Study the Effect Doping (Al$_2$O$_3$) Nanoparticles on Optical Properties for PVA Polymer

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Abstract

Polyvinyl alcohol polymer is a harmless substance of great importance to the medical and optical fields. In this paper, we saturated PVA with Al$_2$O$_3$ nanoparticles with different weights 0, 0.01, 0.03 and 0.05% at a temperature of 25°C and 1 atm pressure, The optical constants had been characterized by measuring the transmittance in the visible spectrum, the ultraviolet field, the absorption, and the rest of the optical properties such as the damping and refraction coefficient, in addition to the real and imaginary part of the dielectric constant and finally the optical conductivity of the samples. We observed that the band gap width (E$_g$) decrease when we increase the Al$_2$O$_3$ (doping ratio).

Introduction

In recent years, nano-materials have attracted widespread interest in industrial applications (Zaid A. Hasan, 2021; Zaid A. Hasan, 2019; Abdelaziz, 2011). Alloying polymers have received great attention for bringing certain properties of modified materials, such as enhanced thermal stability, response to influence, flexibility and toughness (Abbasi and Dorranian, 2015). Nanoparticles are the primary element in building nano-structures. In addition, nanoparticles have several physical and chemical properties more than bulk metals in terms of melt point, surface area, optical and mechanical properties, and others (Horikoshi et al, 2013). Al$_2$O$_3$ and various oxides are founded in many uses including luminescent compounds (Caiut et al, 2007) additives for polymer (Hanemann, 2006; Alhareb and Ahmad, 2011); on another hand, Alumina is the cost effective and used material in others applications. It also has high properties such as abrasion resistant, high electrical insulation, good thermal conductivity and hardness (Kamal et al, 2008). Alumina is also used in other applications such as gas laser tubes and high-temperature and high-voltage electrical insulators (Morrell, 1985; Ashby and Jones, 1996). Polymer compounds exhibit unique properties that enable them to be used in a number of applications with easy processing techniques and optical properties. The most famous water-soluble polymer is the poly-vinyl alcohol polymer used in optoelectronic devices with good optical properties (Aslam et al, 2018; Gaaz et al, 2015; Deshmukh et al, 2017). It is a semi-crystalline vinyl polymer with good dielectric, high transparency and low light scattering with low refractive index (Tanio et al, 2000).

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Experimental

Samples were prepared in the form of films (polyvinyl alcohol: Al_2O_3) by doping with percentages ranging (0, 0.01, 0.03 and 0.05%), where the purity was (98.98%), and the measurements (25-27 nm) were from (merk) The chloroform-treated (alumina) particles were dissolved in polyvinyl solution in the previously mentioned proportions in a container (30 ml) in a mixer and placed in a Petri dish with a diameter (9 cm) where the Petri dish was sterilized with water and using ultrasound. The samples were dried after evaporation, and the thickness of the measured sample was ($105*10^3$ nm).

Results

The optical behavior of the material was used to determine its optical constants (such as the absorption coefficient α, the refractive, index n_o, the extinction coefficient K_o, the electrical dielectric constant ε as well as the photo transmittance, 6_{op}), since there are several methods for measuring these constants, we chose this from them Absorbance spectrophotometric method, using the spectrophotometer. We calculated the following quantities:

Transmittance T

Assuming that intensity of the light passing through film I_o, the intensity of the light on surface of a thin film, its thickness d, and the absorption coefficient in α, we write the following exponential relationship (according to lambert) (Zaid A. Hasan; Tariq, 2010) $T = I_t / I_o = e^{-\alpha d}$ the absorbance was defined with equation:

$A = \log 1/T$. Reading the knowledge of the values of the absorbance coefficient A. The transmittance can be calculated from the formula: $T = e^{-2.303A}$. Figure. (1) shows the transmittance coefficient for films.
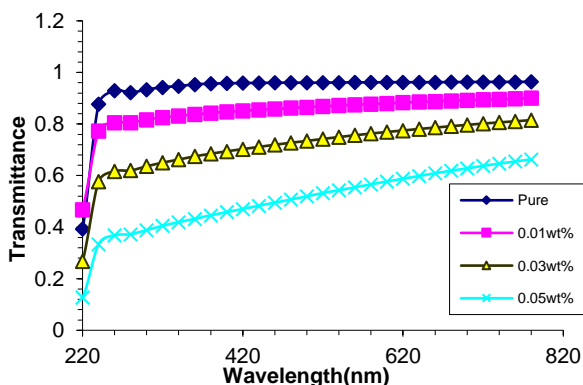

Fig. 1. Changes of transmittance coefficient as a function of wavelength λ(nm) for films

Figure 1 shows as the concentration of aluminum oxide nanoparticles decreases the permeability decreases, and this is due to the increase in the size of the crystal grains (Saadaty et al, 2010). The low value of transmittance in rang (200-400 nm) had been explained by absorption of photons. However, it rose in the near infrared range at about 800 nanometers.

