Linear and Non-Linear Optical Properties of Nematic Liquid Crystal Thin Film

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Abstract—The linear and nonlinear optical properties of nematic liquid crystal thin film has been found, using a highly sensitive method known as Z-Scan technique. Z-Scan experiment was performed using a continuous wave (CW) diode solid state laser at 473 nm wavelength, and 20 mW power, the first part has been done using a close aperture, and the second part was carried out using an open aperture. The sample were prepared on glass substrates by using spin coating method. Several testing were done to study the characteristics of the sample, including X-ray diffraction, as well as Atomic Force Microscopy (AFM). Results suggest that nematic liquid crystal thin film is a promising material for third order nonlinear applications due to its large nonlinear optical properties.

Index Terms—Nematic liquid crystal, Z-Scan technique, non-linear optical properties.

I. INTRODUCTION

Liquid crystals (LC) are known to exhibit large optical nonlinearities which have been the subject of considerable study in recent years, from both experimental and theoretical points of view. So far, almost all the research has been focused on thermotropic liquid crystals (TLC) [1]. Since LC molecules typically have delocalized π electrons, they are believed to be potential sources of fast and large nonlinearities. Due to bulk anisotropy of nematic LC, nonlinear optical parameters (e.g., nonlinear refraction index \(n_2\) and nonlinear optical absorption \(β\)) are expected to depend on the geometrical configuration between the light polarizing direction (E) and the nematic director \(\widehat{n}\) [2].

Z. Xiaqiang et al. the nonlinear optical properties of a series of azobenzene liquid-crystalline materials, which have different side-chain lengths in their molecular structure from one to another, were investigated using Z-scan method under picosecond pulse laser at 532 nm, 1064 nm and CW 488 nm excitation study. Nonlinear optical properties of a series of azobenzene liquid-crystalline materials [3].

E. Saievar et al. studied the suspension of magnetic particles in nematic liquid crystals (NLCs), usually called ferro-nematic (FN). The FN studied in this work are E7 dopa spherical FeO₄ nps was based on efficient chemical with small compositional percentage of FeO₄ nps (5% W/W). Synthesis of the co-precipitation technique [4].

S. Patil et al. study the third order nonlinear optical properties of organic nonlinear optical material, 3,4-Dimethoxy-4-methoxycalcone (DMMC) in Dimethyl formade (DMF) solvent has been investigated using Z-scan technique with femtosecond (fs) Ti:sapphire laser pulses at 800 nm wavelength. The crystal shows optical-limiting effects for femtosecond laser pulses at 800 nm. The result suggest that the nonlinear properties investigated for DMM can be desirable for nonlinear optical applications [5].

In this paper, we have investigated nonlinear optical properties of nematic liquid crystal thin film which is prepared by spin coating method, by using Z-Scan technique with (CW) diode solid state laser at 473 nm wavelength and 20 mW power.

II. EXPERIMENTAL WORKS

1. Preparation of nematic liquid crystal
   (Bis-4-Methoxy-Benzyl-dene-Hydrazine)

Bis-4-Methoxy-Benzyl-dene-Hydrazine was prepared by mixing (1.001 g; 0.02 mol) of hydrazine hydrate dissolve in (10 mL) of absolute ethanol with (2.72 g; 0.04 mol) of \(p\)-methoxy benzaldehyde dissolved in (10 mL) of absolute ethanol, then mixture three drops of glacial acetic acid were added to the prepared and left under reflux for two hours, producing yellowish shining solid product. The solid product formed was separated by filtration, purified by recrystallization from ethanol, washed with ethanol, and then dried.

2. Thin film preparation

Solution of concentrations (1x10⁻³M) of Bis-4-Methoxy-Benzyl-dene-Hydrazine in ethanol solvent were prepared. The powder was weighed by using an electronic balance type (BL 210 S), Germany, having a sensitivity of four digits. Different concentrations were prepared according to the following equation:

\[
W = \frac{M_{dil} \times V \times C}{1000}
\]

Where, \(W\): Weight of the dissolved in material (g), \(M_{dil}\): Molecular weight of the material (g/mol), \(V\): Volume of the solvent (mL), \(C\): The concentration (M). The prepared solutions were diluted according to the following equation:

\[
C_1V_1 = C_2V_2 \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots (2)
\]

Where: \(C_1\): Primary concentration, \(C_2\): New concentration, \(V_1\): The volume before dilution, \(V_2\): The volume after dilution.

