Optical Properties of Zinc Phosphate Glass Doped With Aluminum Oxide for Optical Filter

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Phosphate glass system doped with Al_2O_3 of chemical formula 49.5% P_2O_5-20%Na_2O-(30-x)%ZnO-x%Al_2O_3-0.5%CuO (x=0, 2.5, 5, 7.5, 10) was prepared by conventional melt quenching technique. XRD analysis shows the glassy nature of the prepared samples. The measured density and calculated molar volume reveal nonlinear dependence, however follow opposite trend. Optical transmittance of all prepared samples show absorption edge. Obtained optical transmittance was used to estimate band gap E_g. E_g shows nonlinear dependence on the Al content. The analysis of optical data reveals the indirect transmission mechanism. Refractive index and dielectric constant show a slight change.

1. Introduction:

Phosphate glass system has marvelous interest because of their properties, such as low melting and softening temperature, high thermal expansion coefficient, low dispersion, high electrical conductivity and optical properties [1-3]. The poor chemical durability of phosphate glass is one of the main disadvantages of using this type of glass former[4,5]. However addition of some modifier like transition metal oxide increase the benefits of glasses. [6]. Addition of ZnO improves the chemical durability, melting properties and opacity of glass which is very important for the optical applications[7]. Copper phosphate glasses exhibit an optical absorption band in the visible and near infrared region and fundamental optical absorption edge in the ultraviolet region[8].

The aim of present study is to examine the effect of Al additive at the expense of zinc oxide and Copper doped phosphate glasses can act as a good band pass filter

2.Experimental Work:

2.1. Glass Preparation:

Phosphate glass of chemical composition 49.5%P_2O_5-20%Na_2O-(30-x)%ZnO-x%Al_2O_3-.5%CuO, since x=0, 2.5, 5, 7.5 and 10% was prepared from starting materials Na_2CO_3, ZnO, $(NH_4)H_2PO_4$, $Al_2(CO_3)_3$ and CuO using conventional melt quenching technique as shown in Table1. The desired amounts of starting materials were mixed and grinded using mortar for each sample to obtain a homogenous fine powder. All samples were calcinated in porcelain crucible using muffle furnace for 1hour 300^0C to release gases. Then the samples were heated at 1000^0C for half hour. Molten sample were shaken several times to obtain a homogenous glass sample. The molten samples were quenched in copper mold by pressing plate to have thin disks. The obtained glassy sample is a thin transparent blue color.

2.2. Density Measurements:

Density measurements were carried out at room temperature, using Archimedes' method with toluene as the immersion fluid and applying the following relation [9]:

$$\rho = \rho_l \frac{w_a}{w_a - w_l} \tag{1}$$

since ρ_l is the density of toluene, w_a and w_l are the sample weight in air and in toluene, respectively.

2.3. X-ray Diffraction Analysis:

XRD was carried out on glass powders to confirm the amorphous nature of the glasses. Measurements were carried out on a Bruker-D8 Advance Diffractometer (Brüker, UK) in flat plate geometry, using Ni filtered Cu Kα radiation. Data were collected using a Lynx Eye detector at 2θ values from101 to 901.

2.4. UV–Visible Measurements:

Ultraviolet and visible optical transmission spectra were immediately measured for perfectly polished glass samples using a recording double beam spectrophotometer (type JASCO Crop., V-570, Rel-00, Japan) covering the wavelength range from 190 to 1100 nm.

3. Results and Discussion:

3.1- Structural Analysis Using XRD

Glassy nature of the prepared samples was confirmed by XRD studies as shown in Fig.(1). Diffractogram of glass samples shown in Fig.(1), shows a standard trace of glassy materials where there is no appearance of diffraction lines indicating to crystalline nature of the prepared materials.