Absorption A

The light ray, which is neither transmitted nor reflected, is absorbed by the atoms of the material, while the energy is preserved through the following equation (Zaid A. Hasan; Jaaraj et al, 2002): T+R+A=1; where R (Reflection), T: (Transmittance), (A: Absorption). The following figure shows absorbance changes as a function of wavelength.
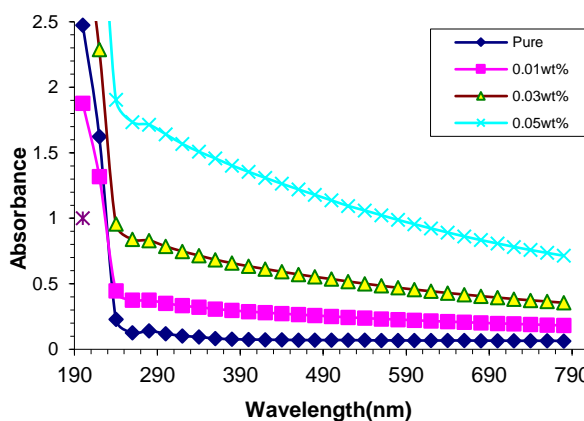

Fig. 2. The absorbance changes terms of wavelength λ(nm)

Absorption coefficient α:

We obtained values for the absorption coefficient (α) for prepared films based on the transmittance spectra according to the following formula (Venkatachalam et al, 2006, Ezema, 2004): $\alpha = \frac{1}{d} 2.303 \, log \, (\frac{1}{T})$ where T: Transmittance, d: thickness.
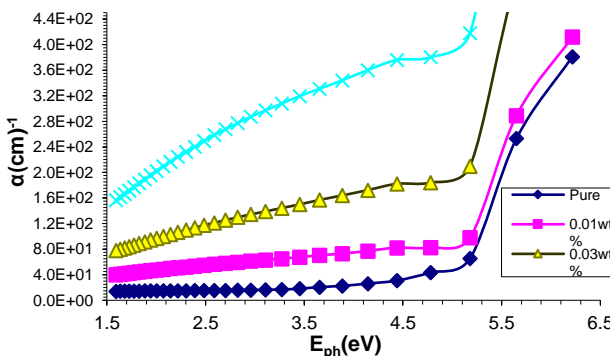

Fig. 3. The absorption coefficient variated in terms of photon energy

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Figure 3 shows that the highest value of absorption is at a concentration of 0.03% of aluminum oxide, then it decreases when the concentration increases, especially at high energies, and it changes rapidly near the edge of light absorption. As the concentration increases, the edges of the absorption shift towards higher photonic energies. We also note that the absorption of the samples is the greatest possible at short wavelengths and then decreases with increasing wavelength to reach a low value in the visible field.

Extinction coefficient K_o

K_o is defined by the amount of energy absorbed by the electrons of the atoms, where the absorption coefficient is calculated from the formula: $\alpha = 2.303\ A/d$, then we find the damping values from the formula (Tigau et al, 2004): $K_o = \frac{\alpha\lambda}{4\pi}$ and the extinction coefficient Ko. From the refractive index relationship, the imaginary damping index of the refractive index given by formula (Zaid A. Hasan; Khaleel et al, 2011).
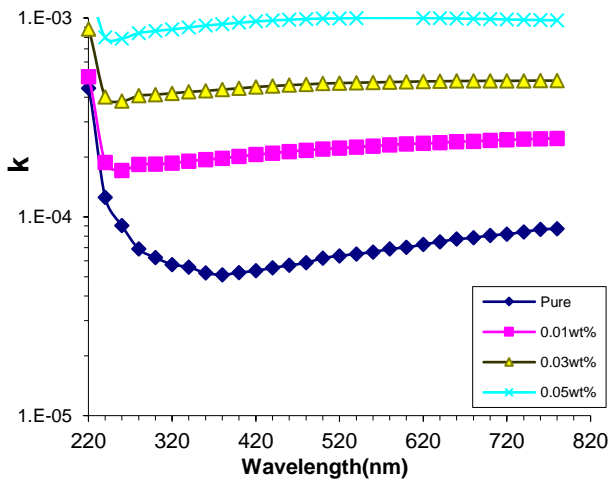
$$n = n_o - iK_o \qquad (1)$$

Fig. 4. Changes of extinction coefficient terms of wavelength λ(nm) for films.

