



Fabrication and Optical Characterization of Polyvinylidene Fluoride/Neodymium Oxide Nanocomposite Films

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Abstract

Polyvinylidene fluoride (PVDF) is employed in a wide range of devices based on its excellent mechanical, optical, high thermal, piezoelectric, pyroelectric, and ferroelectric characteristics. In the current investigation, the pristine and neodymium oxide (Nd₂O₃) nanoparticles embedded polyvinylidene fluoride (PVDF) thick films were prepared via solution casting method. The Nd₂O₃ nanoparticles were synthesized via hydrothermal technique. The functional groups were identified in the nanocomposite films via infrared vibrational spectroscopy. It revealed the presence of ferroelectric β -phase in the annealed nanocomposite films. All-important optical constants have been determined for the first time via UV-VIS transmission spectroscopy for the nanocomposite films in the ferroelectric phase.

Subject Areas

Atomic Physics, Modern Physics

Keywords

PVDF, Neodymium Oxide, Nanocomposite Films, Optical Characterization

1. Introduction

Ferroelectric materials are called “smart materials” as they can be configured to store, release, or interconvert electrical and mechanical energy in a well-controlled manner via their respective characteristics. They have large piezoelectric com-

pliances, pyroelectric coefficients, dielectric susceptibilities, and electro-optic properties. Ferroelectric polyvinylidene fluoride (PVDF) is utilized in a wide range of devices due to their excellent mechanical properties, optical, high thermal and chemical stability, piezoelectricity, pyroelectricity, and ferroelectric responses [1]. In the present investigation, the pristine and neodymium oxide (Nd_2O_3) nanoparticles embedded polyvinylidene fluoride (PVDF) thick films were fabricated via solution casting/intercalation technique. The Nd_2O_3 nanoparticles were synthesized via hydrothermal technique. The Fourier Transform Infrared Spectroscopy (FTIR) has been recorded in the range 400 to 4000 cm^{-1} , and functional groups were identified in the nanocomposite films. Infrared vibrational spectroscopy (FTIR) revealed the presence of ferroelectric β -phase intrinsically in the annealed nanocomposite films. All-important optical constants have been determined for the first time via UV-VIS transmission spectroscopy for the nanocomposite films in the ferroelectric phase.

With the rapid growth of technologies, electroactive polymers (EAPs) are gaining an immense amount of interest as smart materials. There are different EAPs, namely, Nylon-11, polylactide and aniline pentamer copolymer, poly(lactic-co-glycolic acid) (PLGA), and poly(vinylidene fluoride) (PVDF) and its copolymers with trifluoroethylene (TrFE) [2]-[7]. Amongst them, PVDF and PDVF-TrFE exhibit the best electroactive properties, such as piezo-, pyro- and ferroelectricity and optoelectronic. As a result, PVDF and its copolymers are the polymer of choice for the increasing number of possible microelectronics applications, such as electro-optic transducers, waveguides, sensors, actuators, energy harvesting, electro-optic memory, and biomimetic robotic, etc. [2]. PVDF is inherently polar. With respect to the carbon atom in the unit, the hydrogen atoms are positively charged, and the fluorine atoms are negatively charged. The repeat unit of $(-\text{CH}_2-\text{CF}_2)$ or $\text{CH}_2\text{CF}_2)_n$, in which the carbon-hydrogen bonds with the electrically polar carbon-fluorine, can take up a number of stable configurations determined by the treatment of the polymer. PVDF can be crystallized into at least four different polymorphous phases, depending on the film preparation conditions. Two forms β (or I) and α (or II) are of particular importance. In form α , PVDF (formed from slow-cooled melts or an acetone solution) is non-piezoelectric, the bonds are in a trans-gauche-trans-gauche configuration, and the molecules are stacked, giving a nonpolar unit cell. Form α can be converted into form β by stretching and electrically poling with a suitable field [3]. In form β , the molecular groups are in an all-trans configuration, and the molecules are assembled to give a polar unit cell. Form β is orthorhombic with point group $A\text{ mm}^2$.

