

## Determination of optical properties of Neodymium-doped Zinc-Phosphate glasses.

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**Abstract:** Zinc-Phosphate glasses have superior physical properties such as high thermal expansion coefficients, low melting temperatures and high ultra - violet transmission. They also find application as a potential substrate for femtosecond Laser writing. Their further applications are probably not rising due to their poor chemical reactivity and low light absorbance. In the present work, a series of Nd doped Zinc-Phosphate glasses have been studied for the estimation of their optical parameters. The refractive index and the dispersion data has been derived from the transmission spectrum of the samples using Swanepoel envelope method and Wemple-DiDomenico model. The value of absorption coefficient derived from the Optoacoustic absorption spectrum leads towards the estimation of Energy band gap and Urbach energy of the samples.

**Keywords:** Transmission Spectrum, Envelope Method, Optoacoustics, Refractive index, Urbach Edge.

### Introduction

Ceramics find number of key technological as well as industrial applications, due their high thermal stability, corrosion resistance and the easy availability of raw material. Zinc-Phosphate glasses offer enough design flexibility options, leading them to various optoelectronic and insulating applications. Knowledge of the optical parameters of a glassy material is quite important for examining the potential of the material to be used in above mentioned applications. The optical constants also provide the information about the electronic band structure, the band tail and localized states<sup>1</sup>. The analysis of the glassy state is based primarily on the theory of semiconducting and insulating crystals. The definitive prediction of the various optical parameters of the ceramic family in the fundamental region is quite complicated, since it requires detailed knowledge of the wave function of whole material. More complications are caused by some basic problems like crystal imperfections, presence of lattice phonons at experimental temperature and surface states etc. In the present work, two different methods are utilized for the complete investigations of the various optical parameters of the samples. Firstly, the transmission spectrum was recorded for all the samples individually, which led to the determination of refractive index and few dispersion parameters of the samples. Secondly, the Optoacoustic (OA) absorption spectrum was recorded for all the samples, through which the Energy band gap and Urbach energy were calculated. An Optoacoustic absorption spectrum has an edge over the normal absorption spectrum as it depends upon the non-radiative transitions taking place inside the sample. This aspect of the technique becomes strikingly important when we have to analyze less light absorbing samples like those of the present work. Also, the method of optoacoustics is always the first choice over other photothermal detection techniques, due to its simple and elegant experimental set-up and its capability to provide material parameters with great accuracy<sup>2</sup>. The method of Optoacoustics is based upon the non-radiative de-excitations produced in the sample, after

absorbing a monochromatic chopped electromagnetic radiation. The heat generated in the sample creates pressure fluctuations in the adjacent coupling gas compartment and can be detected using a microphone or piezoelectric transducer. This technique has efficiently been used for studying the weakly light absorbing samples<sup>3-5</sup>. Various workers<sup>6-9</sup> used OA technique for the determination of Optical energy gap and other various properties of semiconductors and glasses.

Rosencwaig and Gersho<sup>10</sup> were the first to present a quantitative derivation for the optoacoustic signal in terms of optical, thermal and geometrical parameters of the system. A rigorous mathematical treatment<sup>11</sup> to the Rosencwaig - Gersho (RG) theory gives following relationship between optoacoustic signal and optical absorption coefficient.

$$\alpha = \frac{1}{\mu_s} \frac{[q^2 + q(2 - q^2)^{1/2}]}{(1 - q^2)} \quad \text{-----(1)}$$

Where q = Normalized Optoacoustic Signal

Urbach<sup>12</sup> suggested that at small values, absorption coefficient varied with both frequency and temperature.

$$\alpha = \alpha_0 \exp \left[ \frac{\gamma \{h\nu - E_g(0) + \beta T\}}{kT} \right] \quad \text{-----(2)}$$

Where  $\alpha$  is the absorption coefficient, which depends on temperature T and the light energy  $h\nu$ ,  $\alpha_0$  and  $\gamma$  are constants,  $E_g(0)$  is the energy gap value of the glass and  $\beta$  is the energy-gap temperature coefficient, which is determined from equation

$$E_g(T) = E_g(0) - \beta T \quad \text{-----(3)}$$

In the quantum mechanical sense, for allowed direct transitions in glass, we may write<sup>13,14</sup>.

