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Optical Parametric Investigation on a Poled PVDF Thin-Film for Optoelectronic Devices

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Abstract: Optical quality poly(vinylidene fluoride) film thin film has been selected and all-important optical constants have been determined for the first time via UV-VIS transmission spectroscopy for pure poly(vinylidene fluoride) film in the ferroelectric phase. The ultraviolet-visible spectra showed that the film has wide optical transparency in the entire visible region. The calculated optical parameters include the absorption and extinction coefficients, refractive index, optical density and conductivity, real and imaginary dielectric constants, the dielectric loss tangent, direct and indirect bandgaps of the film. The Raman Infrared Spectroscopy has been recorded in the range 200 to 2250 cm^{-1} and the functional groups/phases of a film have been identified. The fabricated film is found to be Raman active and the measurement revealed the characteristics β phase Raman band at about 839 cm^{-1} which is consistent with literature value.

Keywords: PVDF, Ferroelectric, Electrooptic, Piezoelectric, Optical constants, Raman spectra, Optical bandgap.

1. Introduction

With the rapid growth of technologies, electroactive polymers (EAPs) are gaining an immense amount of interest as smart materials [1]. 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) [2-10]. 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, wave guides, sensors, actuators, energy harvesting, electro-optic memory, biomimetic robotics [11-13], etc. 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 (–CH2–CF2_) or CH2CF2)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 a, 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. In form b, 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 mm^2.

In the recent past, PVDF has attracted the interest in the photonics area because of the possibility to be used as hosts for lanthanides photonics ions [14]. 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 PVDF pristine poled thin film in UV-Vis range. Thus, this publication presents all the important optical constants, including optical bandgap of pristine 52 μm thin film of poled PVDF.

2. Methodology

Raman spectral analysis in the range from 250-2250 cm^{-1} was carried out by using a Raman spectroscopy system (Enwave Optronics Inc.) operating at 785 nm laser wavelength. The optical transmittance in 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:

$$Optical\ Conductivity = \frac{\alpha n c}{4\pi}, \quad (4)$$

where c is the speed of light, n is the refractive index and α is the absorption coefficient.

The optical density is given by:

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

The extinction coefficient k can be obtained from the equation:

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

From the optical constants n and k, real (ε'), imaginary (ε'') of dielectric constants and dielectric loss ($Tan\delta$) can be calculated according to the following relations:

$$\epsilon' = n^2 - k^2 \quad (7)$$

$$\epsilon'' = 2nk \quad (8)$$

$$Tan\delta = \frac{\varepsilon''}{\varepsilon'} \quad (9)$$

3. Results and Discussions

3.1. Raman Spectral Analysis

The Raman scans for pure PVDF is shown in Fig. 1. Most of the peaks at frequency corresponds to α and β phase. The peaks at 610 cm^{-1}, 760 cm^{-1} and 1420 cm^{-1} belong to α phase. Consistent with earlier reports [15-16], the other peaks at 508 $cm^{-1}$and 839 cm^{-1} are related to the characteristics β phase spectra of the Raman bands. The ferroelectric, pyroelectric and piezoelectric properties of the electroactive β phase PVDF films are found to be superior to α, γ, δ and ε phases [16-17]. Due to this remarkable property, and its biocompatibility, it has been widely investigated for various applications including biomedical sensors and devices [17-18].

3.2. UV-VIS Transmission Spectral Analysis

The optical property of the material gives information regarding the composition of, nature and the quality of the material. The transmittance, absorbance, and absorption coefficient are shown in the Fig. 2 to Fig. 3. The regular/neat variation of the parameters demonstrates good quality of the PVDF films investigated. This property enables the material for optoelectronic applications.

