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Effect of ZnCl_2 and CaCl_2 Concentration on the Optical and Structural Properties of Perovskite Structure CaZnO_3

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ABSTRACT

Thin films of cubic perovskite (CaZnO_3) was deposited using Spry pyrolysis deposition (SPD) method. The effect of many precursors concentration on the structural and optical properties of (CaZnO_3) thin films have been studied using scanning electron microscope SEM, X-Ray spectrum and UV- spectrum respectively. The transmittance and absorbance of the prepared films with wave length show a clear variation with precursors concentrations, in addition, the energy gap of the films were also varied from 2.7eV to 3eV. The SEM images and x-ray spectrum of the films shows also clear difference in the shape and structure of the films.

Keywords: crystal structure; energy gap; perovskite; stability; CaZnO_3 thin film,

1. Introduction

Perovskite materials are considered a good semiconductor that can replace silicon and germanium. Perovskite has many structures, but the most common is ABX_3 (figure 1), which is made up of five atoms, where "A" has a rather large diameter. "B" is a cation of small diameter, a "transitional or noble metal," and "X" is an oxygen atom; it can be a halogen or a nitrogen [1–3]. Perovskite can be easily prepared using several methods, such as chemical bath deposition (CBD) [5], chemical vapor deposition (CVD) [6], the silar method [7], the spin coating method [8], and spray pyrolysis deposition [9]. Perovskite materials have been used in many industries and fields, including capacitors and memories [10], transistors [11], light-emitting diodes (LEDs) [12], measuring doses during radiotherapy in x-rays [13], transparent ceramics [14], photovoltaic cells [15], fuel cells [16], and in the preparation of superconducting materials at relatively high temperatures [17]. In the present study, a different concentration of precursors ZnCl_2 and CaCl_2 were used to prepare thin films of inorganic perovskite structure CaZnO_3 . The structural properties and morphological surface of these layers were examined using a scanning electron microscope (SEM) and an X-ray spectrum; in addition, the transmittance, absorbance, refractive index, and extinction coefficient were also investigated.

2. Experimental details

The films were deposited on glass slides as substrates. The cleaning process included several steps: they were cleaned ultrasonically with alcohol

and methanol, washed with distilled water, and finally left to dry. Three different concentrations of calcium chloride, CaCl_2 (0.2, 0.6, and 0.8 gm), zinc chloride, ZnCl_2 (0.2, 0.6, and 0.8 gm), and a constant concentration of potassium hydroxide, KOH (0.8 gm), have been used to prepare thin films of " CaZnO_3 ," as shown in table (1). Each compound was dissolved in 50 ml of distilled water, and then the solutions of CaCl_2 and ZnCl_2 compounds were added simultaneously to the KOH solution. The mixture was stirred using a magnetic stirrer device for 1 hour at 80°C . The later solution was used to prepare thin films of CaZnO_3 on the glass slides at 300°C using spry pyrolysis deposition (SPD). During the deposition process the substrate temperature was kept at 300°C , Atmospheric, pressure 7.5 bar and ten spray steps with period 5sec

3. Results and discussion

The optical and structural properties of the layers were examined using a spectrophotometer, a scanning electron microscope (SEM) and an X-ray spectrum. The optical properties show a clear variation for all concentrations, as shown in figure 2), the transmittance inversely proportional with ZnCl_2 and CaCl_2 concentration while the absorbance and reflectance decreases. The refractive index spectrum shows a stable value for all concentrations along the range (300-550 nm) and then decreases over the range (550-600 nm). Also, the extinction coefficient was inversely proportional to concentration from 300 nm to 550 nm and then decreases for all concentrations.

by using Bragg's law [18] and Scherer's Formula used to calculate the crystalline size C.S of the films [19, 20]:

$$2d_{hkl} \sin\theta = n \dots (1)$$

$$C.S = \frac{0.9\lambda}{\beta \cos\theta} \dots (2)$$

β (FWHM): width of the diffraction peak at half maximum intensity.