$$\alpha h\nu = A(h\nu - E_g(0))^{1/2} \quad \text{-----(4)}$$

So, the plot between  $(\alpha h\nu)^2$  and  $h\nu$  will then give a straight line and we can estimate the band gap energy  $E_g(0)$  from the intercept on x axis. The Urbach energy corresponds to the width of the tail of localized states within the optical band gap. It is linked to the absorption coefficient in the lower energy region of fundamental edge and can be described by-

$$\alpha = \alpha_0 \exp \left( \frac{h\nu}{E_u} \right) \quad \text{-----(5)}$$

Here,  $E_u$  = Urbach energy

## Materials and Methods

For the preparation of glass samples, Sodium di hydrogen orthophosphate and Zinc Oxide, in the ratio 3:1 by weight are taken in a beaker and stirred continuously with the help of an electrically driven stirrer, so as to obtain a homogeneous mixture. The mixture is then put in to an electric furnace (capable of achieving temperature up to 1200°C) in a platinum crucible at a temperature ranging from 850°C to 950°C for half an hour. The molten mass is then allowed to cool for about 10 minutes and then rapidly quenched by placing in between two well-polished, preheated brass plates so as to obtain glass discs of about 2 mm thickness and with a diameter of about 1 cm (little smaller in size with the sample cavity of OA cell). For recording the transmission spectra, the thin films were deposited by evaporating the bulk glass sample prepared in the previous step, onto pre-cleaned glass substrates kept at room temperature, using a conventional coating unit (Edwards coating system E-306) under vacuum of about  $2 \times 10^{-5}$  Torr. The transmittance spectra of all the samples were recorded using Shimadzu UV-VIS NIR Spectrophotometer, in the wavelength range 200 nm-1500 nm.

For recording the optoacoustic spectra of these samples, the glass discs obtained in the first step above were placed inside the sample cavity of the Optoacoustic cell one by one. The details of the experiment are given elsewhere<sup>15</sup>. An Optoacoustic Spectrometer allows us to measure the optoacoustic signal at varying wavelengths of incident light from Xenon-arc lamp in between 200 nm to 1000 nm at a fixed modulation frequency.

## Results and Discussions

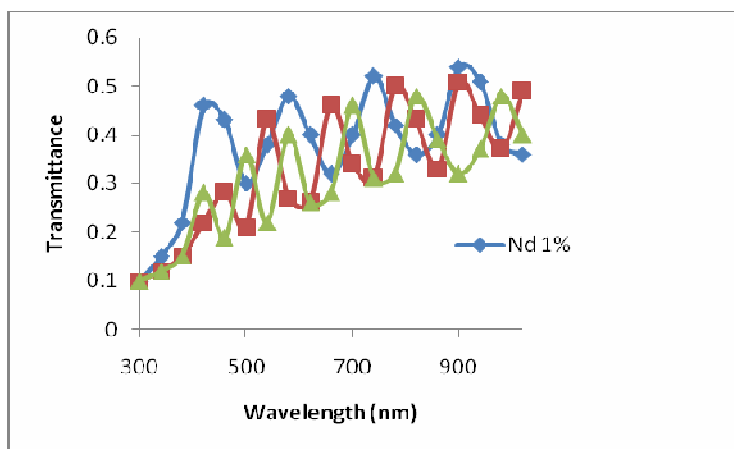
### a. Determination of Refractive Index by Swanepoel method-

The determination of the refractive index ( $n$ ) was done using the envelope method suggested by Manifacier *et al*<sup>16</sup> and Swanepoel<sup>17</sup>. The spectral envelopes of the transmittance  $T_{\max}$  and  $T_{\min}$ , which are assumed to be the continuous functions of the wavelength, were computed using a polynomial interpolation between extremes. The transmittance spectra in the range of 300 to 1100 nm, for all the samples of the present work are shown in figure 1. In the graph, the oscillating part of the curve is due to the interference effect of multiple reflections of incident beam inside the film. For the determination of optical parameter like refractive index, values of upper and lower envelopes ( $T_{\max}$  and  $T_{\min}$ ) were determined and which ultimately gave the value of refractive index. The Swanepoel method establishes that, in transparent region, where the absorption coefficient is nearly zero, the refractive index  $n$  is given by-

$$n = [H + (H^2 - n_s^2)^{0.5}]^{0.5}$$

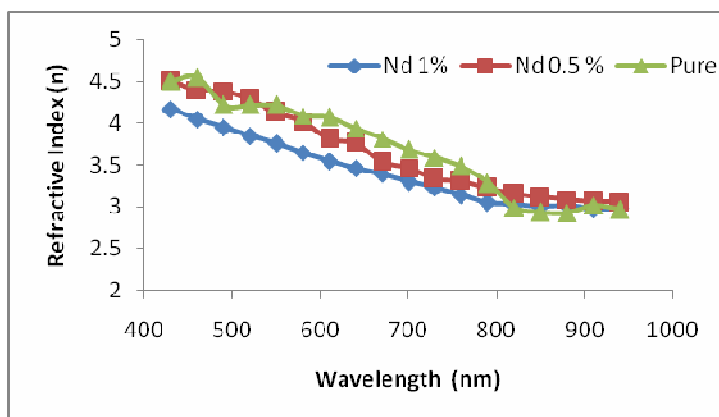
$$\text{Where, } H = \frac{2n_s(T_{\max} - T_{\min})}{(T_{\max}T_{\min})} - \frac{n_s^2 + 1}{2}$$