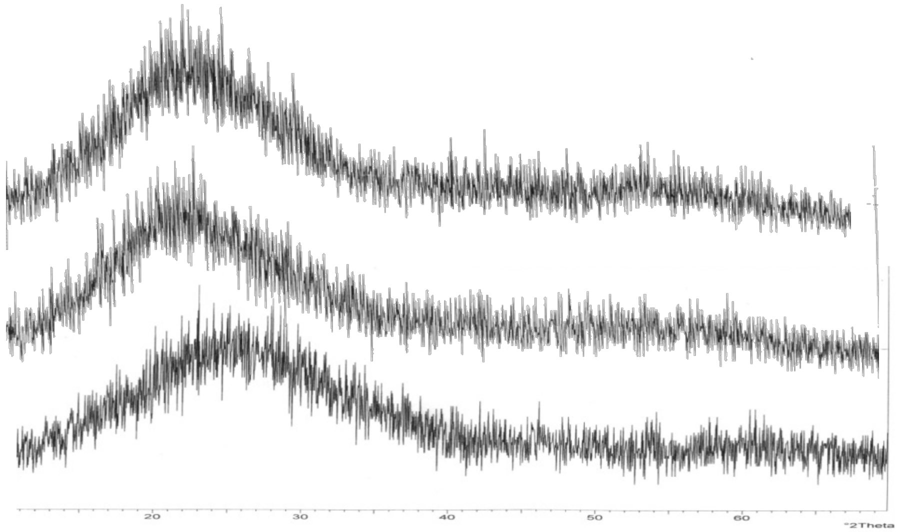


Fig.(1): XRD pattern for the prepared glass.

3.2-Density:

The dependence of density ρ and molar volume M_v of glass sample on Al_2O_3 oxides concentration are shown in Fig.(2) and Table1. The data reveal that both ρ and M_v follow opposite trend, i.e., follow the normal behavior. However the dependence of ρ and M_v on Al content is non-linear. This non-monotonically behavior is most likely due to the fact that Al is an intermediate oxide which can act as glass former or modifier according to also concentration[10-13].

Table (1): Composition of P_2O_5-Na_2O-CuO -ZnO -Al_2O_3, density (ρ) and molar volume (V_M):

Sample	Glass composition (mol%)					Ρ gcm^{-3}	VM $cm^{-3}mol^{-1}$
	P_2O_5	Na_2O	CuO	ZnO	Al_2O_3		
S_1	49.5	20	0.5	30	0	3.5	53.2
S_2	49.5	20	0.5	27.5	2.5	3.3	56.57
S_3	49.5	20	0.5	25	5	3.97	47.29
S_4	49.5	20	0.5	22.5	7.5	3.82	49.18
S_5	49.5	20	0.5	20	10	3.49	53.921

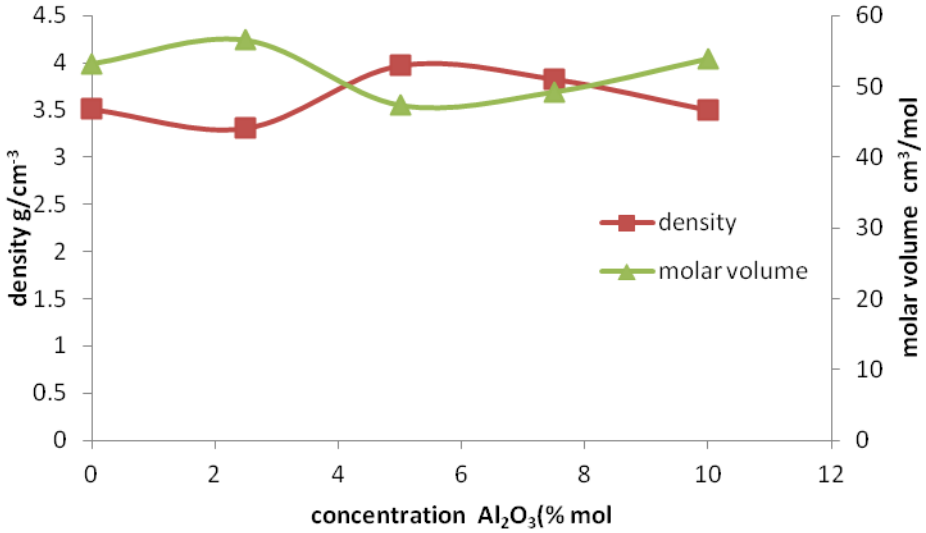


Fig.(2): Density and molar volume as a function of Al content.

3.3-Transmission:

The spectra show broad high transmittance region. This is easily understood by considering the fact that copper divalent ions as to absorption bands at UV and infrared region and hence the transmission region is obtained which give this composition band pass filtering effect Fig.(3), [14-16].