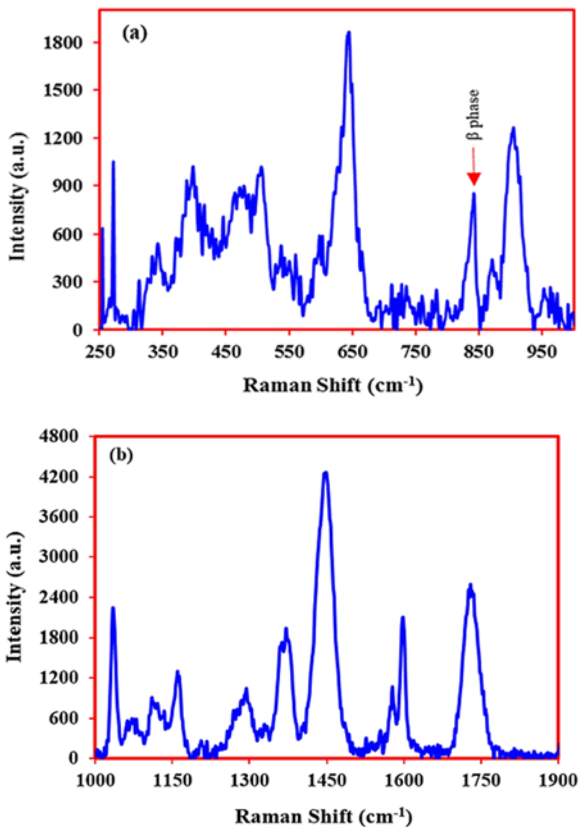

Fig. 1. Raman spectra of PVDF thin film measured with Raman system equipped with 785 nm wavelength laser.

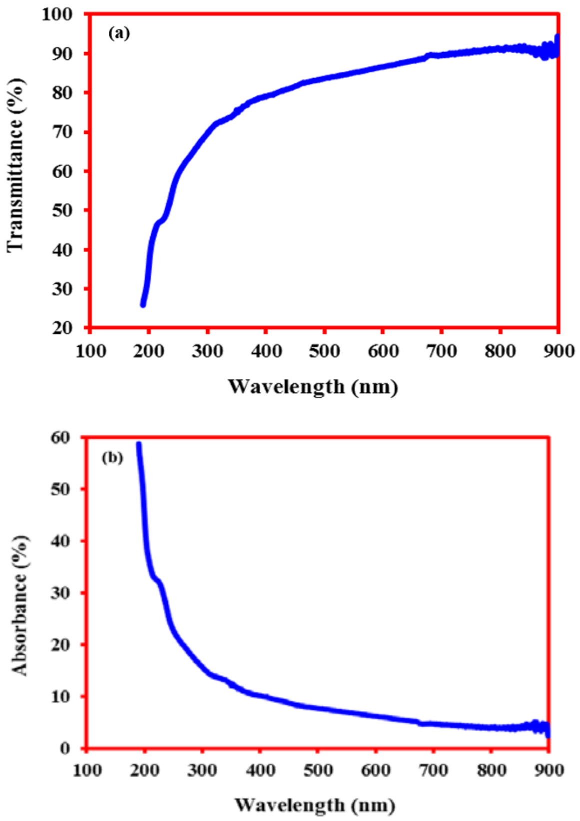

Fig. 2. Variation of transmittance (T) (a), and absorbance (b) of thin film of PVDF with the wavelength.

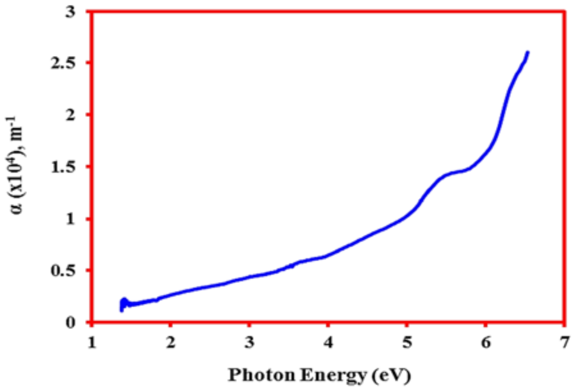

Fig. 3. Variation of absorption coefficient (α) with the photon energy of pristine PVDF thin film.