Figure 4 shows a decrease in the damping coefficient at low energies, then it increases with the increase in the photon energy and then when the concentration ratio increases from 0.01 to 0.05, where we find a rapid rise in the spectrum at low wavelengths, which is an indication of the high absorption and therefore the increase in the damping coefficient K.

Refractive Index n_o

The real refractive index n is defined speed of light in a vacuum to its speed in the material: n = C/ν It is calculated from following equation:
$n_o = [(1+R/1-R)^2 - (K_0^2 + 1)]^{1/2} + (1 + R/\ 1-R)$. The n_o depends on the type of material, and on the morphological structure. And as we mentioned in the previous paragraph, the refractive index n is basically a complex quantity given by the formula (1), where (n_o: the real refractive index), which is the amount that we calculate. Figure. (3) represents the changes of the refractive index n_o with a dependency $h\upsilon$.
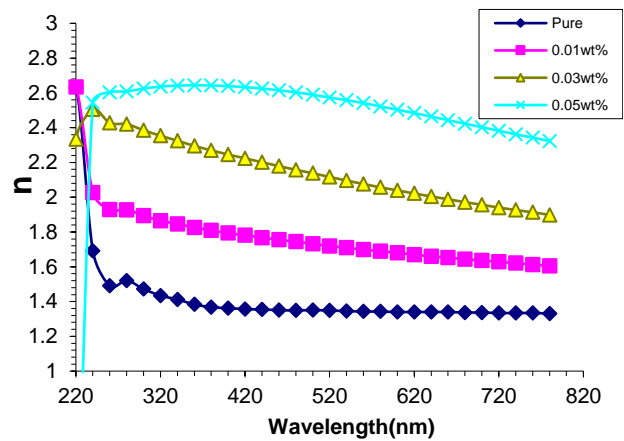
Fig. 5. Changes n in terms of photon energy wavelength λ(nm) for films

The fig. 5 shows that the refractive index curve of the pure sample increases with increasing wavelength (anomalous dispersion) to reach the peak, then the curve begins to decrease (regular dispersion) as we notice a decrease in the values of (n) with increasing wavelength due to decreasing of absorption (Abdul Kader, 2017).

Dielectric Constant ε

The charges of the material are polarized when the beam falls on the material and it interacts with the charges. This polarization expresses the dielectric constant ε, that is ability of electrons of the material to respond to light. We cannot directly calculate each of damping, dielectric and refraction coefficients, except from their respective equations, but we can calculate both absorbance and permeability directly, and the complex dielectric constant can be calculated from the formula (Abdul Zahra, 2013) $\varepsilon = \varepsilon_r + 4\pi i 6_{op}$. Where ε_r denotes the properties of bound charges, while 6_{op} denotes free charges. On the other hand, ε has the following complex: $\varepsilon = \varepsilon_r - i\varepsilon_i$ (Khaleel et al, 2011). Where ε_r (real part),

and ε_i (imaginary part) of the value of ε. The complex refractive index n is related to the extinction coefficient K_o. and on the other hand, the dielectric constant ε according to the following formula (Khaleel et al, 2011) $n = n_0 - iK_o = \sqrt{\varepsilon}$ and squared both sides of this formula:

$\varepsilon = (n_o - iK_o)^2 = n_0^2 - K_0^2 - 2\,in_oK_o$. By equality the formulas, we find:

$$(\varepsilon_r = n_0^2 - K_0^2) \qquad (2)$$
$$\varepsilon_i = 2n_oK_o \qquad (3)$$

Figure. (4) represents the variations of the real dielectric constant ε_r as a function of wavelength λ(nm) for films.
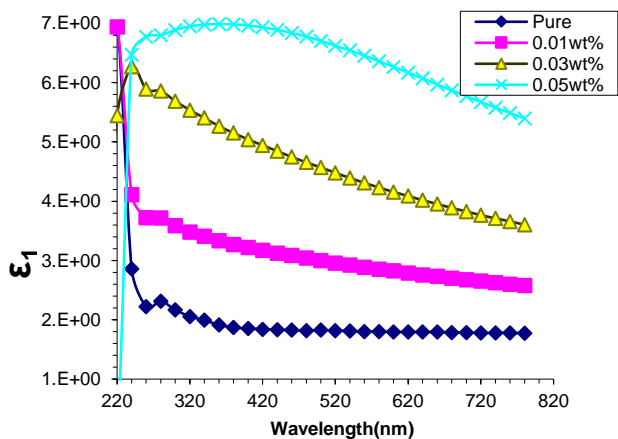

Fig. 6. Spectra of the real electrical dielectric constant ε_r as function of wavelength λ(nm).