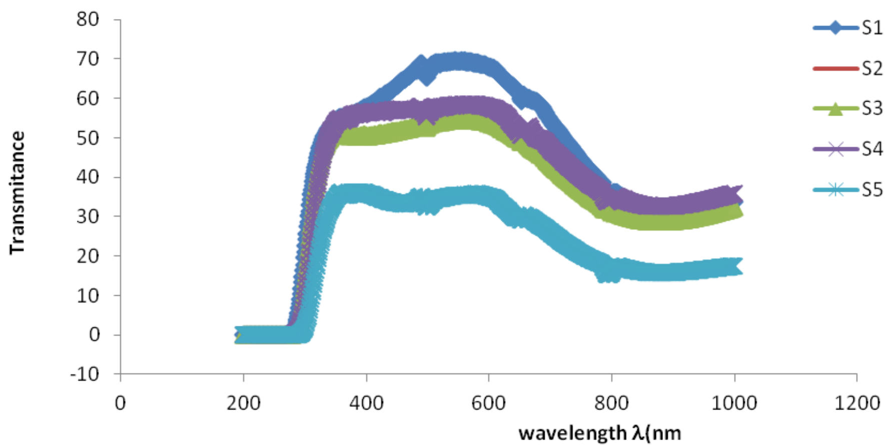


Fig.(3): The transmission as a function wavelength of the glass samples.

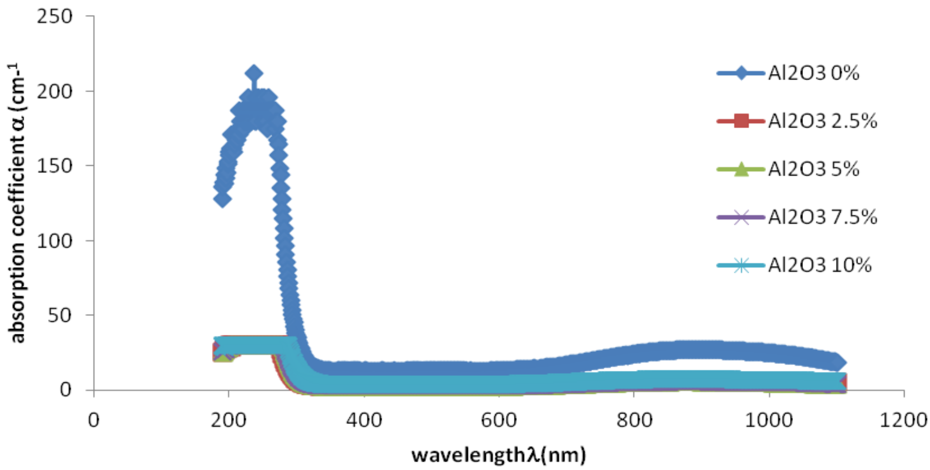
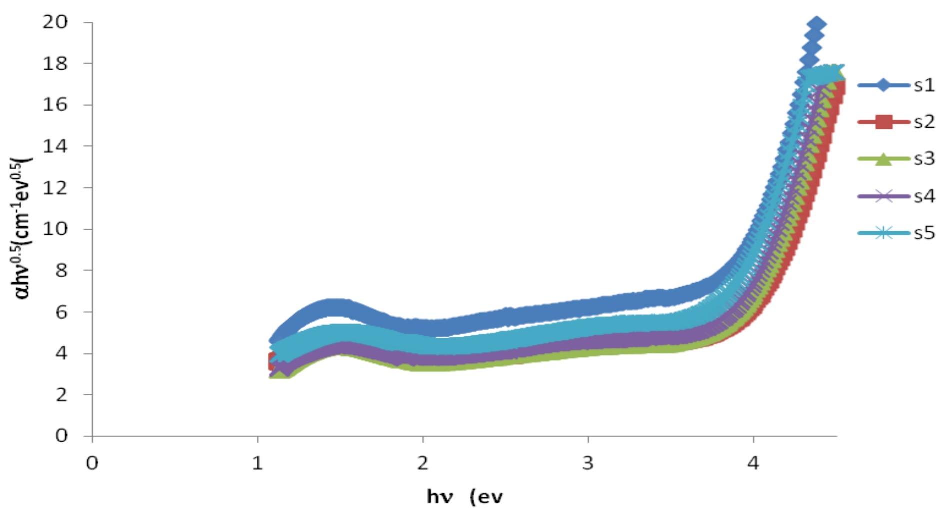


Fig.(4): The absorption coefficient against wavelength.