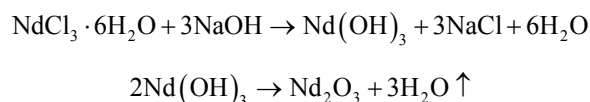
In the recent past, PVDF has attracted interest in the photonics area because of the possibility to be used as hosts for lanthanides photonics ions [4]. In designing the above mentioned emerging optical devices and sensors, the variation of all the standard basic parameters and constants with photon energy are warranted and justified to be investigated. However, few works can be found in the

literature about the study of the complete optical properties of Nd₂O₃ nanoparticles embedded PVDF thick films in UV-Vis range [5]. Thus, this publication presents all the essential optical constants, including optical bandgap of nanocomposite PVDF films with various amounts of Nd₂O₃ nanoparticles.

2. Experimental

2.1. Preparation of Nd₂O₃ Nanoparticles

Nd₂O₃ nanoparticles were prepared using 0.1 molar aqueous solution of neodymium chloride hexahydrate and 0.5 molar aqueous solution of sodium hydroxide without any surfactants. An equal amount of the precursors were mixed and cooked in the Teflon lined autoclave at 200°C for 9 hours and brought into ambient temperature by slow cooling. The precipitate neodymium hydroxide is centrifuged, cleaned thoroughly with Millipore water several times and heated to 300°C in the air in a muffle furnace resulting in the formation of neodymium oxide leaving behind water vapors according to the reaction.



2.2. Preparation of PVDF-NdO Films

500 mg of PVDF is dissolved in 20 ml of DMF solvent and Nd₂O₃ nanoparticles in the different wt% ratio (2 wt% and 4 wt%; coded as Nd2 and Nd4) is added to this solution with vigorous agitation to obtain a clear solution of the mixture. It is then poured in the petri dish and kept at 60°C in a vacuum oven for the evaporation of the solvent. Self-standing films of the PVDF-Nd₂O₃ composite with different wt% without any inclusions were used for different studies.

2.3. Optical Studies on PVDF-NdO Films

FTIR spectra of the films have been recorded in the range 400 to 4000 cm⁻¹. The optical transmittance in the UV-VIS region of the samples was recorded using Hitachi U-2900 (2J1-002) dual-beam spectrophotometer in the wavelength range 200 - 800 nm. The surrounding medium was air and all the measurements were performed at room temperature.

The measured transmittance (T) was used to calculate the absorption coefficient (α) using the formula:

$$\alpha = \frac{2.303 \log\left(\frac{1}{T}\right)}{t} \quad (1)$$

where, t is the thickness of the sample. It is known that, if multiple reflections are neglected, the reflectance R of the sample can be calculated from the measured values of the transmittance T and absorbance A using the following equation:

$$R = 1 - (T + A) \quad (2)$$

The refractive index (n) of the material was calculated from reflectance values using the expression:

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

The optical conductivity is one of the powerful tools for studying the electronic states in the material and is given by the following relation:

$$\text{Optical Conductivity} = \frac{\alpha nc}{4\pi} \quad (4)$$

where, c is the speed of light.

The optical density is given by:

$$\text{Optical Density} = \alpha * t \quad (5)$$

The extinction coefficient k can be obtained from the equation:

$$k = \frac{\alpha \lambda}{4\pi} \quad (6)$$

3. Results and Discussions

FTIR spectra of the film are illustrated in **Figure 1**. The FTIR analysis revealed the electroactive β phase of the fabricated films at around 845 cm^{-1} .

Figure 2(a) to **Figure 2(b)** show the absorption and transmittance spectra of NdO films, respectively. The figure indicates that the transmittance of PVDF films decreases with the addition of Nd_2O_3 nanoparticles. The decrease in transmittance may be due to light scattering of caused by nanoparticles. **Figure 3** shows the variation of absorption coefficient with wavelength of Nd-0, Nd-2 and Nd-4 films fabricated.