The curves of real dielectric constant here are almost similar to the refractive index in the figure. 5 because of their connection together with formula. (2) and in which the effect of the extinction coefficient is weak.
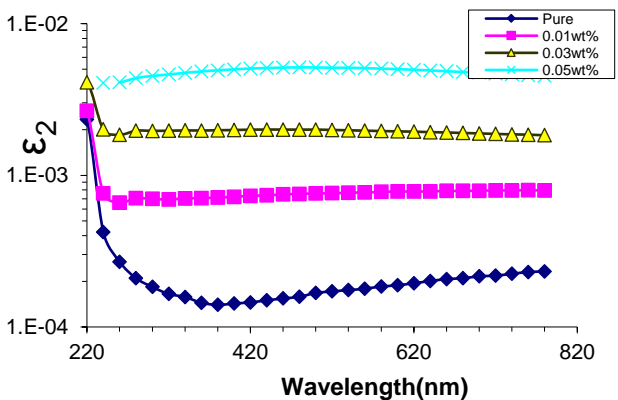
The imaginary dielectric constant (ε_2) represents the energy lost due to the movement of dipoles when shedding an external field. We notice from Figure.7 that the value of (ε_2) for (pure-0.01-0.03 %) samples is almost constant at long wavelengths, while for the sample (0.05 %) it is low at short wavelengths and then increases at long wavelengths.

Calculate of the width of E_g: There are two basic types of direct electronic transitions in the energy structure of the material: allowed electronic transitions, and forbidden electronic transitions. Absorption coefficient (α) of two transitions had been calculated from following formula: $(\alpha h\upsilon = B(h\upsilon - E_g)^r \ldots\ldots(4)$, where: B (constant) relates to the properties of the valence and conductivity bands, $h\upsilon$: the absorbed photovoltaic energy.

The value of the exponent (r) depends on the nature of the transitions. In the allowed direct transfers, its value is 1/2, and formula. (4) takes the form: $(\alpha h\upsilon)^2 = B^2(h\upsilon - E_g)$

In the case of forbidden direct transitions, its value is 2/3, and formula (4) takes the form: $(\alpha h\upsilon)^{3/2} = B^{3/2}(h\upsilon - E_g)$, and the value of the energy gap E_g corresponding to direct electronic transitions is determined graphically from the graph of the graph of $(\alpha h\upsilon)^m$ changes terms of ($h\upsilon$) Then the best and farthest linear part of the curve is taken and plotted as a straight line tangent to it.

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So that an extended intersection of this tangent with the horizontal axis ($h\upsilon$) corresponds to the value of the energy gap E_g, and becomes $(\alpha h\upsilon)^m = 0$. Figures. (6), (7) represents the energy gap of the films in allowed and forbidden direct electronic transitions.

Fig. 7. Spectra of imaginary electrical dielectric constant ε_i in terms wavelength λ(nm) for films.
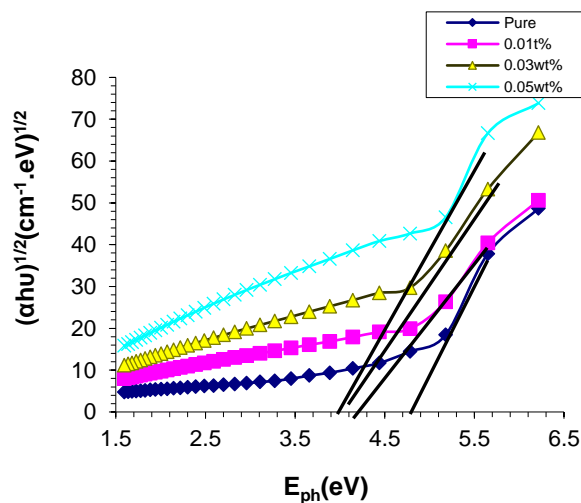