Optical absorption spectra as a function of wavelength is shown in Fig(4). The measured absorption spectra follow the normal behavior where an absorption edge is observed at short wavelength side. Such edge extends over wide range of wavelength as expected for non-crystalline systems. To estimate the absorption mechanism should apply the well-known relation[17]:

$$(\alpha h\nu)= A(h\nu-E_g)^n \qquad (2)$$

where α is the absorption coefficient. The value of n depends on the absorption mechanism and the structure of the investigated system, i.e., amorphous or non-crystalline. The linear relation observed in case of $\sqrt{\alpha h\nu}$ against $h\nu$, indicating that the most probable absorption mechanism is indirect allowed transition. This is expected in non-crystalline system as a result of the absence translation symmetry and conservation of linear momentum.



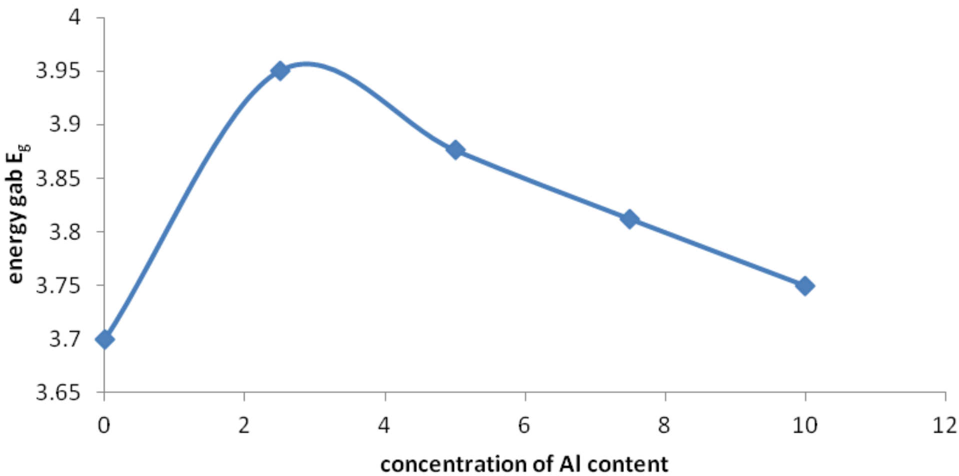


Fig.(5): Variation of energy gap as a function of Al content in mol%.

The estimated band gap E_g plotted as a function of Al content as shown in Fig.(5). The observed behavior shows the increase in the band gap from 3.7eV to 3.96eV with increasing Al content from 0 to 2.5 mol%. For Al content higher than x=2.5% the band gab decrease monotonically. This is usually related to the role of Al content in the present glass matrix, i.e., Al as former or as modifier [17].

The refractive index n calculated using the following equation of reflectance R[17, 18]:

$$R=\frac{(n-1)^2}{(n+1)^2} \tag{3}$$

Since:

$$R+A+T=1 \tag{4}$$

Where T and A are the transmittance the absorbance respectively.
reflectance and refractive index calculated from Eqn 4 & Eqn3 respectively. Refractive index n plotted as a function of wavelength as shown in the Fig.6.

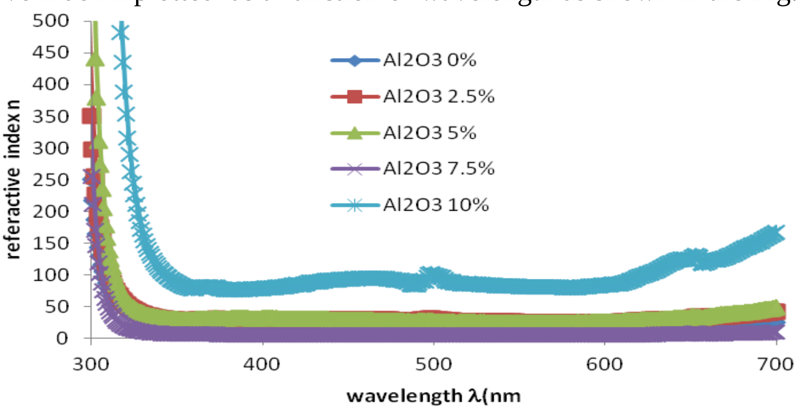


Fig.(6): Refractive index as function of wavelength.

