Preparation and Characterization of Benzimidazole Thin Films for NLO Applications

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PHYSICS

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CERTIFICATE

This is to certify that the dissertation entitled "Preparation and Characterization of Benzimidazole thin films for NLO applications" submitted to Bharathidasan University, Tiruchirappalli under the Choice Based Credit System (CBCS) in partial fulfillment of the requirements for the award of the degree of Master of Science in Physics is a bonafide record of the work carried out by **Mr. P.A. Praveen** under my supervision and guidance during the fourth semester period of the programme (2009 – 2011).

Head of the Department   **Research Advisor**

<u>DECLARATION</u>

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Tiruchirappalli

5th April, 2011

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I do here by declare that this dissertation entitled "Preparation and Characterization of Benzimidazole thin films for NLO applications" is an original work done by me and it has not formed the basis for the award of any Degree\ Associateship\ Fellowship\ or other similar title to any candidate of any other University and that this work has not been submitted elsewhere for any other degree.

Signature of the candidate

(P.A. Praveen)

Acknowledgement

Contents

Preface

Organic materials are of great interest for various applications, as they have many advantages over their inorganic counterparts. They may often be solution-processed allowing the ease-of fabrication. Organic molecular thin films hold great promise for the rational development of organic NLO materials. Their long-range order not only reveals the performance limits of organic materials, but also provides unique insight into their electro-optic properties.

Already organic NLO's such as DAST and DAN has surpassed various inorganic NLO's in performance. On the other hand, one must need some versatile deposition technique in order to coat the organic thin films. Since most of the organic materials posses low melting and boiling points, they always preferred to chemical processing, instead of physical vapor techniques, where the temperature plays vital role. In chemical processing, the chemical bath deposition (CBD) is a simple, robust when properly monitored and a low cost technique for producing thin films of wide variety of compounds in micro to nano sizes.

The present dissertation entitled "Preparation and Characterization of Benzimidazole thin films for NLO applications" deals with optimizing the conditions for depositing BMZ thin layers on micro glass substrates and characterizing its properties.

The first and second chapters give a brief introduction to nonlinear optical materials and organic nonlinear optical thin films. The third chapter unfolds the various deposition techniques which are widely used to deposit organic thin films. The fourth chapter gives the details of deposition of BMZ thin films by CBD in brief. The fifth and final chapter brings about the various characterization studies such as structural, optical, thickness measurement and NLO properties of the deposited BMZ thin films.

Chapter 1

The burgeoning field of computer science has shifted our view of the physical world from that of a collection of interacting material particles to one of a seething network of information. In this way of looking at nature, the laws of physics are a form of software, or algorithm, while the material world—the hardware—plays the role of a gigantic computer.

~ P.C.W. Davies

1   INTRODUCTION TO NONLINEAR OPTICS

1.1 Introduction

Nonlinear optics is the study of intense electromagnetic fields with materials to produce the modified fields that are different from the input field in phase, frequency or amplitude. It was observed for the first time by Franken co et al in 1961. They observed ultraviolet light at twice the frequency of a ruby laser light (λ=6493 A˚), when the light was made to traverse a quartz crystal [1]. This experiment has grabbed the great attention of many researchers and the progress made in this domain can be measured by looking at some of the very important resulting applications. For example, many commercial tunable laser sources are based on the use of nonlinear process such as parametric oscillations or parametric amplification. Breakthroughs are still awaited in nonlinear optics, especially their capability to be used for ultrafast data processing for future optical integrated circuits [2, 3].

Since from 1990 the study of nonlinear effects in microstructured materials has become a very active research domain. Structuring the matter at the scale of the wavelength of the light enables the engineering of its dispersion properties, such as phase and group velocity [1]. This possibility can be used, for instance, to make optical waves at very different wavelengths propagate in a very dispersive medium at the same phase velocity to fulfil the phase matching condition and at low group velocities to obtain greater nonlinear interactions.