The complex refractive index is the representation of the optical constants of material and in 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 (Fig. 4). This may be due to a change in density and/or the polarization in the film.

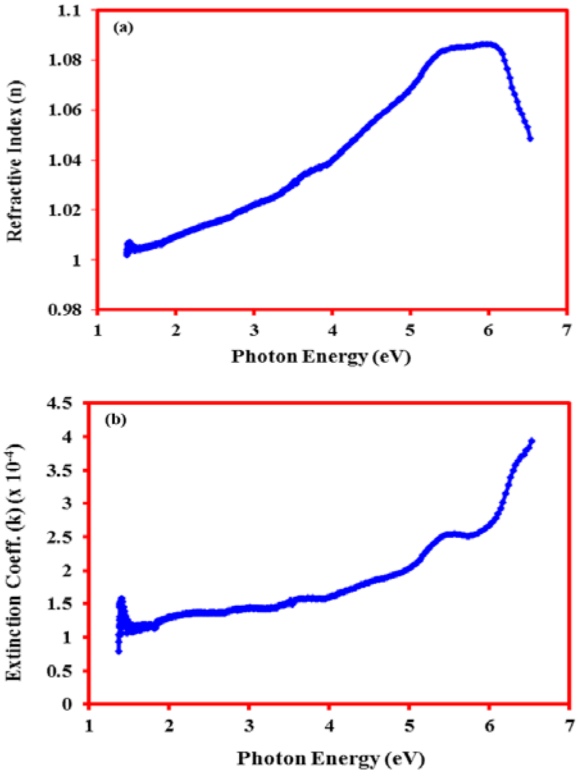

Fig. 4. Variation of refractive index (n) (a), and Extinction coefficient (k) (b) as a function of photon energy of PVDF poled thin film.

The optical conductivity is one of the powerful tools for studying the electronic states in materials.

The plot between the optical conductivity (O.C) against photon energy is depicted in Fig. 5(a). The spectrum indicates that optical conductivity increases with the increase of photon energy Fig. 5(b). The behavior of optical density (O.D) is similar to the variation of O.C with photon energy in pure PVDF film.

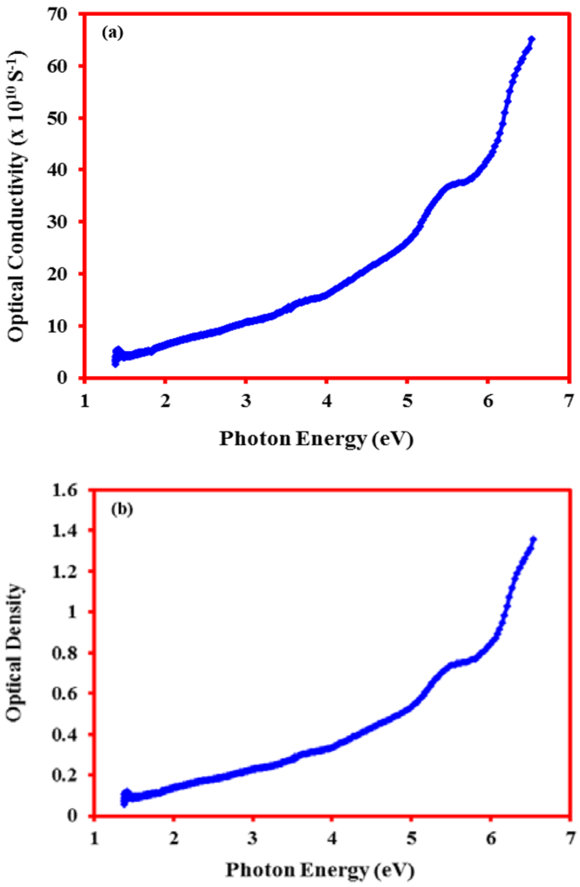

Fig. 5. Variation of optical conductivity (O.C) (a), and optical density (O.D) (b) as a function of the photon energy of pure PVDF thin film.