The extinction coefficient shown in Fig.(7), calculated using the following relation[17-18]:

$$K = \frac{\alpha\lambda}{4\Pi} \qquad (5)$$

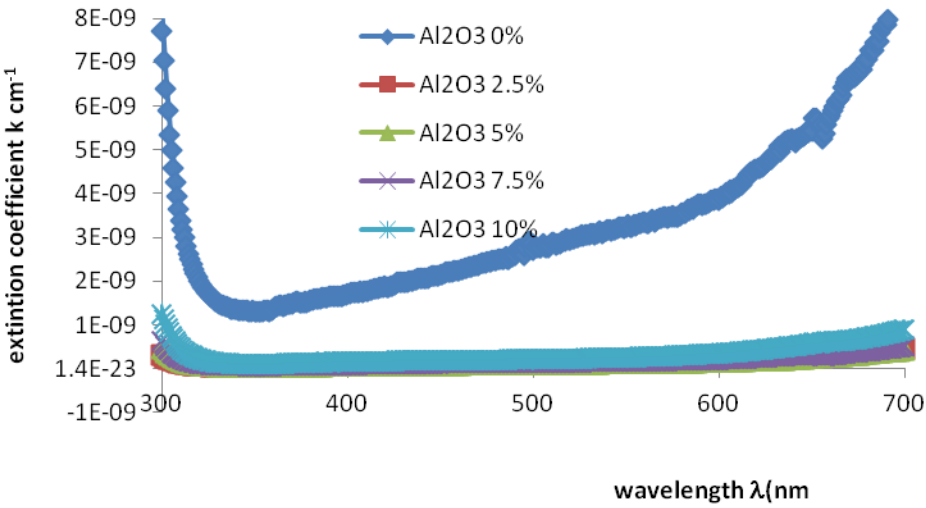


Fig.(7): Extinction coefficient as function of wavelength.

Real and imaginary parts of dielectric constants shown in Fig.(8 & 9) calculated using the following relations [17-18]:

$$\varepsilon^{\backslash} = n^2 - K^2 \qquad (6)$$
$$\varepsilon^{\backslash\backslash} = 2nK \qquad (7)$$

Where $\varepsilon^{\backslash}$ and $\varepsilon^{\backslash\backslash}$ are the real and imaginary part of dielectric constant.