1.2 Harmonic generation

A dielectric medium when placed in an electric field is polarized, if the medium does not have a transition at the frequency of the field. Each constituent molecule acts as a dipole, with a dipole moment P_i. The net dipole moment per unit volume is given by

$$P = \sum_i Pi \qquad\qquad \text{- - -(1.1)}$$

The orienting effect of the external field on the molecular dipoles depend both the properties of the medium and the field strength. Thus, we can write,

$$P = \varepsilon_0 \chi \mathbf{E} \qquad\qquad \text{- - - (1.2)}$$

Where χ is called the *polarizibility or dielectric susceptibility* of the medium.

This relation is valid for the field strength of conventional sources. The quantity χ is a constant only in the sense of being independent of $\mathbf{E}$; its magnitude is a function of the frequency. With sufficiently intense laser radiation the above relation does not hold good and has to be generalized to

$$P = \varepsilon_0 \left(\chi^{(1)} \mathbf{E} + \chi^{(2)} \mathbf{E}^2 + \chi^{(3)} \mathbf{E}^3 \right) \qquad\qquad \text{- - - (1.3)}$$

Where $\chi^{(1)}$ is the same as χ. The coefficients $\chi^{(2,)} \chi^{(3)} \ldots$ define the degree of nonlinearity and are known as nonlinear susceptibilities. If the field is low, as it is in the case of ordinary light sources, only the first term of the above equation can be retained. It is for this reason that the prelaser optics is known as *linear optics*. Higher the value of the electric field, more significant becomes the higher order terms. It may be noted that optical characteristics of a medium, such as dielectric permittivity, refractive index, etc., which depend upon susceptibility, also become functions of the field strength $\mathbf{E}$, if it is sufficiently high[4]. The medium of which the polarization is described by a nonlinear relation of the type (1.3) is called a "nonlinear medium."

Suppose now that the field incident on a medium has the form

$$E = E_0 \cos \omega t \qquad\qquad \text{- - - (1.4)}$$

Substituting this in (1.3), we have

$$P = \varepsilon_0 \left(\chi^{(1)} \mathbf{E}_0 \cos \omega t + \chi^{(2)} \mathbf{E}^2_0 \cos \omega t + \chi^{(3)} \mathbf{E}^3_0 \cos \omega t + \ldots \right) \qquad\qquad \text{- - - (1.5)}$$

Using the trigonometric identities we can transform (1.5) to the form

$$P = 1/2\ \varepsilon_0\ \chi^{(1)}\ \mathbf{E}^2_0 + \varepsilon_0\ (\ \chi^{(1)} + 3/4\ \chi^{(3)}\ \mathbf{E}^2_0\ )\ \mathrm{E}_0\ \cos\omega\ t \qquad\qquad \text{- - - (1.6)}$$

$$+ 1/2\ \varepsilon_0\ \chi^{(2)}\mathbf{E}^2_0\ \cos 2\ \omega\ t + 1/4\ \varepsilon_0\ \chi^{(3)}\mathbf{E}^3_0\ \cos 3\ \omega\ t + \ldots$$

The first term is related to the dc field across the medium; the effect of which is of comparatively little importance. The second follows the external polarization and is called as the first or *fundamental harmonic of polarization*. The third oscillates at frequency 2ω and is called as *second harmonic of polarization*, the fourth is *third harmonic of polarization*, and so on.
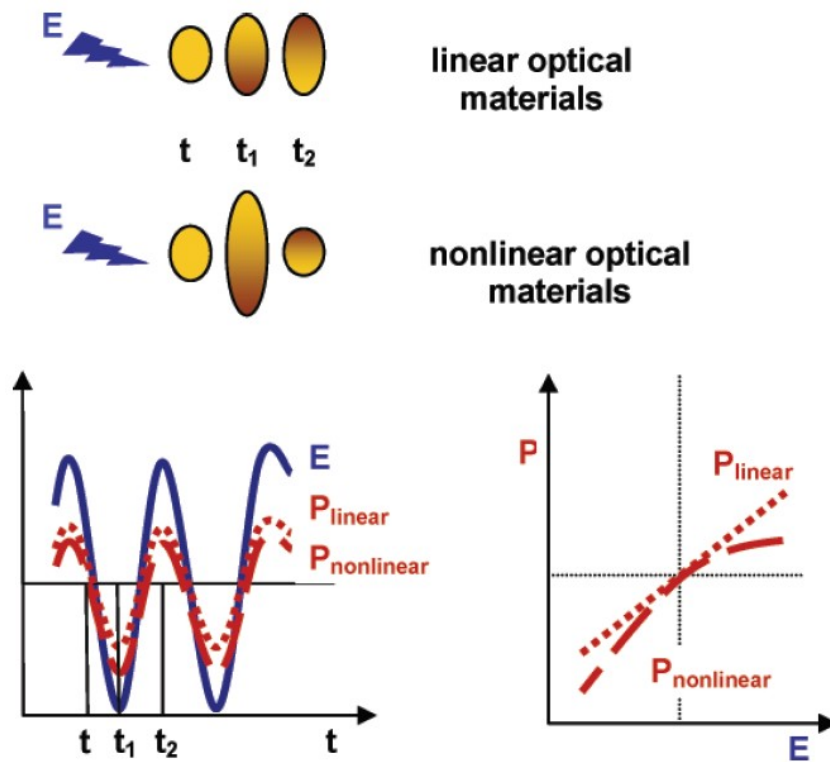
Fig. 1.1 *Linear and nonlinear polarizability comparison*