Microstrain (ϵ) for fabricated thin films can be calculated from the equation below:

$$\epsilon = \frac{\beta \cos\theta}{4} \dots (3)$$

The dislocations density (δ) is defined as the length of dislocation lines per unit volume of the crystal and it can be determine from the formula below [21]:

$$\delta = \frac{1}{(C.S)^2} \dots (4)$$

The optical properties of thin films have been studied, and "transmission and absorption spectra" in the range between 400 and 1000 nm have been noted. Lambert law has been used to determine the absorption coefficients and the energy gap respectively from the absorption spectrum [22, 23]:

$$\alpha h\nu = D (h\nu - E_g)^r \dots (5)$$

$$\alpha = 2.303 A / \dots (6)$$

α : the absorption coefficient, $h\nu$ the incident photon energy, r : a parameter for the type of the optical transition. A : absorbance, t : thickness D is a constant depends on the temperature and the properties of the valence & conduction bands.

Optical Constants such as n refractive index, k : extinction coefficient, real part ϵ_r & imaginary part ϵ_i of dielectric constant can be considered by the relations below: [24, 25, 26]:

$$n = \frac{4R}{(R-1)^2} K^2 J^{1/2} - \frac{(R+1)}{(R-1)} \dots (7)$$

$$k = \alpha\lambda/4\pi \dots (8)$$

$$\epsilon_r = n^2 - k^2 \dots (9)$$

$$\epsilon_i = 2nk \dots (10)$$

From all the above equations, the band gap decreases with increasing concentration; for the first concentration (the highest concentration), the energy gap was 2.8 eV, then increased to 2.9 eV for the second concentration, and finally became 3 eV for the third concentration (figure 2). The variation in the energy gap is due to the continued changes in the structure and grain size of the films (table 2) [27]. Scanning electron microscope images of the layers show that the grains' sizes are proportional to precursor concentrations. The image of the first concentration shows the formation of Nano roads structure with diameter of about (90-125 nm), the second concentration image show the formation of a cubic shape grains as a result of the grains aggregation and grow, while the third concentration image show the formation of

uniformly distributed grains with size of about 80 nm figure (2).

The x-ray spectra show that all the films have amorphous structure with the presence of several peaks belonging to the single crystal phase with different intensities at the same 2θ , in addition to the appearance of other peaks in the spectrum due to the different orientation in the structure of the prepared films (figure 3).

4. Conclusions

The absorbance and reflectance inversely proportional with $ZnCl_2$ and $CaCl_2$ concentration while the transmittance increases with concentration of both compounds. The refractive index spectrum shows a stable value for all concentrations along the range (300-550 nm) then decrease over the range (550-600nm), also the extinction coefficient decreases for all concentrations. The band gap for the first concentration was 2.8eV then increase to 2.9 eV for the second concentration and finally become 3eV for the third concentration. Scanning Electron Microscope images and for all concentrations show a high variation in the structure of the films. Finally, the results showed the possibility of obtaining a thin film from semiconductor of Pervoskite and therefore can be used in the manufacture of solar cells.

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Table1: show the of concentration variation $CaCl_2$, $ZnCl_2$ and KOH

	$CaCl_2$ gm	$ZnCl_2$ gm	gm KOH
1 st Concentration	0.8	0.8	0.8
2 nd Concentration	0.6	0.6	0.8
3 rd Concentration	0.2	0.2	0.8

Table 2: Show the grain size and energy gap with concentration

	Average grain size nm	energy gap eV
1 st Concentration	387.4476	2.8
2 nd Concentration	135.6373	2.9
3 rd Concentration	88.4817	3

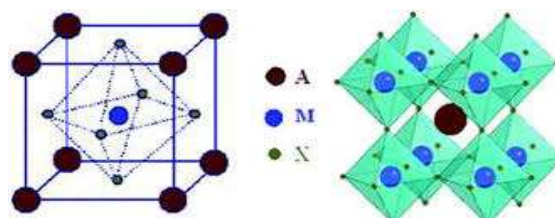


Fig. 1: The perfect stricture of pervoskite "ABX₃" which forms a three-sided network "BX₆" [4]

