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Effects of molarity concentrations on structural and optical properties of MgO thin films prepared by co-precipitation method

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Abstract*—Nano magnesium oxide MgO NPs powder was synthesized in three different molarity concentrations (0.03, 0.05 and 0.07) mol by co-precipitation method. Stoichiometric amounts of Magnesium chloride hexahydrate and ammonium carbonate were used for this purpose. The effects of molarity concentrations on the optical ,structure ,topographical and electrical properties of MgO NPs were investigation by using UV-Vis spectroscopy ,atomic force microscopy AFM. X-ray measurements showed that the grains size of MgO powder increases as molarity consternation increasing. Scanning Electron microscopic SEM images of MgO nanoparticles showed three different of shapes Nanoflower-like, Nanorod and Nanosheet according to the mole concentrations (0.03, 0.05 and 0.07) mol respectively. Spectral transmit-ttance of MgO thin films were measured in the range of (200-1100) nm. Optical band gaps were calculated from Tauc' plots and found they decrease with molarity increase. The average surface roughness was measured by Atomic Force Microscopy (AFM) and shows that increases with molarity increasing.*Keywords*— *MgO nanostructure; concentration; grain size; band gap; morphology, XRD ,SEM , AFM***

1. Introduction

In the preparation of nano-structured materials, it is important to optimize synthesis parameters in order to obtain the desired material. The physical and chemical properties of Nano-MgO crystallites are directly connected with their sizes, shapes and size dispersion, therefore a new and inexpensive method to synthesize nano-MgO with narrow size distribution, controllable structure, morphology, and large specific surface area is necessary. This work investigates in the role of concentration of starting materials on the size of MgO particle and what are the consequent impacts on the structural and optical properties. Magnesium oxide (MgO) is characterized with physical and chemical properties make it of great importance for numerous applications in many fields. MgO possesses great stability at high frequencies and elevated temperature due to its properties such as high permittivity (9.8), large band gap (7.3-7.8eV)**[1]** and higher breakdown field (12 MV/cm)**[2,3]**, in addition to that, easy and multiple routes to its preparation. There are several routes to synthesize MgO nanostructures such as precipitation, chemical vapour deposition, electrochemical and other methods **[4, 5]**. Each method has its own advantages and disadvantages. A type of preparation method and

a kind of raw materials which are used to obtain MgO have their own influence over the shape and size of nanoparticles. Not only that, but by control a concentration of these substances can

2. Experimental details

2.1. Synthesis of MgO nanostructure by co-precipitation method

In this synthetic method, (0.03 mol) of Magnesium chloride hexah-ydrate ($MgCl_2.6H_2O$) was dissolved in (100 ml) of distilled water (solution A) likewise (0.03 mol) of ammonium carbonate $(NH_4)_2CO_3$ also was dissolved in (100 ml) of distilled water (solution B). Then the solution B was added to solution A with vigorous stirring for 6hr, thereafter the white precipitate are filtered and washed several times with distilled water followed by ethanol. The product was dried at 100º C and then calcined at 700º C for 5hr to obtain MgO nanostructure. This procedure was repeated for other two molarity concentrations (0.05 and 0.07 mol).

2.3 Characterization techniques

X-ray measurements of the MgO powder at three different molarities were performed using a Shimadzu XRD-6000 X-ray powder diffract-tometer using CuKα radiation λ 1.5406 Å at 40 kV and 30 mA for the X-ray tube. The scanning rate was 5°/min to analyze the phase type and content. For each measurement, a complete 2θ scan was made between 10° and 80°. For morphological investigations, AFM images were recorded using (SPM) scanning probe microscope controller in a tapping mode. Field emission electron microscopy (FESEM) of determination a particle size and shape required for magnesium oxide and getting a best properties.

2.2. prepared of MgO Thin Films

From MgO powders which have been prepared in the first stage can be used to fabricate MgO thin film by dissolving amounts of the MgO powder for each sample (0.03, 0.05, and 0.07) separately in distilled water, then the MgO solutions was dropped on a clean quartzite substrates at temperature 80ºC. The deposited MgO thin films were then dried at 200ºC in a furnace for 10 minutes and these processes were repeated for several times in order to achieve the desired films thickness. Finally the films were then annealed in furnace at 500° C for three hours [5], thereby was obtained three different molarity samples of MgO thin films.

the sample was carried out using a ZEISS LSM 880 high-resolution transmission electron microscope operated at 100 kV. To study the chemical composition, measurement of the molar content of MgO was performed using an energy dispersion X-ray spectroscopy (EDS) attached to ZEISS LSM 880 high-resolution transmission electron microscope. The optical properties of the MgO films were determined using the UV-VIS spectrum. (Shimadzu, UV-1201) was used to study the change of the molarity of absorption, transmittance and band gap energy.