1.3 Second harmonic generation

The polarization oscillating at frequency 2ω radiates an electromagnetic wave of the same frequency, which propagates with the same velocity as that of the incident wave. The wave, thus produced has the same characteristics of directionality and monochromacity as the incident wave and is emitted in the same direction. This phenomenon is known as the *Second Harmonic Generation* (SHG).

In most crystalline materials, the nonlinear polarizability $\chi^{(2)}$ depends on the direction of propagation, polarization of the electric field and the orientation of the optic axis of the crystal. Since in such crystalline materials the vectors **P** and **E** are not necessarily parallel and the coefficients χ must be treated as tensors. The second order polarization, therefore, may be represented by the relation of the type

$$P_i^{(2)} = \varepsilon_0 \sum_{i,j} \chi^{(2)}_{ijk} E_j E_k \qquad \text{- - - (1.7)}$$

Where i, j, k represent the coordinates x, y, z. Most of the coefficients $\chi^{(2)}_{ijk}$, however, are usually zero and we have to deal only with one or two components.

It must be mentioned here that second harmonic generation cannot occur in an isotropic medium such as liquids or gases nor in centrosymmetric crystals. Only the crystals lack inversion symmetry exhibit SHG [4].

1.3.1 Applications of second order nonlinearity

Second order nonlinear effects are involved in numerous applications especially to obtain laser sources at wavelength that are not available with "standard" sources.

Parametric amplification leads to parametric gain for the signal field. Using parametric material in a resonant cavity (at least for signal frequency), a parametric oscillator can be obtained. This kind of source is equivalent to a laser source in which stimulated emission is replaced by parametric emission. Parametric sources can be widely spectrally tunable by changing the phase matching conditions with an exterior parameter like temperature or light incident angle on the nonlinear crystal [5].

There is also a quadratic phenomenon which is the parametric equivalent to spontaneous emission: parametric fluorescence. This effect consists of the spontaneous creation in nonlinear crystal of two photons with frequency ω_1 et ω_2 from one photon at ω_3. This phenomenon can be used in light sources for quantum cryptography protocols [6].

1.4 Third harmonic generation

As stated in (1.2), in the case of centrosymmetric materials, the expression (1.3) will lack terms in even powers of E and it will reduced to

$$P = \varepsilon_0 (\chi^{(1)}E + \chi^{(3)}E^3 + \dots) \qquad \text{- - - (1.8)}$$

 in Vector notation

$$P = \varepsilon_0 (\chi^{(1)}\mathbf{E} + \chi^{(3)}E^2\mathbf{E} + \dots) \qquad \text{- - - (1.9)}$$

Third harmonic generation (THG) is, therefore, possible in crystals that exhibit inversion symmetry. The development of q-switched lasers had made it possible to generate third harmonic crystals. However, the energy conversion efficiency in such cases is very low. For example, in calcite the maximum energy conversion efficiency in the third harmonic was 0.01%.