Thin films of Bis-4-Methoxy-Benzyl-dene-Hydrazine, were prepared on a clean glass slide via repeat-spin-coating method, with solution of (10⁻³ M) concentration and dried at room temperature for (30 min), the thickness of thin film is about (0.125 µm), the thickness of the thin films were measured with by optical method it’s done by Optical thin-film measurement model (LIMF-10, Lambda Scientific Pty ).
III. RESULTS AND DISCUSSION

1. X-ray diffraction analysis
Thin films of Bis-4-Methoxy-Benzylidene-Hydrazine examined by (XRD) to identifying the crystalline composition. The crystal structure was determined by using International Center for Diffraction Data (ICDD), and it found that it is a mixture of orthorhombic and monoclinic structure. Spacing (d) between the crystalline levels that is corresponding to diffraction angles values bounded between (10° - 60°), and average wave height (Full Width at Half Maximum (FWHM)). Miller indices of crystalline levels, were calculated, and crystalline size (average grain size) of the diffraction peaks is (52.172 nm), as shown in Figure (1).

Fig. (1): X-Ray Diffraction Pattern of The Thin Film.

2. Atomic Force Microscopy (AFM)
The 3-D AFM images and granularity accumulation distribution charts for nematic liquid crystal thin film deposited on glass substrate with thickness of (0.125 µm) , the average grain size were found to be (88.98 nm), the Roughness is (2.38 nm), as shown in Figure (2).

Fig. (2): 3D AFM Image and Granularity Accumulation of The Thin Film.

3. Z-Scan Measurement
The Z-scan is a simple and popular experimental technique to measure the intensity and a direct method to characterize both the nonlinear refraction index and nonlinear absorption. It is based on a single beam method and refers to the process of inserting a sample in a focused Gaussian beam and translating it along beam axis through a focal region. The far field intensity is measured as a function of the sample position by properly monitoring the transmittance change through a small aperture at the far field position (closed aperture) by moving the sample through the focus and without placing an aperture at the detector(open aperture) [6,7].

4. Linear Optical properties
For study the linear optical properties. The absorption spectrum of (Bis-4-Methoxy-Benzylidene-Hydrazine) as solution in ethanol solvent, and as thin film was analyzed using UV-VIS spectrophotometer model (Aquarius 7000, Optima Japan), at room temperature recorded for wavelengths (190 to 1100) nm, as shown in Figure (3),(4) respectively.

Fig. (3): Absorption Spectra for solution of (Bis-4-Methoxy-Benzylidene-Hydrazine) at Concentration (10⁻⁴ M).

Fig. (4): Absorption Spectra for Thin Film at Concentration (10⁻³ M).

The linear absorption coefficient (α°) was determined by using formula[8]:

\[ α° = \frac{\ln(\frac{1}{T})}{t} \] .......................... (3)

where (t) is the thickness of sample and T is the transmittance.
The refractive index (n°) can be found from transmittance spectrum of the film according to the following equation[8]:

\[ n° = \frac{1}{T} + \left[ \left( \frac{1}{T^2} - 1 \right) \right]^{1/2} \] .......................... (4)

The linear absorption coefficient and refractive index are shown in Table (1). From this table we noted that the value of the linear absorption coefficient of thin film of nematic liquid crystal is larger than of its value for the same material as solution.
5. Nonlinear Optical Properties

The nonlinear refractive index, there are two cases were chosen at (473 nm), Figure (5) and (6) respectively shows the closed-aperture $Z$-scan results for (Bis-4-Methoxy-Benzylidene-Hydrazine) as solution and thin film.

![Solution (Bis-4-Methoxy-Benzylidene-Hydrazine) Z-Scan](image1)

![Thin film (Bis-4-Methoxy-Benzylidene-Hydrazine) Z-Scan](image2)

As shown in Figure (5) and (6), the transmittance started with a linear behavior at different distances from the far field of the sample position ($-Z$) with respect to the focal plane at $Z=0$ mm. At the near field the transmittance begins to increase until it reaches the maximum value ($T_{\text{peak}}$) at approximately ($Z=-5$ mm). Afterward, the transmittance begins to decreased until it reaches the minimum value ($T_{\text{valley}}$) at approximately ($Z=-5$ mm). Again, the transmittance begins to increase toward the linear behavior at the far field of the sample position ($+Z$).