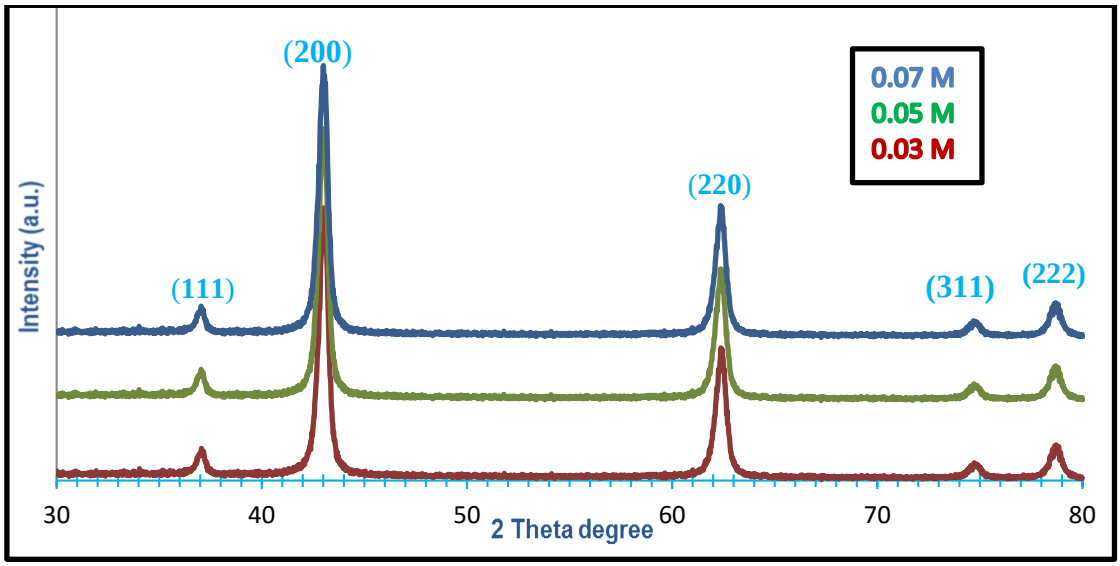
3. Results and discussion

3.1. Structural and surface morphology

Figure 1 shows X-ray diffraction spectra of the MgO nanostructures with Miller planes of (111), (200), (220), (311) and (222) for three concentrations (0.03, 0.05 and 0.07) mol and its corresponding angles of diffraction (36.86 º, 42.8, 62.2 º, 74.57 º, 78.5º) respectively. The crystal structure of the samples is attributed to the single phase of face centered cubic (Fcc) MgO, with the lattice constant of a = 4.213 Å, which is in good agreement with the reported data (JCPDS card No. 87- 0653). The sharp and intensive peaks further indicate that the MgO nanostructures are well crystallized. The other phases were not observed, which means that the synthesized MgO nanostructure have a high purity. The crystallite size for the synthesized MgO nanostructure was calculated by Scherer's formula **[2, 3]**

$$D = \frac{0.94\,\lambda}{\beta\,cos\theta} \qquad (1)$$

Where λ is the wavelength of (XRD), β is the full width at half maxima of diffracted line in radian. θ is angel Bragg diffraction.