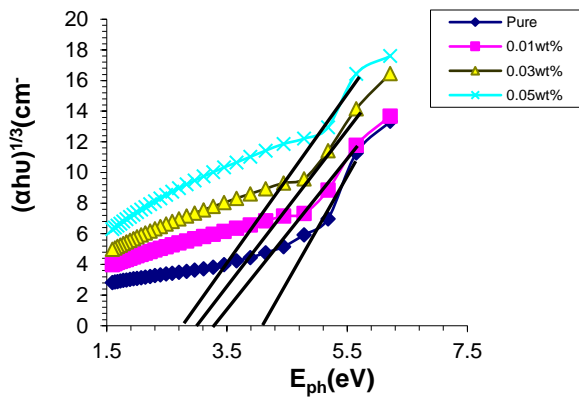**Fig. 8.** Energy gap values of allowed direct transitions

Fig. 9. Energy gap values for forbidden direct transitions.

We note from the two figures (8,9) that the forbidden band gap of the allowed and for bidden direct electronic transitions decrease with the increase in the concentration of aluminum oxide nanoparticles, as the increase in concentration leads to a deflection of the absorption edge towards lower energies. This is due to the fact that the rate of grains size increases with increasing concentration, and consequently, the concentration of charge carriers increases, and thus value for band gap field decrease (Bakry and Mahmoud, 2010). The following table shows the energy gap values of the allowed and forbidden direct transitions of the samples.

sample	Allowed energy gap (ev)	forbidden energy gap (ev)
Pure	4.30	3.42
0.01 %	3.85	3.28
0.03 %	3.40	2.96
0.05 %	2.85	2.62

Optical Conductivity σ_{op}

It is defined as the increase in the number of charge carriers (electrons or holes) as a result of the falling of a light beam on material. The σ_{op} had been calculated from following formula (Abdul Zahra, 2013):

$$\sigma_{op} = \frac{\alpha n_0 c}{4\pi} \qquad (5)$$

The optical conductivity σ_{op} had been calculated from formula (5), notice from this equation that it is directly proportional to the refractive index n_0 and absorption coefficient α.
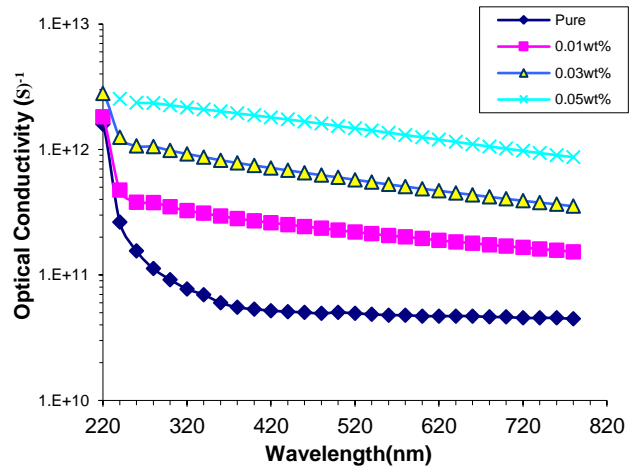
Figure. (8) shows Optical conductivity changes.

Fig. 10. Optical conductivity changes σ_{op} in terms of hv for films.

The figure. 10 shows value of optical conductivity decreases with increases wavelength, while it increases at low wavelengths because connection of optical conductivity (σ_{op}) with absorption coefficient (α).

Conclusion

A series of (PVA: Al₂O₃) films had been prepared by new method. The ultraviolet and visible spectroscopy had been improved of optical properties. We noticed that the transparency decreases with increasing doping concentration with aluminum oxide nanoparticles. on the other hand, we find that the absorption coefficient increases significantly with increasing the concentration of doped especially at high energies, and it changes rapidly near the edge of light absorption. As the concentration increases, the edges of the absorption shift towards higher photonic energies. We note that Eg the allowed and forbidden electronic transitions decrease with the increase in the concentration of doping, this is due to the fact that the rate of grains size increases with increasing concentration, and consequently, the concentration of charge carriers had been increased, and thus value of band gap increases, that value of optical conductivity decreases with increasing wavelength, while it increases at short wavelengths due to the connection of optical conductivity with absorption coefficient.

References

Bakry AM, Mahmoud SA. *Effect of substrate Temperature on the optical Dispersion of sprayed Nickel oxide thin films.* University of Hail 2010.

Jazmati AK, Abdallah B. Optical and structural study of ZnO thin films deposited by RF magnetron sputtering at different

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thicknesses: a comparison with single crystal. *Materials Research* 2018: 21.