Here  $n_s$  = Refractive index of glass substrate (1.52 in present case)



**Fig. 1 The transmittance spectra for Pure Zn-P glass sample, Zn-P glass doped with 5 % of Nd and Zn-P glass with doped 1 % of Nd**

Further, the variation in the refractive index  $n$  as a function of wavelength  $\lambda$  for different doping concentration is shown in the figure below. It is mostly observed that the incorporation of Nd decreases the refractive index of the films. The same behavior was also predicted earlier<sup>18,19</sup>.



**Fig. 2 Variation of refractive index for various sample plotted with the wavelength**

### b. Determination of dispersion parameters (Dispersion energy and Single Oscillator energy)-

The obtained values of refractive indices ( $n$ ) of the samples can be fit in to Wemple-DiDomenico single oscillator dispersion model<sup>20</sup>.

$$n^2 = 1 + \frac{E_d E_0}{[E_0^2 - (h\nu)^2]}$$

Where  $E_d$  is the dispersion energy or oscillator strength and  $E_0$  is the single oscillator energy. Dispersion energy is the measure of the strength of interband optical transitions and is related to the coordination number of the atoms. Single oscillator energy defines average energy gap between the centers of both the conduction band and valence bands. Therefore, a graph of  $(n^2-1)^{-1}$  vs  $(h\nu)^2$  will give the value of  $E_0$  and  $E_d$ . The slope of the graph gives the value of  $(E_d E_0)^{-1}$  and intercept on vertical axis gives the value of  $E_0/E_d$ .

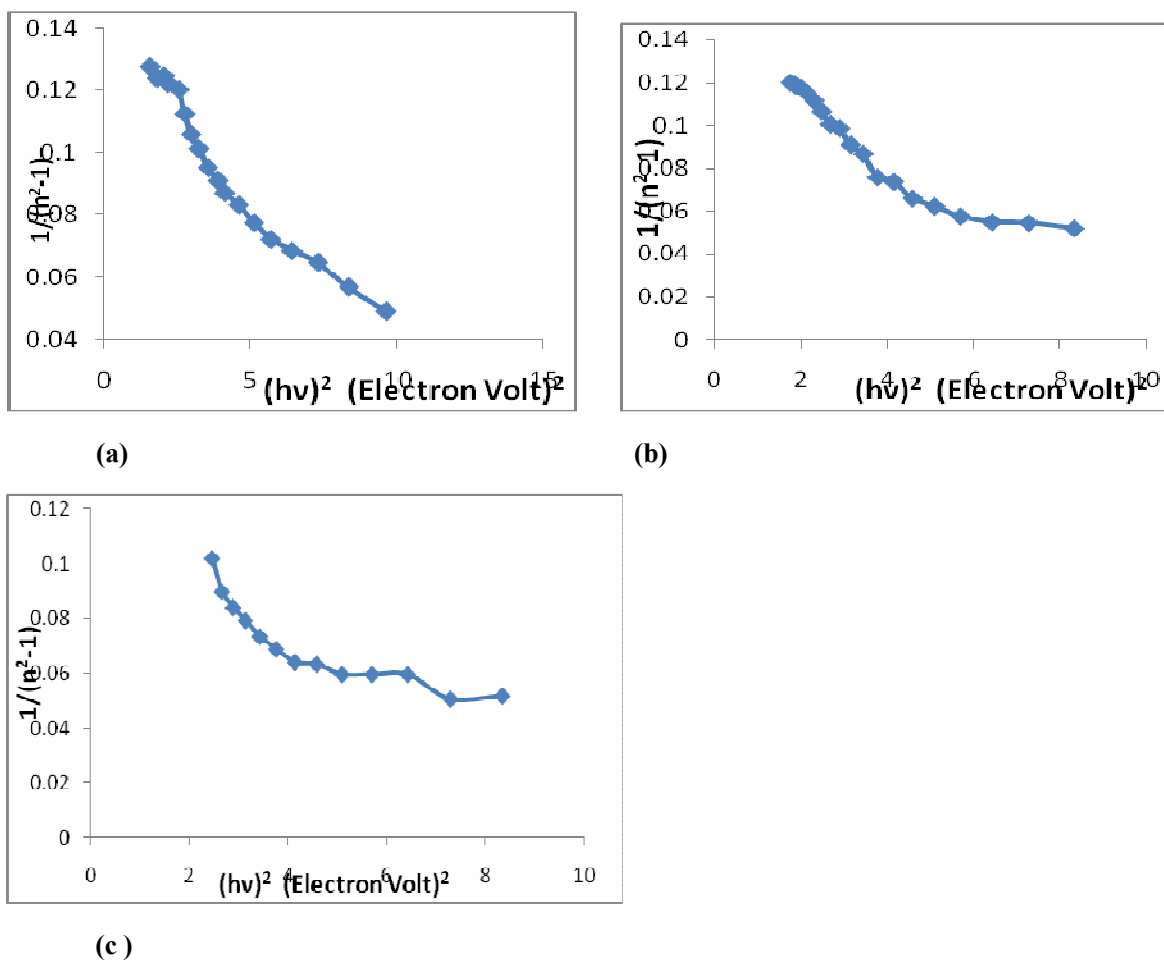
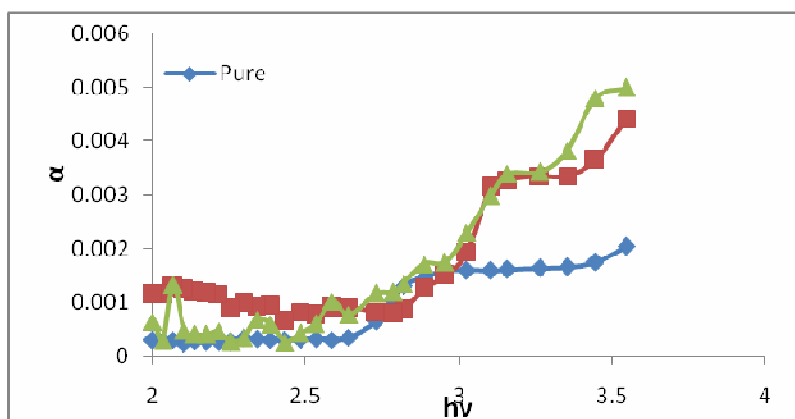