(Fig.1) X-ray pattern of the MgO nanostructure (0.03, 0.05, and 0.07) M

(Table 1) grain size value for (0.03, 0.05, 0.07) MgO nanostructure

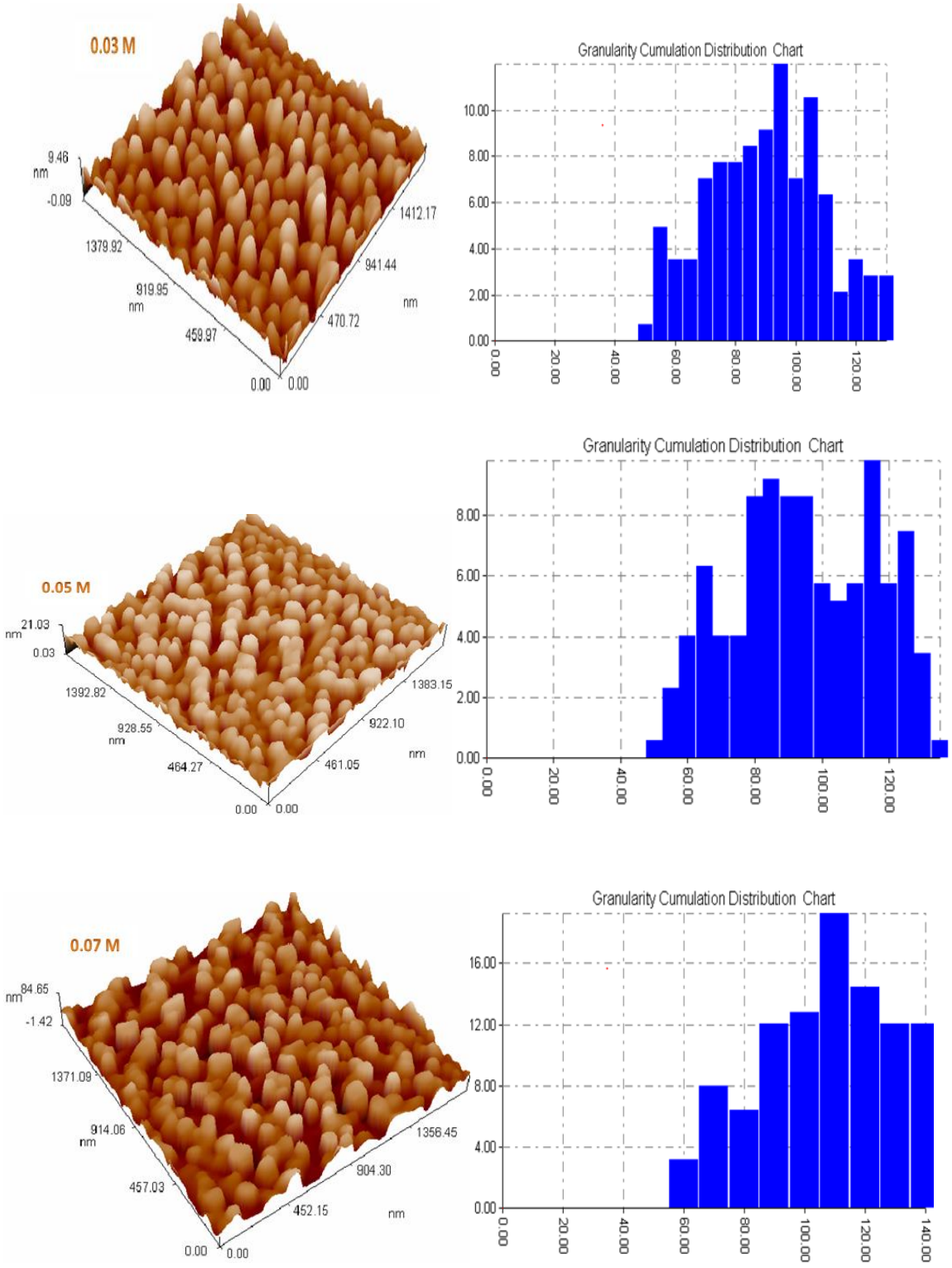
Molarity	hkl	2θ (deg)	β (deg)	D (nm)
0.03 M	(111)	36.95	0.42	19.95
	(200)	42.9	0.4735	18.03
	(220)	62.27	0.5009	18.53
	(311)	74.61	0.6133	16.29
	(222)	78.56	0.5	20.53
0.05 M	(111)	36.86	0.3737	22.41
	(200)	42.84	0.3883	21.98
	(220)	62.21	0.3881	23.91
	(311)	74.58	0.4687	21.31
	(222)	78.52	0.4268	24.04
0.07 M	(111)	36.84	0.3393	24.68
	(200)	42.81	0.3623	23.566
	(220)	62.18	0.3549	26.14
	(311)	74.55	0.326	30.63
	(222)	78.49	0.3511	29.22

The grains size of MgO nanostructures prepared for all molarity and at each orientation found as shown in Table 1. Results indicate that the grains size of MgO nanostructure is increasing whenever the concentration of reactive raw materials was increased.