The complex refractive index is the representation of the optical constants of

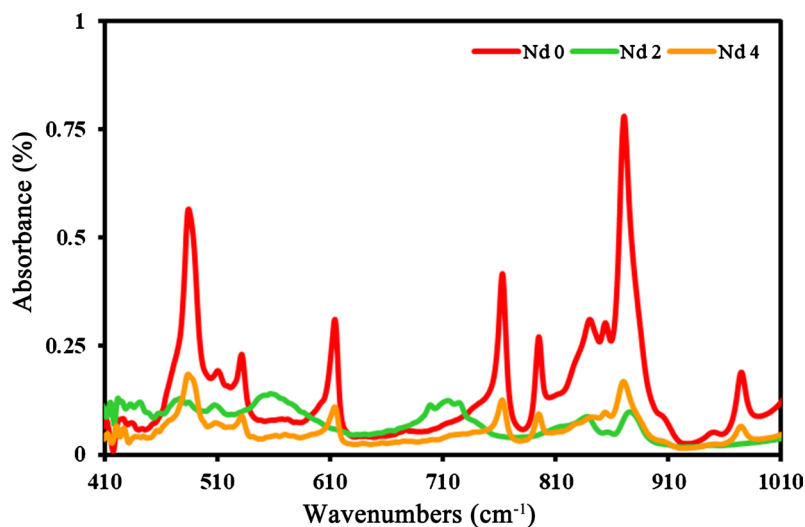


Figure 1. FTIR spectra of Nd-0, Nd-2 and Nd-4 samples.

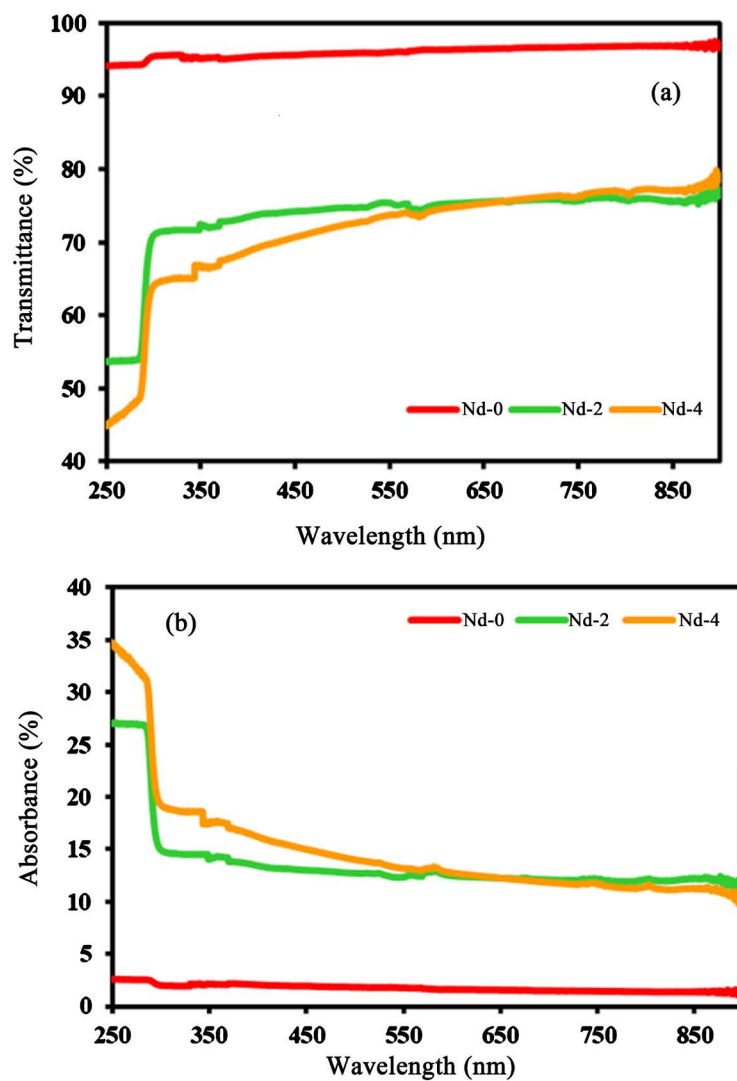


Figure 2. Variation of transmittance (T) (a), and absorbance (b) of the thin films.

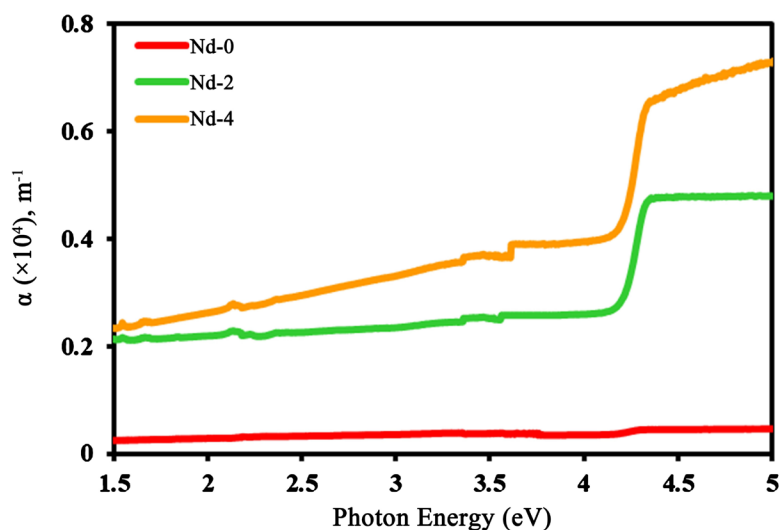


Figure 3. Variation of absorption coefficient (α) with the photon energy of pristine PVDF thin film.