The dielectric function ($\varepsilon_T = \varepsilon' + i\varepsilon''$) 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.

From the optical dielectric curve (Fig. 6), it is evident that ε' and ε'' increase with increase of photon energy. The calculated dielectric loss tangent (tanδ) of the PVDF film represents the depletion of the electrical energy [19]. 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 material is determined by the absorption spectra. According to the Tauc relation, the absorption coefficient α for a material is given by [20]:

$$A h\nu = A(h\nu - E_g)^n, \quad (10)$$

where Eg is the optical energy gap. A is a constant and is different for different transitions. hν is the energy of photon and n is an index which assumes the values 1/2, 3/2, 2 and 3 depending on the nature of electronic transitions responsible for absorption.

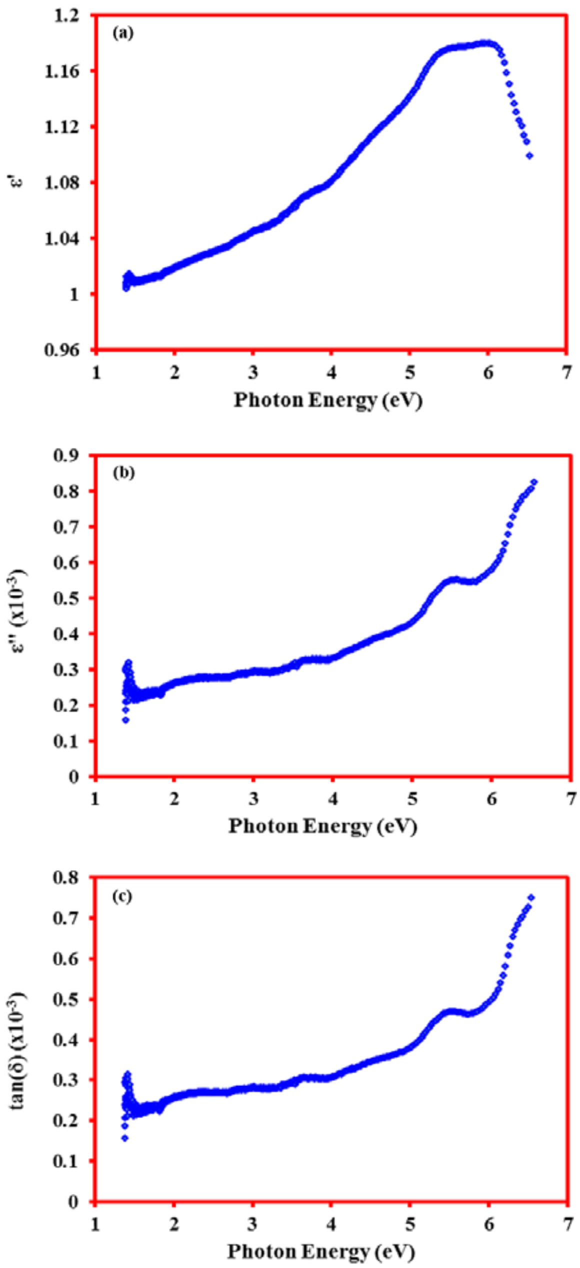

Fig. 6. Variation of ε' (a), ε'' (b), and tanδ (c) as a function of photon energy.

Thus the bandgap is obtained by plotting $(\alpha h\nu)^{1/n}$ versus hν in the high absorption range followed by extrapolating the linear region of the plots to

$(\alpha h\nu)^{1/n} = 0$. The analyses of our data showed that the plots of $(\alpha h\nu)^{1/n}$ against hν with n = 1/2. This indicates the allowed direct transition is responsible for the inter-band transition in the doped crystal. Fig. 7 shows the plot of $(\alpha h\nu)^2$, against photon energy hν for the pure PVDF film. The value of optical bandgaps (Eg) for pure PVDF film for $(\alpha h\nu)^2$, $(\alpha h\nu)$ and $(\alpha h\nu)^{1/2}$, were found to be 5.8, 5.4 and 4.45 eV respectively (Fig. 7(a), (b), (c)).