Experiments for observation of third harmonic were also performed by Maker and Terhune using giant pulse lasers. Zwernemann and Beeker have observed experimentally the enhancement of third harmonic generation (THG) at 9.33 μm in CO by having the interaction take place in wave guide [7]. They have presented a theoretical determination of the most suitable waveguide in which the interaction can takes place.

1.4.1 Applications of third order nonlinearity

Among all the nonlinear process, the optical Kerr effect is certainly one of the most important for applications [8 ,9]. Indeed, this effect is involved in a great number of phenomena such as:

-   Self-focussing and self-defocussing: this comes from nonlinear refractive index variation in space.

-   Self-phase modulation: it is presently used in optical fibre transmission systems to compensate chromatic dispersion of silica in order to propagate temporal solitons[8].

- Four wave mixing degenerated in frequency: Two powerful pump waves at the frequency of ω interfere to create a nonlinear refractive index grating. A third wave of weak intensity (probe at ω frequency) is then partially diffracted by the grating which gives birth to the fourth wave[9].

Nonlinear spectroscopy: It constitutes a fundamental application of nonlinear optics for the study of excitations in natural media (atoms, solids …) and their dynamics[10]. The nonlinear effects generally associated with nonlinear spectroscopy are:

- Stimulated Raman spectroscopy

- Stimulated Brillouin scattering

- Stimulated Rayleigh scattering

Some other well known applications of third order generation are:

- Continuum generation in microstructured optical fibres

- Optical reconfiguration of two dimensional photonic crystal slabs
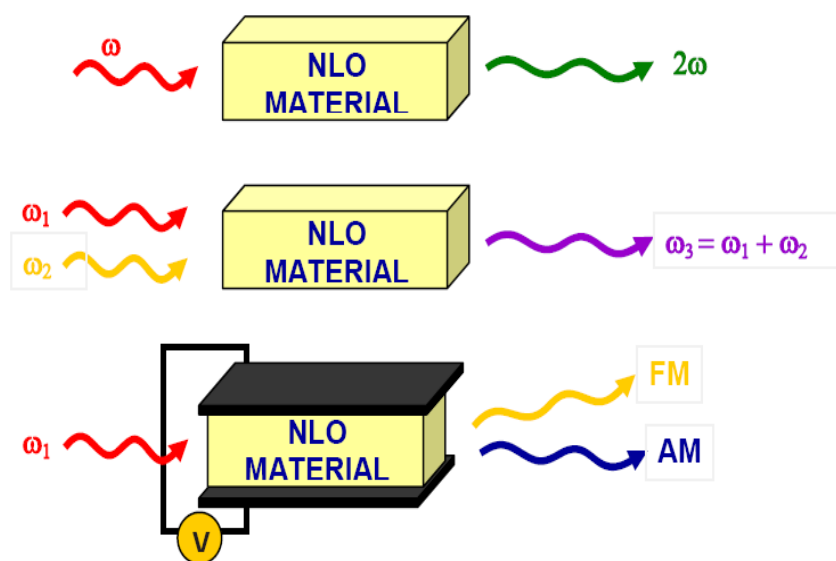
Fig. 1.2 *Schematic representation of important nonlinear optical and electro-optic effects.*

1.5 NLO materials

Research on NLO has mainly focussed on second and third order effects, which are suited to different applications and also have different material requirements. The ideal material for applications in NLO devices should have a combination of physicochemical properties such as appropriate values for given parameters, high damage threshold, high mechanical strength and thermal stability, fast response, processability, ease of fabrication and optical transparency [1,3].

1.6 Summary

In this chapter, our goal was to give the reader a glimpse of the potential of the nonlinear optics. We illustrated this with examples that second and third order nonlinear interactions could be enhanced in materials. Engineering the nonlinear properties and managing phase and group velocity is key to producing efficient nonlinear effects. In return organic nonlinear optical materials offer numerous new functionalities such as spectral tunability and ultrafast reconfiguration. This will be discussed in the next chapter.

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Chapter 2

A fact is a simple statement that everyone believes. It is innocent, unless found guilty. A hypothesis is a novel suggestion that no one wants to believe. It is guilty, until found effective.