material and is represented by $n^* = n + ik$. The real part “ n ” is the index of refraction, defines the phase velocity of light in material: $v = c/n$, where v is the speed of light in materials and c is the speed of light in vacuum. The imaginary part “ k ” is the extinction coefficient, determines how fast the amplitude of the wave decreases. The variation of n and k both decrease with wavelength as shown in **Figure 4(a)** and **Figure 4(b)**, respectively. This may be due to a change in density and/or the polarization in the film.

The optical conductivity is one of the powerful tools for studying the electronic states in materials. The plot between the optical conductivity (O.C) and optical density (OD) against photon energy is depicted in **Figure 5(a)** and **Figure 5(b)**, respectively. The spectrum indicates that optical conductivity increases with the increase of photon energy. The behavior of optical density (O.D) is similar to the variation of O.C with photon energy in pure PVDF film.

The dielectric function ($\epsilon_T = \epsilon' + i\epsilon''$) is a complex quantity and a fundamental intrinsic property of the material which consists of both the real and imaginary parts (ϵ' and ϵ''). The real part indicates how the speed of light in the material can be slowed down while the imaginary part deals with the absorption of energy by a dielectric from the electric field due to dipole motion.

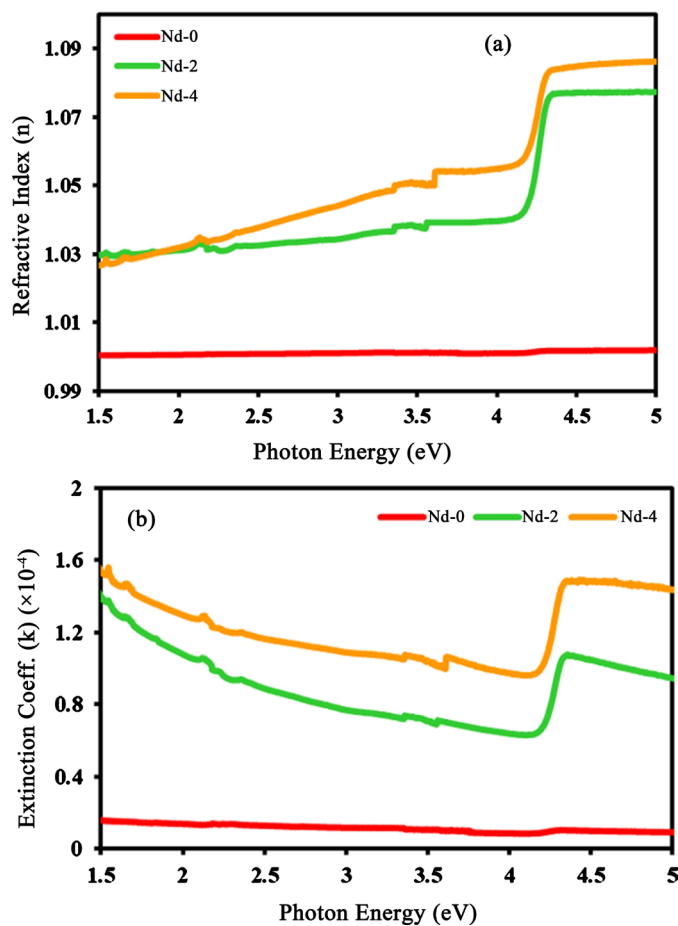


Figure 4. Variation of refractive index (n) (a), and extinction coefficient (k) (b) as a function of the photon energy of PVDF poled thin film.