Fig. 3 Graphs between  $(h\nu)^2$  and  $(n^2-1)^{-1}$  for- (a) 1%Nd (b) 0.5 % Nd (c) Pure Zn-P Glass

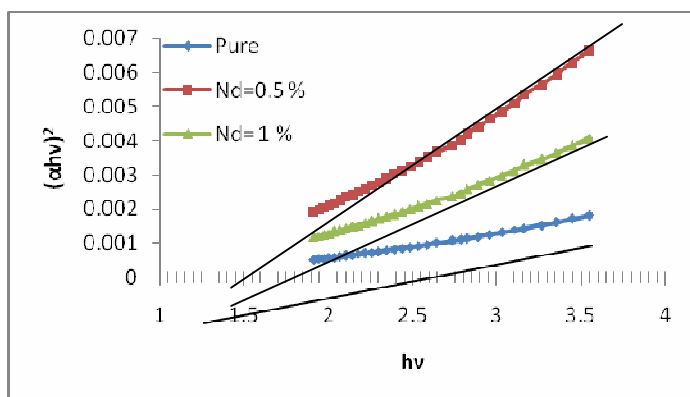
### c. Absorption coefficient, Energy Band gap and Urbach Energy-

The estimation of optical absorption coefficients, particularly near the fundamental absorption edge, is a standard method for the investigation of optically induced electronic transitions. The Optoacoustic spectroscopy method is used for the determination of absorption spectra of the samples of present work. The value of absorption coefficient ( $\alpha$ ) can be determined through the experimentally recorded value of Optoacoustic signal using eqn (1). Fig. 4 shows the variation of absorption coefficient with the photon energy of incident beam. In all curves, we observe an absorption edge. Glasses generally show the absorption edge in the UV range, but if any of the glass

contains heavy atoms like that in present work, the absorption edge shifts to the visible or even to the infrared region<sup>21</sup>. Pardeset al<sup>22</sup> also reported the same kind of shifting of absorption edge from ultraviolet to visible region when the composition of anhydrous boric oxide was increased in the soda-lime glasses. The presence of this absorption edge in the spectra of any glass is mainly depends upon the content of network modifier. The absorption edge of a non-metallic, crystalline or non-crystalline material is determined by the fundamental absorption<sup>12</sup>. When electron hole interactions are neglected, the density of states profile is well shaped and is proportional to some power of energy.