The 3D AFM images and granularity accumulation distribution chart of MgO NPs synthesized at different molarity (0.03, 0.05 and 0.07) M shown in Fig. 2. As can be seen that surface of MgO films become rougher as the molarity increase and when the molarity reaches at 0.07M the surface roughness of films be the highest, that's due to the agglomerated particles occurred due to non-dispersion of the particle **[7]**. The MgO Nanoparticles are agglomerated and formed larger partcles as shown in figure 2.The average grain size listed in Table 2 are disagree with those estimated from X-ray diffraction due to the fact that atomic force microscopy results measure the average dimeter regardless of the degree of nanostructure defects but those which estimated by XRD is based on size of defect free volume.

Table 2 data of AFM measurement

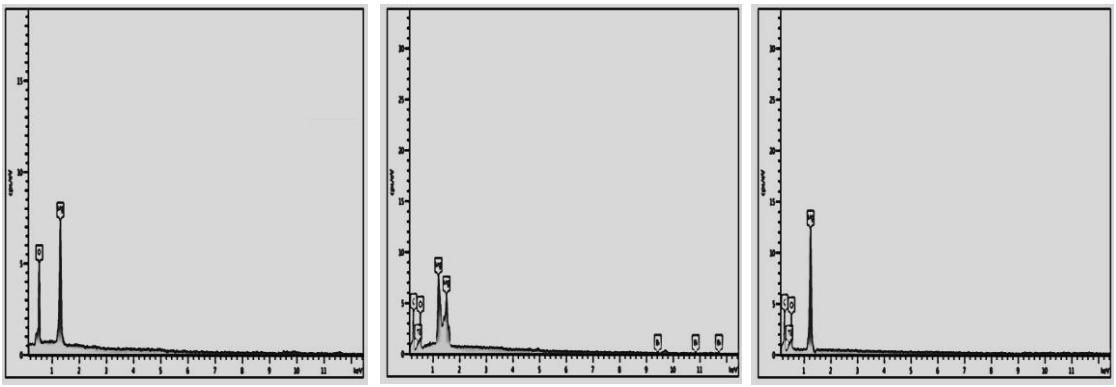
Molarity consternation %	Roughness density (nm)	Average grain size(nm)	RMS (nm)	thickness (nm)
3	1.52	87.66	1.82	9.46
5	3.06	92.48	3.61	21.03
7	13.5	101.87	15.9	84.65



(*Fig. 2): AFM images and Granularity accumulation distribution chart of MgO films prepared at different molar concentration*

The shapes and the grain size of the MgO prepared by precipitation method at different molarity (0.03, 0.05 and 0.07) are shown in figure 3, where were seen as Nanoflower-like, Nanorod, Nanosheet respectively. These changes in shapes with molarity increase as mentioned earlier are due to the change of crystalline construction when the number of unit cells

increase inside grain for which its size be larger when the molarity increase. Also the test of FESEM showed that the average of grain size increases with molarity increasing and this confirms the test of XRD and AFM. In order to confirm the chemical compositions of the MgO nanostructures, energy dispersive X-ray (EDS) analysis was performed. EDS spectra of the synthesized MgO nanostructures indicate that there are strong peaks for magnesium (Mg) and oxygen (O), which indicates the formation of purely MgO, this result agrees with X-ray test where did not show any foreign peaks. The atomic ratio of Mg to O estimated from the EDS results was determined to be about 1:2, which matches well with that of bulk MgO and Fig. 4 shows that these ratios.



(Figure 4) ***EDX spectrum of MgO nanoparticles at different molarity***

Table 3: *The grains size according to XRD, AFM and SEM measurement*

Molarity	Average grain size (nm)		
	XRD	AFM	SEM
0.03	18	87.66	60
0.05	22	92.48	75
0.07	23.5	101.87	85