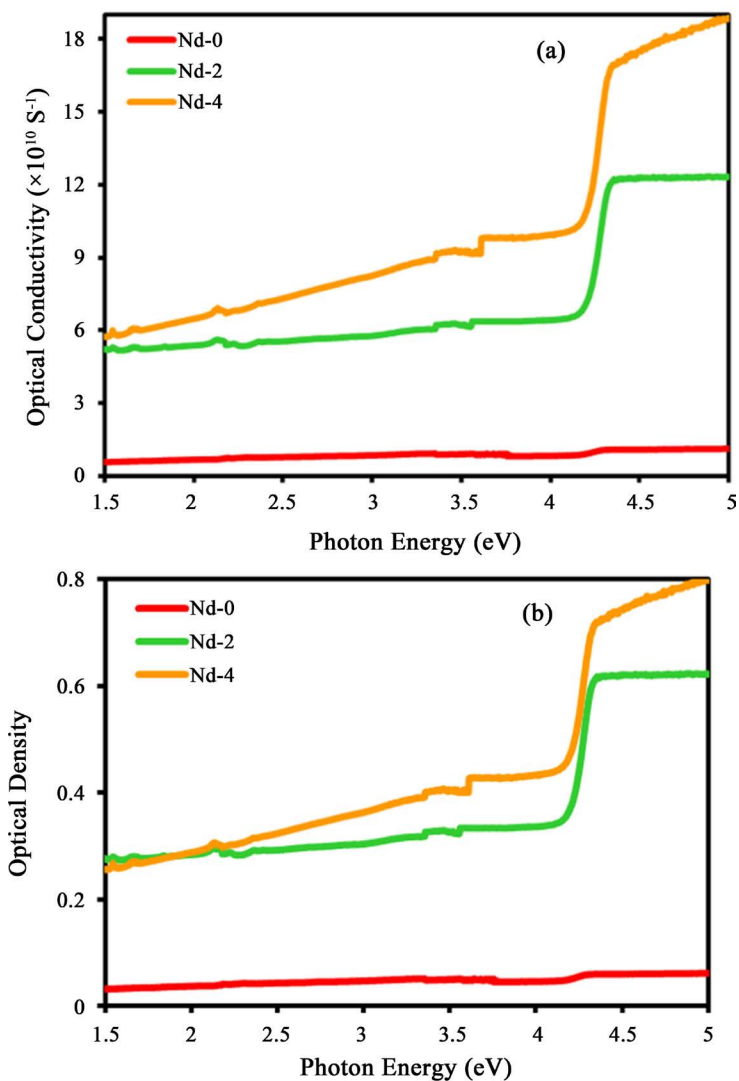


Figure 5. Variation of optical conductivity (O.C) (a) and optical density (O.D) (b) as a function of the photon energy of pure PVDF thin film.

From the optical dielectric curve shown in **Figure 6**, it is evident that ϵ' increases with an increase of photon energy. The calculated dielectric loss tangent ($\tan\delta$) of the PVDF film represents the depletion of the electrical energy [2] [6]. The study of the absorption edge is essential in connection with the theory of electronic structure, which leads to the prediction of whether the band structure is affected near the band extreme. So the main aim is to determine the magnitude and the nature of the optical energy band gap of pure PVDF thin film. The optical energy gap of the films is determined by the absorption spectra. According to the Tauc relation, the absorption coefficient α for the material is given by [2] [6]:

$$Ah\nu = A(h\nu - E_g)^n \quad (7)$$

where E_g is the optical energy gap; A is a constant and is different for different transitions; $h\nu$, is the energy of photon; and n is an index which assumes the