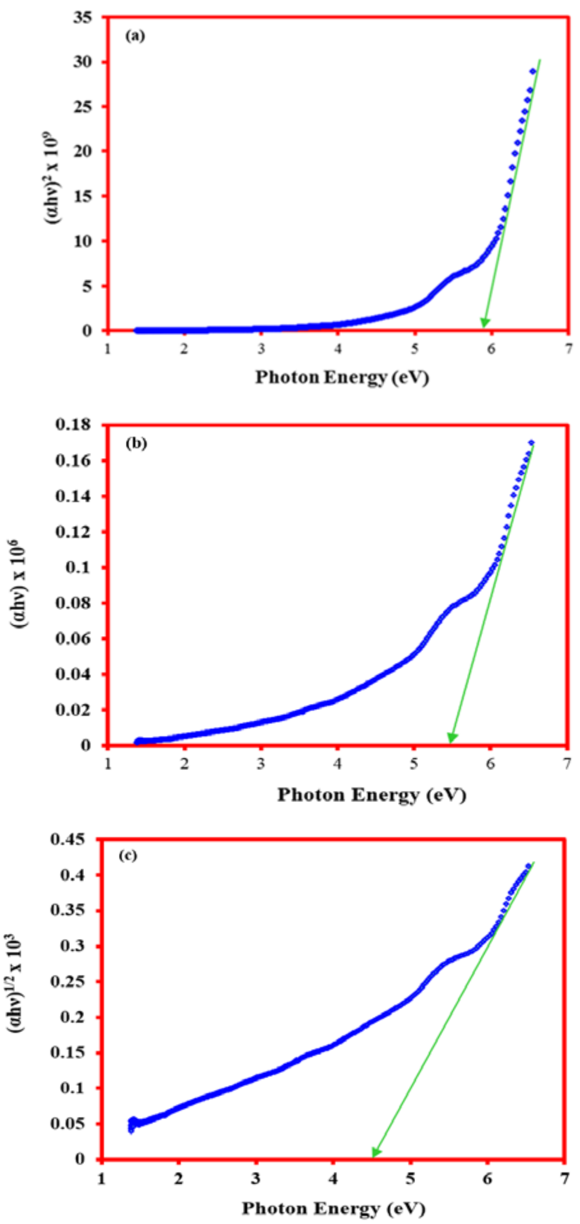

Fig. 7. Direct and indirect optical bandgap as a function of photon energy.

4. Conclusions

In this study, optical quality PVDF thin film with has been fabricated and the optical constants, such as the direct and indirect optical bandgaps (Eg), absorption coefficient (α), refractive index (n), extinction coefficient (k), and real and imaginary dielectric constants (ε' and ε'') and the electric loss tangent (tanδ) were calculated to analyze the optical properties of poled pristine PVDF thin film. The results of the UV-VIS spectroscopy measurements show the absorption and transmission property of the PVDF thin film, and the Raman analysis revealed the electroactive β phase of the fabricated film. These parameters investigated will of importance in numerous optoelectronic applications such as lens, optical waveguides, optical switches, light emitting diodes, optical grating, modulators for optical signal treatment and displays. Furthermore, use of novel tunable PVDF-based optical elements for MEMS applications have great technological and scientific values.

Table 1. Summary of optical constants for pure PVDF thin film.

Optical constants of pure poled PVDF thin film @ 620 nm (2 eV)						
n	**K ($\times 10^{-4}$)**	**O.D**	**O.C ($\times 10^{+10}$)**	**ε'**	**ε'' ($\times 10^{-3}$)**	**tan(δ) ($\times 10^{-3}$)**
1.0095	1.3067	0.1374	6.4754	1.01906	0.26376	0.25888
Optical constants of pure poled PVDF thin film @ 310 nm (2 eV)						
1.0399	1.6008	0.3373	16.1092	1.08131	0.33292	0.30789

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