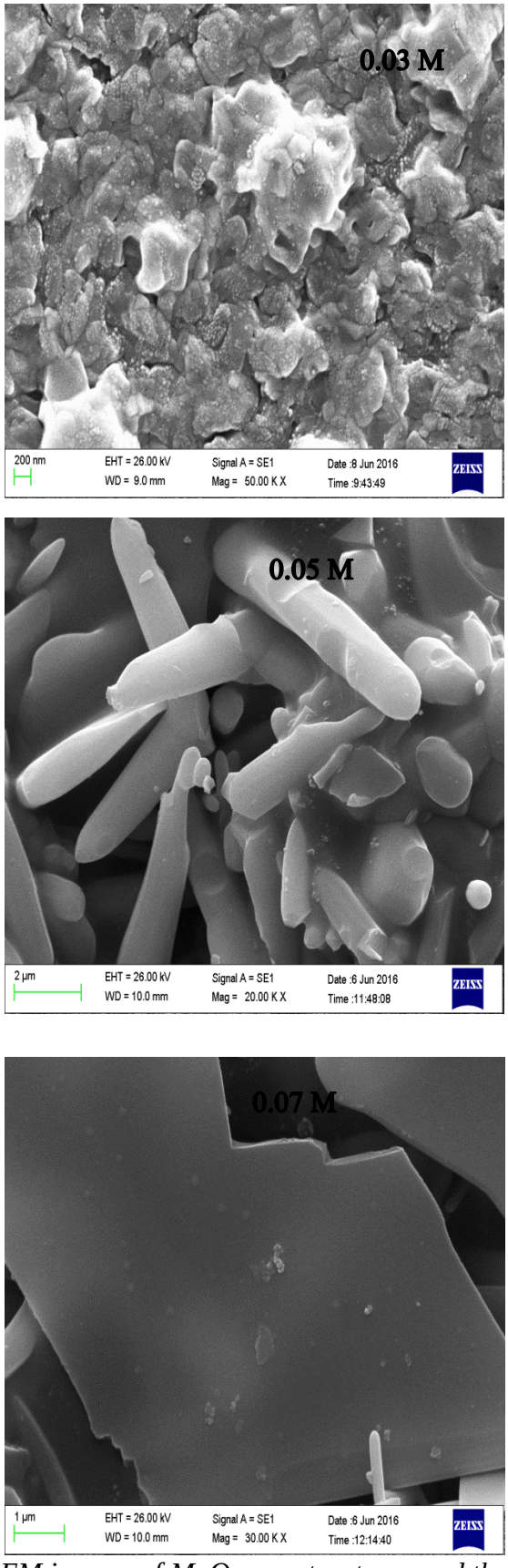


Fig. 3 : FESEM images of MgO nanostructures and their grain size

Particle size has been estimated by three different tools XRD, AFM and SEM, all results pointed that molarity increasing leads to particle size increasing, but the grains size measured by XRD is much smaller than those measured by AFM and even SEM for the same sample.

The results show that Increases the grains size when the molarity consternation increasing due to the surfactant which means (a substance that tends to reduce the surface tension of a liquid in which it is dissolved) thereby the surface tension of the solvent becomes not enough to break the bonding between molecules when growing melted substance, as the result, the particle in the solution begin to aggregate whenever molarity increases and this lead to grains size are larger **[6, 7]**.

3.2. Optical properties

The optical measurements of MgO thin films gives an important information about the physical properties such as the, transmittance and energy gap. Transmittance spectra recorded for MgO films as a function of wavelength range (200-1100) nm. MgO films deposited on quartzes substrates at different molarity were illustrated in Fig 4. Less transmittance occurs in UV region at range between 200 nm to 400 nm. Also it can be seen that transmittance decreases with molarity increasing due to increase the film thickness when molarity increasing according to AFM measurement. The optical energy gap was determined by using the absorption coefficient values, figure.5 shows the plot of $(\alpha h\nu)^2$ vs. hν for MgO thin films for different molarity concentrations (0.03, 0.05 and 0.07) M with band gap values (4, 3.6 and 2.8) eV respectively. It's clear that energy gap is narrowing with increasing molarity, namely the energy gap is narrowing when grain size increase, because grain size increasing causes increase in the density of charge atoms and then every electron is effectively surrounded by an exchange and correlation hole that lowers the energy of the electron, and the conduction band is shifted downwards **[8, 9]**.