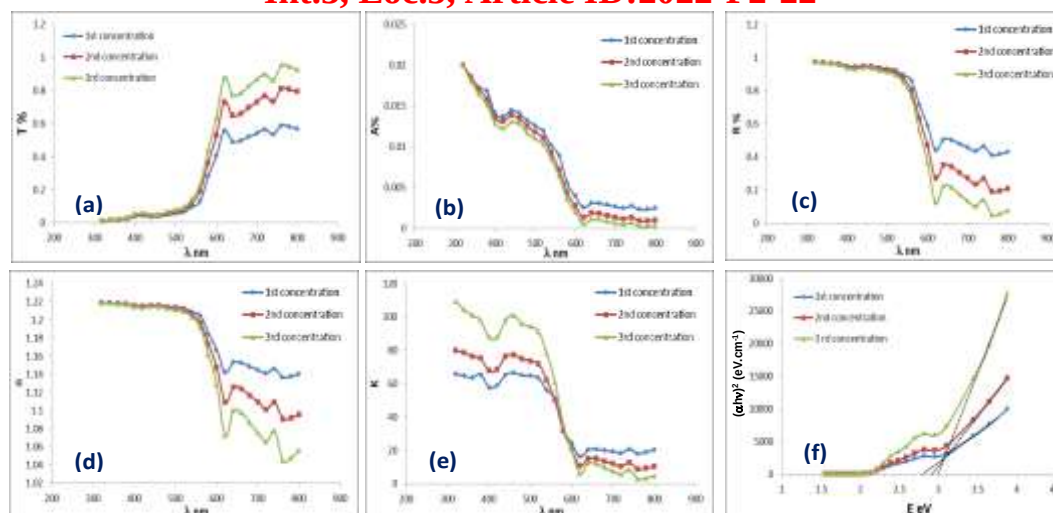


Fig. 2: Effect of concentration on the optical properties a. transition b. absorption c. reflective d. refractive index e. extinction coefficient f. energy gap

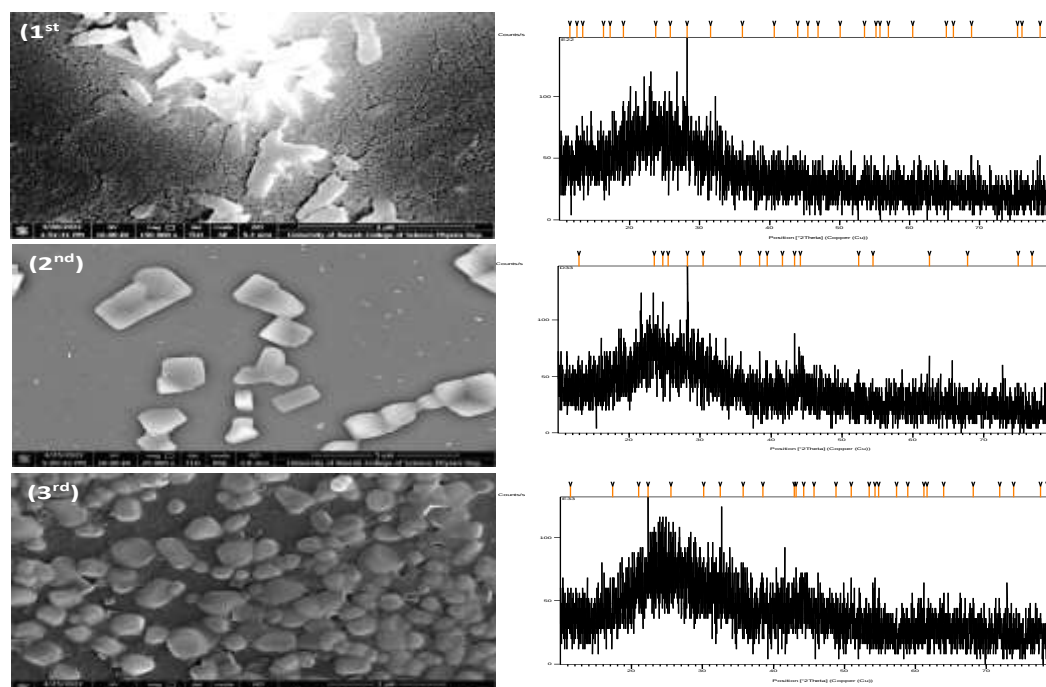


Fig. 3: Scanning electron microscope images and X-ray spectrums of the layers prepared from different concentrations

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