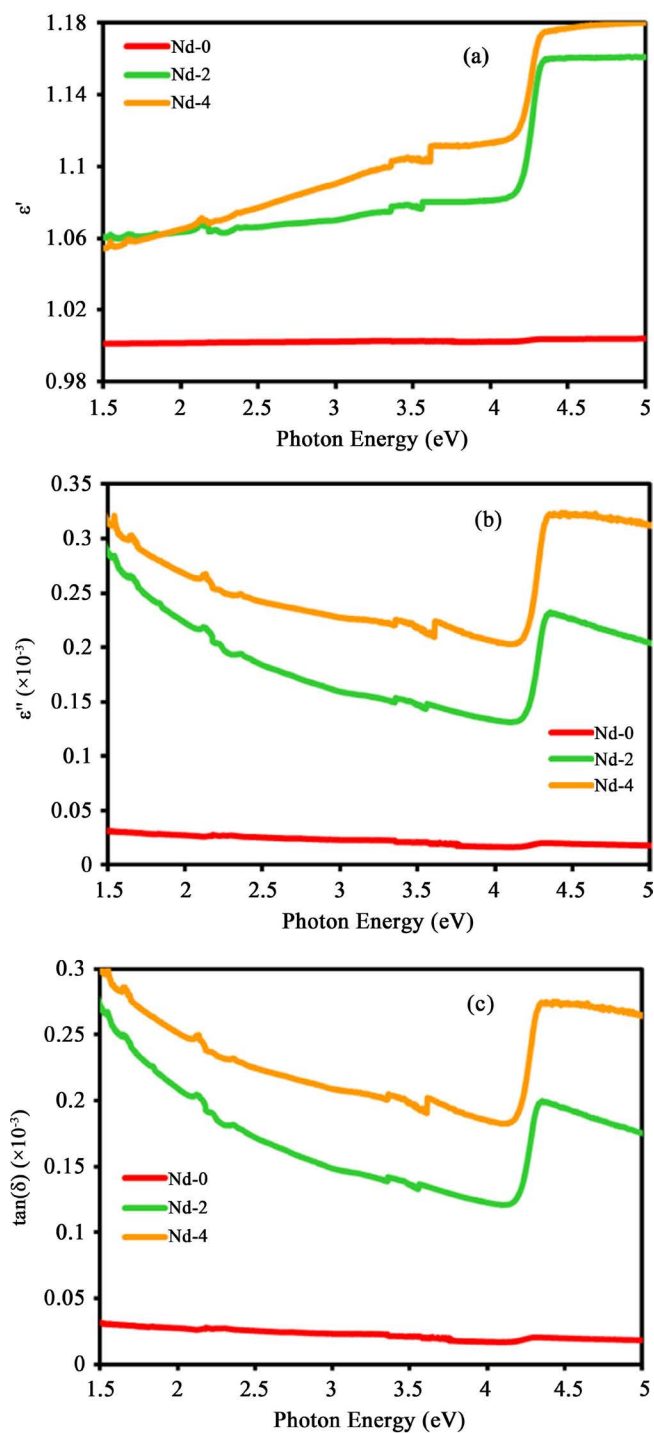


Figure 6. Variation of ϵ' (a), ϵ'' (b), and $\tan\delta$ (c) as a function of photon energy.

values 1/2, 3/2, 2 and 3 depending on the nature of electronic transitions responsible for absorption. Thus, the bandgap is obtained by plotting $(ah\nu)^{1/n}$ versus $h\nu$ in the high absorption range followed by extrapolating the linear region of the plots to $(ah\nu)^{1/n} = 0$. The analyses of our data showed that the plots of $(ah\nu)^{1/n}$ against $h\nu$ with $n = 1/2$. This indicates the allowed direct transition is responsible for the inter-band transition in the doped crystal. **Figures 7(a)-(c)** show the

