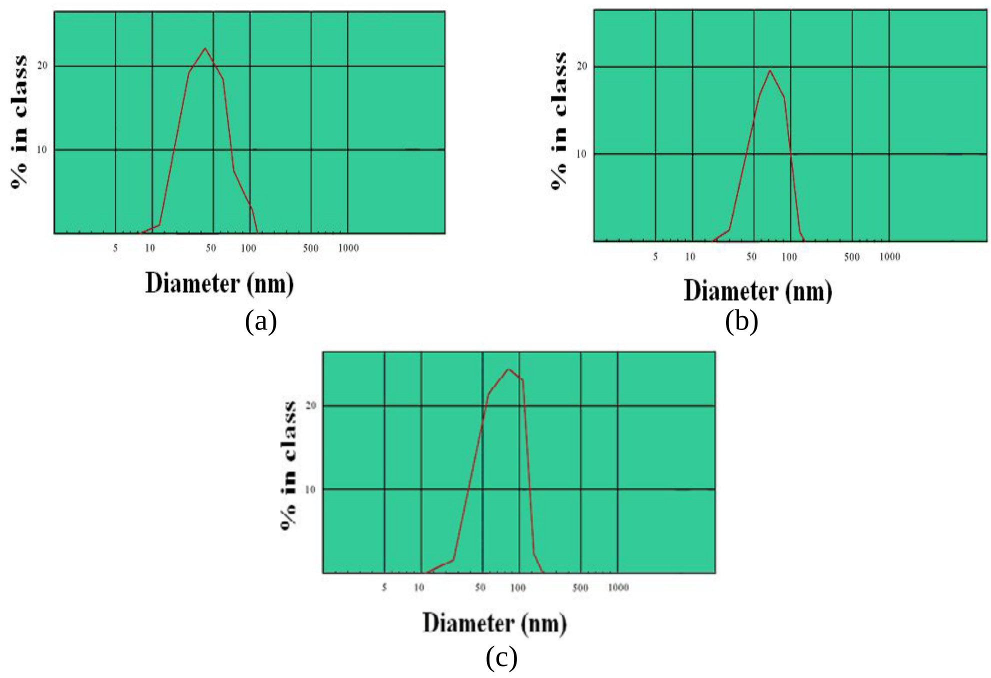


Fig. 7. Particle size Distribution analysis by zeta sizer for combined ZnO/additives nano powders in different calcinations temperatures (a: 400 °C, b: 500 °C, c: 600 °C)

As Figure 8 has been shown ZnO-Bi_2O_3-Sb_2O_3-Cr_2O_3-CoO-NiO-MnO nano powder have been synthesized by gel combustion method in one step.

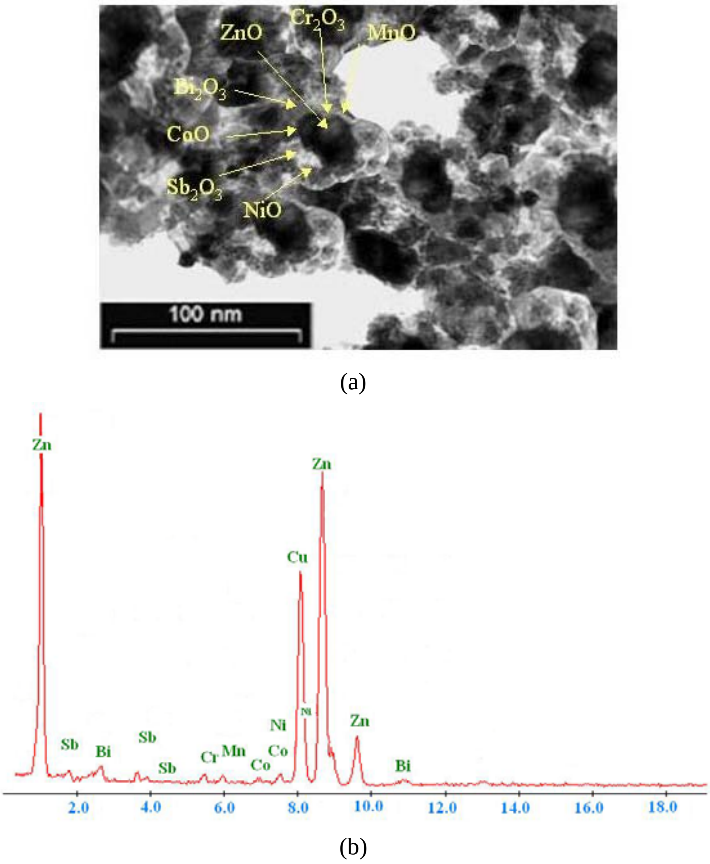


Fig. 8. TEM and EDX pictures of combined ZnO/additives nano powders using citric acid as fuel in gel combustion method

4. Conclusions

In this study the following results were obtained:

1- It is possible to prepare combined ZnO/additives nano powder using gel combustion method.
2- The most desired fuel to raw materials ratio is 0.5 when citric acid is used.
3- Basic pH (pH = 10), in gel combustion process creates fine and homogeneous combined ZnO/additives nano powder.
4- Calcination temperature of 400 ^{o}C is desired for changing amorphous particles to crystal phase in gel combustion method.

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