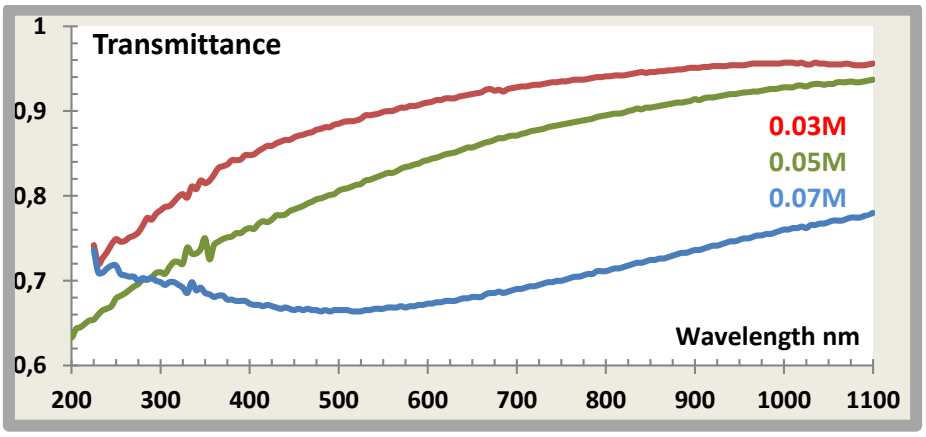


Fig.4 Transmittance versus wavelength of MgO thin films for all molarities

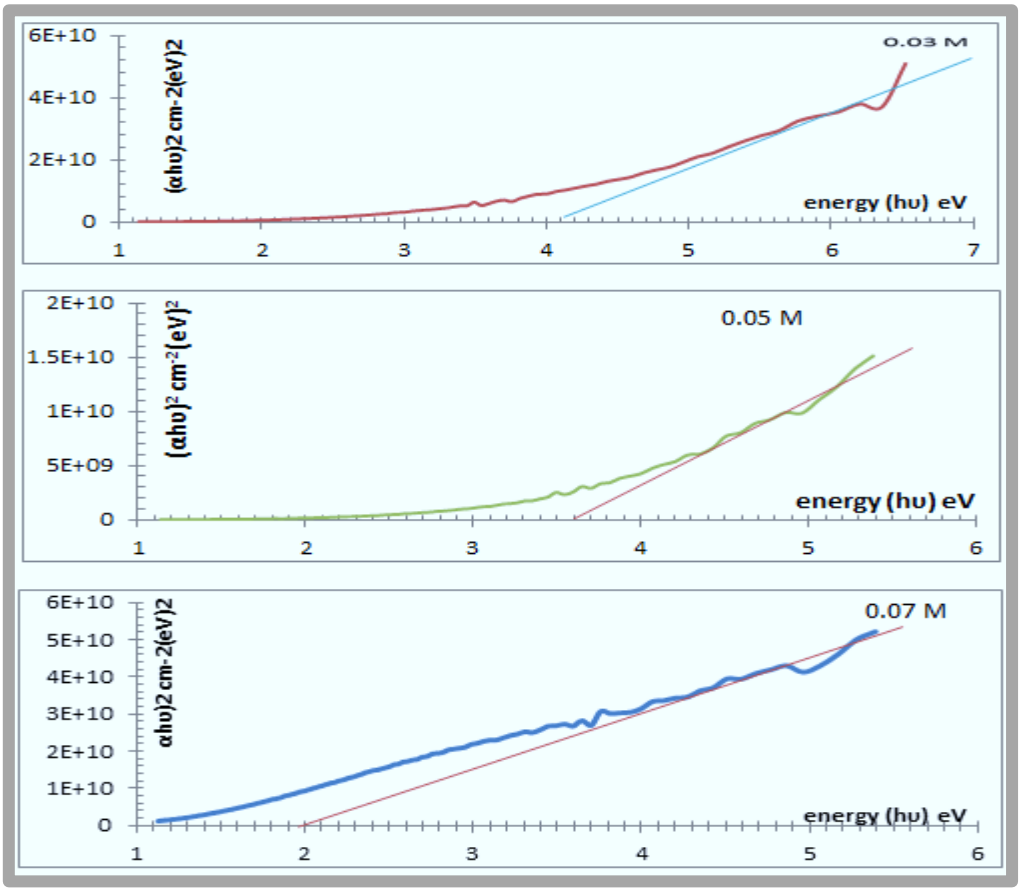


Fig. 5 Tauc's plots for MgO thin films at different molarities

4. Conclusion

MgO nanostructure was successfully prepared in three different molar concentrations by precipitation method. XRD and EDX spectra confirmed the indentation of the material. By Scherrer equation found that grains size increase with molarity increasing. FESEM images showed three different forms of nanostructure are formed Nanoflower-like, Nanorod and Nanosheet for molarity concentrations (0.03, 0.05 and 0.07) respectively. UV-Vis spectra analysis showed that optical energy gap values are decreased as the molarity increasing. Thus it is clear the controlling possibility the MgO properties in terms of shape, size and energy gap is by controlling molarity concentration of the materials used in the preparation of MgO.

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