Zahra SA. Effect of Additive Al on the Optical Properties of Polystyrene-Aluminum Composites. *Ibn AL-Haitham Journal for Pure and Applied Science* 2017; 26(3): 111-121.

Alhareb AO, Ahmad ZA. Effect of Al₂O₃/ZrO₂ reinforcement on the mechanical properties of PMMA denture base. *Journal of Reinforced Plastics and Composites* 2011; 30(1): 86-93.

Ashby MF, Jones DRH. *Engineering materials I.* Ox-ford: Butter worth Heinemann, 1996.

Aslam M, Kalyar MA, Raza ZA. Polyvinyl alcohol: A review of research status and use of polyvinyl alcohol based nanocomposites. *Polymer Engineering & Science* 2018; 58(12): 2119-2132.

Zhang H, Wu J, Zhai C, Du N, Ma X, Yang D. From ZnO nanorods to 3D hollow microhemispheres: solvothermal synthesis, photoluminescence and gas sensor properties. *Nanotechnology* 2007: 18(45).

Deshmukh K, Ahamed MB, Deshmukh RR, Pasha SK, Bhagat PR, Chidambaram K. Biopolymer composites with high dielectric performance: interface engineering. *In Biopolymer composites in electronics* 2017: 27-128.

Saadati F, Grayeli AR, Savaloni H. *Dependence of the optical properties of NiO thin films on film thickness and nano-structure* 2010.

Ezema FI. Optical characterization of chemical bath deposited bismuth oxyiodide (BiOI) thin films. *Turkish Journal of Physics* 2005; 29(2): 105-114.

Gaaz TS, Sulong AB, Akhtar MN, Kadhum AAH, Mohamad AB, Al-Amiery AA. Properties and applications of polyvinyl alcohol, halloysite nanotubes and their nanocomposites. *Molecules* 2015; 20(12): 22833-22847.

Hanemann T. Influence of dispersants on the flow behaviour of unsaturated polyester–alumina composites. *Composites Part A: Applied Science and Manufacturing* 2006; 37(5): 735-741.

Kar KK, Srivastava S, Rahaman A, Nayak, SK. Acrylonitrile-butadiene-styrene nanocomposites filled with nanosized alumina. *Polymer composites* 2008; 29(5): 489-499.

Khleel RI, Alwan TJ. Effect of Doping Ni (etx) 2on Optical Properties of Poly styrene. *Al-Mustansiriyah Journal of Science* 2011; 22(6): 129-136.

Abbasi M, Dorranian D. Effect of laser fluence on the characteristics of Al nanoparticles produced by laser ablation in deionized water. *Optics and Spectroscopy* 2015; 118(3): 472-481.

Abdelaziz M. Cerium (III) doping effects on optical and thermal properties of PVA films. *Physica B: Condensed Matter* 2011; 406(6-7): 1300-1307.

Jayaraj MK, Antony A, Ramachandran M. Transparent conducting zinc oxide thin film prepared by off-axis rf magnetron sputtering. *Bulletin of Materials Science* 2002; 25: 227-230.

Morrell R. Handbook of properties of technical & engineering ceramics. National Physical Laboratory 1985.

Horikoshi S, Serpone N, *Microwaves in Nano-particle Synthesis.* Wiley-VCH, Cambridge, UK; AG & Co. KGaA, Dusseldorf, Germany, 1st edition, 2013.

Venkatachalam S, Mangalaraj D, Narayandass SK. Structural, optical properties and VCNR mechanisms in vacuum evaporated iodine doped ZnSe thin films. *Applied surface science* 2006; 253(11): 5137-5142.

Tanio N, Koike Y. What is the most transparent polymer? *Polymer Journal* 2000; 32(1): 43-50.

Alwan TJ. Refractive index dispersion and optical properties of dye doped polystyrene films. *Malaysian polymer journal* 2010; 5(2): 204-213.

Tigau N, Ciupina V, Prodan G, Rusu GI, Gheorghies C, Vasile E. Structure and optical properties of thermally vacuum evaporated Sb~ 2O~ 3 thin films. *Journal of optoelectronics and advanced materials* 2004; 6: 449-458.

Hasan ZA. Effect Magneto–Optic on Ferromagnetic Nanoparticle Polymer Composite Films. *NeuroQuantology* 2021; 19(6): 25-29.

Hasan ZA. Study the effect of magnetic field on polymer doping Tio2 nanoparticles. *NeuroQuantology* 2019; 17(12): 39-43.

Négadi T. From RNA to the genetic code and back. *NeuroQuantology* 2020; 18(1): 1-7.