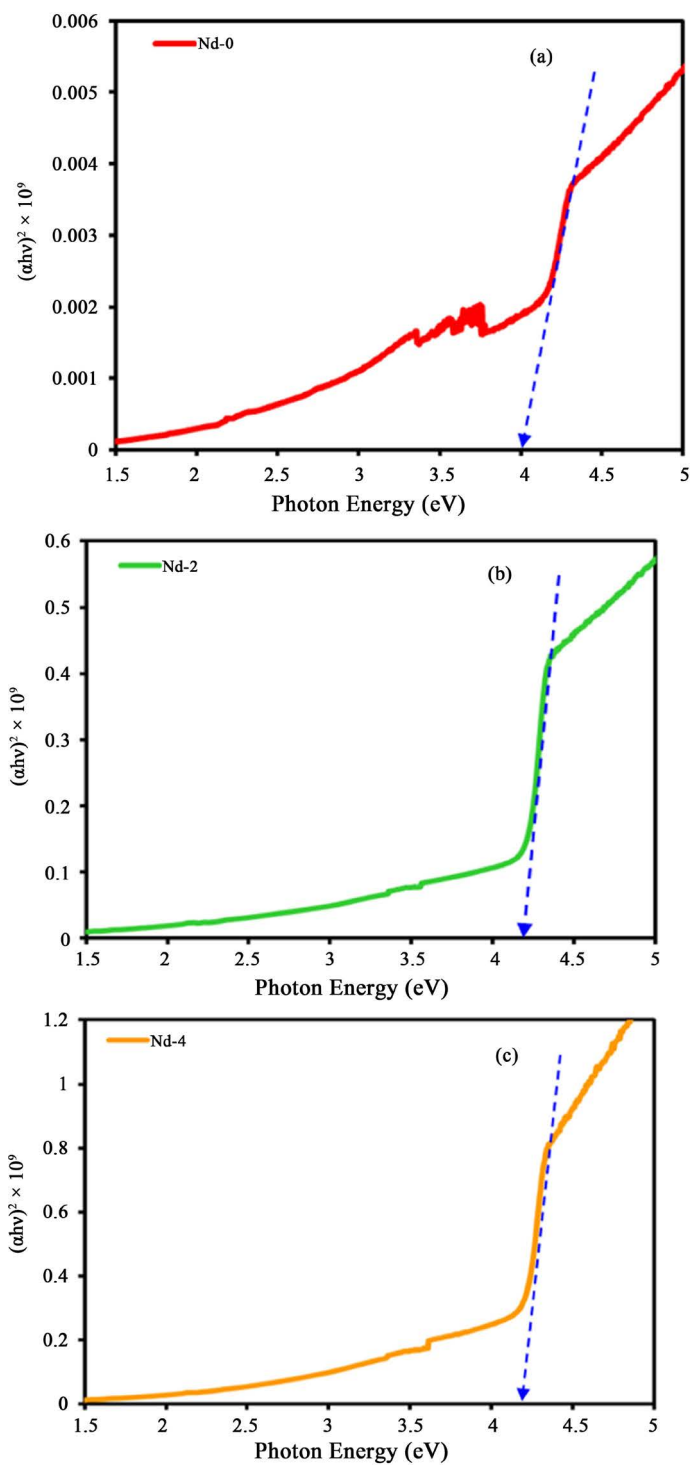


Figure 7. Direct and indirect optical band gap as a function of photon energy for samples Nd-0 (a), Nd-2 (b), and Nd-4 (c).

plot of $(\alpha h\nu)^2$, against photon energy $h\nu$ for the Nd-0, Nd-2 and Nd-4 films. As shown in **Figure 7**, the values of the optical bandgaps (E_g) for $(\alpha h\nu)^2$, of pure PVDF film (Nd-0), Nd-2 and Nd-4, were found to be 4.0, 4.2, and 4.3 eV respectively. **Table 1** summarizes the optical constants obtained at the wavelengths 500

Table 1. Summary of optical constants for samples Nd-0, Nd-2, and Nd-4 at 500, 600 and 700 nm.

Sample	Optical Constants						
	n	$K(\times 10^{-4})$	O.D.	O.C. ($\times 1010$)	ϵ'	$\epsilon''(\times 10^{-3})$	$\tan(\delta)(\times 10^{-3})$
At $\lambda = 500$ nm (2.48 eV)							
Nd-0	1.001	0.128	0.042	0.766	1.002	0.026	0.025
Nd-2	1.032	0.895	0.292	5.542	1.066	0.185	0.173
Nd-4	1.038	1.169	0.323	7.274	1.076	0.243	0.225
At $\lambda = 600$ nm (2.066 eV)							
Nd-0	1.001	0.134	0.036	0.668	1.002	0.270	0.027
Nd-2	1.032	1.053	0.286	5.425	1.064	0.217	0.204
Nd-4	1.033	1.276	0.294	6.584	1.067	0.264	0.247
At $\lambda = 700$ nm (1.771 eV)							
Nd-0	1.001	0.143	0.033	0.614	1.001	0.290	0.029
Nd-2	1.030	1.192	0.278	5.256	1.061	0.246	0.231
Nd-4	1.029	1.384	0.273	6.097	1.060	0.285	0.269

nm, 600 nm and 700 nm respectively.

4. Conclusion

In this study, optical quality PVDF nanocomposites film with has been fabricated and the optical constants, such as the direct and indirect optical bandgaps (E_g), absorption coefficient (α), refractive index (n), extinction coefficient (k), and real and imaginary dielectric constants (ϵ' and ϵ'') and the electric loss tangent ($\tan\delta$) were calculated to analyze the optical properties of PVDF thick films with embedded Nd_2O_3 nanoparticles. The results of the UV-VIS spectroscopy measurements show the absorption and transmission property of the PVDF films, and the Raman analysis revealed the electroactive β phase of the fabricated films at around 845 cm^{-1} .

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Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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