For the calculation of the nonlinear refractive index ($n_2$) the following standard relations were utilized:

$$\Delta T_{p-v} = 0.406 |\Delta \Phi_o|$$

$$n_2 = \frac{\Delta \Phi_o}{I_o L_{\text{eff}} K}$$

$$\Delta T_{p,v}$$, the difference between the normalized peak and valley transmittances, $\Delta \Phi_o$ is the nonlinear phase shift, $I_o$ is the intensity at the focal spot, $L_{\text{eff}}$ is the effective length of the sample, determined from [9]:

$$L_{\text{eff}} = \frac{(1 - e^{-\sigma_o L})}{\alpha_o}$$

The peak – valley configuration revealed a negative nonlinear refraction which is attributed to de-focusing process. The nonlinear absorption coefficient ($\beta$) for (Bis-4-Methoxy-Benzylidene-Hydrazine) as solution and thin film, was determined by performing the open aperture Z-Scan for wavelengths (473 nm), the normalized transmission as function of position as shown in Figures (7) and (8) respectively.

![Solution (Bis-4-Methoxy-Benzylidene-Hydrazine) Z-Scan](image3)

![Thin film (Bis-4-Methoxy-Benzylidene-Hydrazine) Z-Scan](image4)

Two photon absorption phenomenon were observed for our sample as solution in Figure (8), the curve starts linear for different distances from the far field of the transmittance when the sample is at position ($-Z$). At the near field, the transmittance curve begins to increase until it reaches a minimum value at the focal point, where $Z=0$ cm. Afterwards, the transmittance begins to decreased towards the linear behavior at the far field of the sample position ($+Z$). While a saturable absorption phenomenon were observed for our sample as thin film in Figure (8).

The nonlinear absorption coefficient $\beta$ as calculated from the relation [10].

$$\beta = \frac{2\sqrt{2}}{I_o L_{\text{eff}} K} T(z)$$

Where $T(z)$: The minimum value of normalized transmittance at the focal point, $T(z=0)$, the magnitude of $\beta$ depends on the wavelength and on the input intensity, but this dependence is not very strong at low intensities.

The value of nonlinear refractive index and nonlinear absorption coefficient for the thin film is more greater than of the sample as solution, in addition to increasing the value of linear absorption coefficient of thin film with respect to solution, due to increasing the thickness of thin film which
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causes increasing the number of molecules per unit volume as shown in Table (1).

Table (1): The linear and nonlinear optical parameters for solution and thin film of nematic liquid crystal.

<table>
<thead>
<tr>
<th>Nematic Liquid Crystal</th>
<th>C. Mol /L</th>
<th>T%</th>
<th>α cm⁻¹</th>
<th>ΔT(α)</th>
<th>Δα</th>
<th>β</th>
<th>2α/β</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solution</td>
<td>10⁶</td>
<td>0.97</td>
<td>0.022</td>
<td>0.032</td>
<td>0.07</td>
<td>2.8×10⁻⁹</td>
<td>1.11×10⁻⁸</td>
</tr>
<tr>
<td>Thin Film</td>
<td>10⁸</td>
<td>0.90</td>
<td>7950</td>
<td>0.042</td>
<td>0.10</td>
<td>3.2×10⁻⁴</td>
<td>4.65</td>
</tr>
</tbody>
</table>

IV. CONCLUSIONS

In this work, we study structure properties of nematic liquid crystal thin film by using AFM and X-ray diffraction pattern showed that it is a mixture of orthorhombic and monoclinic structure with the average size of (52.172 nm). AFM photograph confirming the average size of thin film were found to be (88.98 nm). Thin film was fabricated by the spin-coating method using nematic liquid crystal material (Bis-4-Methoxy-Benzylidene-Hydrazine).

The present paper demonstrates the linear optical properties of the samples as solution and thin film by using UV-VIS spectrophotometer and nonlinear optical properties by Z-Scan technique respectively. In closed aperture the peak-valley configuration revealed a negative nonlinear refraction which is attributed to de-focusing process for both of thin film and solution, while in open aperture Saturable Absorption phenomenon were observed of thin film, while two photon absorption phenomenon were observed of solution. The values of nonlinear optical properties for thin film is larger than the values of solutions.

REFERENCES