**Fig.4. Variation of the absorption coefficient ( $\alpha$ ) as a function of photon energy ( $h\nu$ ) of various Zinc Phosphate glass samples**



**Fig. 5. Variation of the  $(\alpha h\nu)^2$  as a function of photon energy  $h\nu$  for various Zinc-Phosphate glass samples**

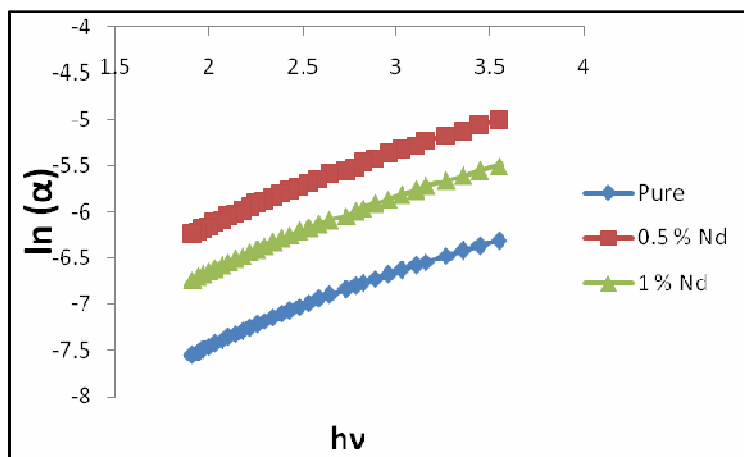
Fig. 5 shows the variations of  $(\alpha h\nu)^2$  with photon energy. In view of equation (4), the intercept on x-axis gives the value of energy band gap. It has been observed in the present study that, the band gap energy slightly decreasing with increasing doping percentage. As we increase the Nd concentration, the unsaturated defects inside the glass are gradually annealed out due to thermal annealing producing large number of saturated bonds<sup>24</sup>. The reduction in the number of unsaturated defects decreases the density of localized states in the band structure, consequently increasing the energy band gap. The energy band gap determined in the present work is in the range that calculated by various other workers for other glass families<sup>24-26</sup>.

The Urbach energy corresponds to the width of the tail of localized states within the optical band gap. It is linked to the absorption coefficient in the lower energy region of fundamental edge. The shape of fundamental absorption edge in the exponential Urbach region can give information on the disorder effects<sup>23</sup>. The relation between the absorption coefficient and Urbach energy is given by<sup>12</sup>-

$$\alpha = \alpha_0 \exp\left(\frac{h\nu}{E_u}\right)$$

Here,  $E_u$  = Urbach energy and  $\alpha_0$  is a constant

Thus a graph between  $\ln(\alpha)$  vs  $h\nu$  can lead to the value of  $E_u$  (reciprocal of slope). Fig 6 shows the variation of  $\ln(\alpha)$  vs  $h\nu$  for the different samples of present case. It has been observed from the graph of different samples, there was no appreciable change in the slope. This indicates that there is no change in the Urbach energy due to the doping of Nd in the Zn-P glass. The calculated values of Urbach energy are tabulated in table 1.



**Fig. 6 Variation of photon energy with  $\ln(\alpha)$  for various samples of the study**

**Table 1: The variation of the optical parameters of the present study with different doping concentration of Nd-**

Sample	$E_0$ (eV)	$E_d$ (eV)	$E_u$ (eV)	$E_g$
Zn-P Glass pure (A4_2)	3.78	36.70	1.31	1.5
Zn-P Glass 0.5 % Nd (A3_2)	3.34	25.14	1.31	1.55
Zn-P Glass 1.0 % Nd (A2_2)	3.65	26.36	1.31	1.6

## Conclusions

Nd doped Zinc-Phosphate glasses were studied for the determination of various optical parameters through a combined technique of Optical transmittance measurements and Optoacoustic absorption measurement. The refractive index and the dispersion parameters are determined under the framework of Swanepoel and Wemple-Di Domenico model. It was observed that the refractive index did not depend significantly on the doping concentration. Parameters like Energy band gap and Urbach energy were determined using Optoacoustic absorption Spectrum. A decrease in the dispersion indicates a strong ionic environment and more static disorders inside the material. Energy band gaps of the samples were calculated by using Urbach method, which indicates towards the semiconducting nature of the present glass series. Also the present work indicated that the Optoacoustic technique may be a potential substitute for the recording of the absorption spectrum of weakly light absorbing samples.

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