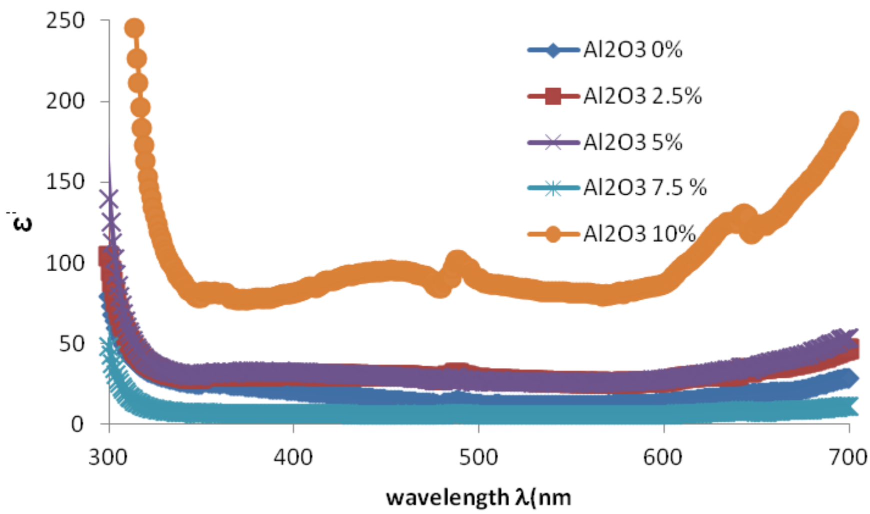


Fig.(8): Real part of dielectric constant as function of wavelength

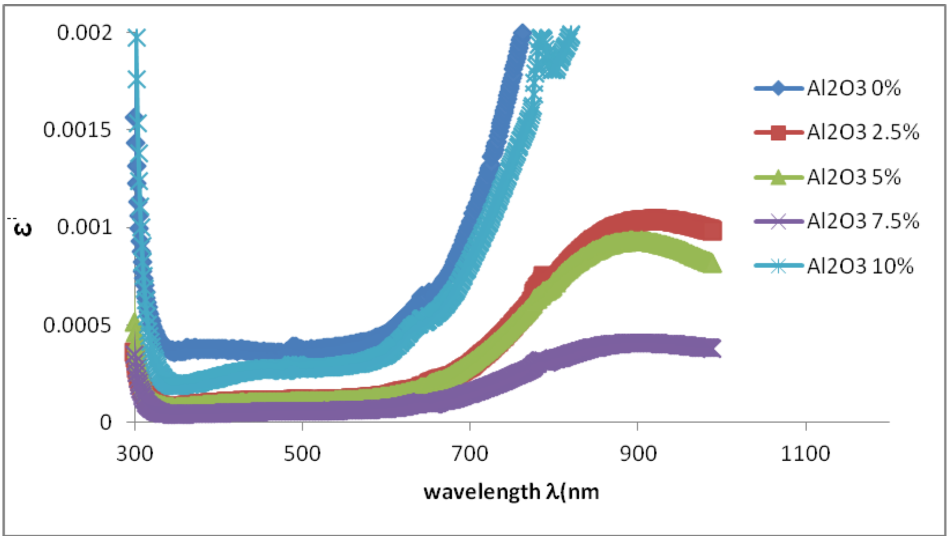


Fig.(9): Imaginary part of dielectric constant as function of wavelength.

From the above observed optical data, it is noted that there is a slightly change in extinction coefficient, refractive index and dielectric constants with wavelength. Determination of these parameters representing great important for the optical application[17].

4. Conclusion:

The present study shows the effect of Al^{+3} ion of phosphate glass on molar volume and density. The behavior of density is nonlinear. The optical transmission was studied. The band gab jumps from x=0mol% to x=2.5mol% then decrease with increasing Al content. The extinction coefficient, refractive index and dielectric constant were studied and show no change remarkable.

References:

1. E. Metwalli, M. Karabulut, D. L. Siderorton, M. M. Morsi, R. K. Brow, *J. Non-Cryst. Solids*, **344** (2004).

2. Yahia H. Elbashar, Ali M. Badr, Haron A. Elshaikh, Ahmed G. Mostafa, Ali M. Ibrahim, *Processing and Application of Ceramics*, **10** (4), 277 (2016)

3. P.P. Proulx, G. Cormier, J.A. Capobianco, B. Champagnon, M. Bettinelli, *J. Phys. Condens. Matter*, **6**, 275 (1994).

4. H. Yung, P.Y. Shih, H.S. Liu, T.S. Chin, *J. Am. Ceram. Soc*., **80**, 2213 (1997).

5. M.R. Reidmeyer, M. Rajaram, D.E. Day, *J. Non-Cryst. Solids*, **85**, 186 (1986).

6. S.T.Reis, M.Karabulut, D.E.Day, *J. Non-Cryst. Solids*, **292**, 150 (2001).

7. G. Buxbaum,G. Pfaff, Wiley-VCH.(1998).

8. B.S.Bae, M.C.Weinberg, *J. Appl. Phys*., **73**, 7760 (1993).

9. S.F.Khor, Z.A, Talib, W.M. Mat Yunus, *Ceram. Int*., **38**, 935 (2011).

10. N. Srinivasa, M. Purnima, S. Bale, *Bull Mater, Sci*, **29**, 365 (2006).
11. H.M. Oo, H.M. Kamari, W.M.D.Wan-Yusoff, *Int. J. Mol. Sci*., **13**, 4623 (2012).
12. S. Kaewjaeng, J. Kaewhao. P. Limuwan, U. Maghanemi, *Procedia Eng*., **32**, 1080 (2012).
13. P. Limkitjaroenporn, *J. Phys. Chem. Solids*, **72**, 245 (2011).
14. B.S. Bae,M.C. Weinberg, *J. Non-Cryst. Solids*, **168**, 223 (1994).
15. H. Takebe,S. Nishimoto, M. Kuwabara, *J. Non-Cryst. Solids*, **353**, 1354 (2007).
16. S.F. Khor, Z.A. Talib, F. Malek, E.M. Cheng, *J. Opt. Mater*, **35**, 329 (2013).
17. H. Elhaes, M. Attallahb, Y. Elbashar, M. El-Okr, M. Ibrahim, *Physica*, **B449**, 251 (2014).
18. M.Y. Nadeem, W. Ahmed, Turk, *J. Phys*, **24**, 651 (2000).