~Edward Teller

2 ORGANIC NONLINEAR OPTICAL THIN FILMS

2.1 Introduction

Thin films, as the name implies, is a layer with high surface-to-volume ratio. For example, the structure may be macroscopically large in length and width but, its thickness is only of the order of micron or less [13]. Thin films have been widely studied over a century. Even though they were first obtained in 1838, they were systematically prepared by Faraday only in 1857. Thin film science has received tremendous attention because of its numerous applications on diverse fields such as electronic industries, solar energy utilization, military weapon systems, space science, high memory computer elements, sensors, microelectronics, hybrid circuits etc., [12].

Research is being done on a new class of thin films, the so called organic thin films. Organic molecular thin films hold great promise for the rational development of organic NLO materials. Nonlinear optical organic crystals are very promising for terahertz (THz) generation and detection and for the development of broadband integrated photonic devices, such as microresonator filters and modulators. Their long – range order not only reveals the performance limits of organic materials, but also provides unique insight into their electro-optic properties [2].

For nonlinear optical applications, organic materials are of great interest due to their large second-order optical nonlinearities, high flexibility in terms of molecular structure, high optical damage threshold, low cost and short response time to optical excitations [3]. They may often be solution – processed which allowing the fabrication of devices such as optical fibres, lithography and radio frequency identification devices on plastic/glass substrates and deposition by unconventional means, such as screen and ink – jet printing. In order to overview

the applications of organic nonlinear optical thin films, one must know the basics of organic materials, their molecular design and the material engineering.

2.2 Organic Materials for Second Order NLO Applications

2.2.1 Molecular Design

In order to develop organic materials for second order NLO effects, an appropriate molecular design should be planned. In this respect one of the most successful and widely used strategies involves highly polarizable structures in which an asymmetric change in the electronic density should be produced by light. The most prevalent approach to provide high β values, where β is the second order nonlinear polarizibility, through chemical structures involves the incorporation of an electron-donating group (D) and an electron-withdrawing one (A) connected by a π-system[3]. In this respect p- nitroaniline can be considered as a model (Fig. 2.1).
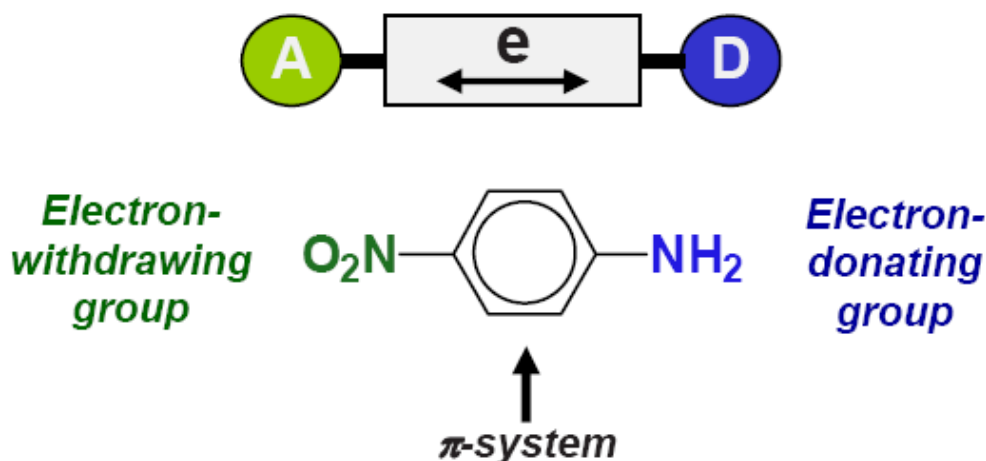
Fig. 2.1 *Typical molecular structure for second-order nonlinear optical applications.*

The total β value is the sum of two contributions:

(i) β_{add} resulting from the interactions between the substituents and the conjugated structure

(ii) β_{CT} arising from the donor-acceptor charge transfer contribution.

The latter contribution is the most important. These NLO-moieties are called NLO- chromophores or NLO-phores and they are easily identified in many materials for nonlinear optics [4].

Nevertheless, in spite of the wide adoption of this approach, a great deal of activity is still devoted to this type of structure, not only in order to improve the NLO response but also to establish a deeper understanding of the structure-activity relationships. There is a desire to open new structural alternatives and in this sense theoretical calculations can be applied, an approach that helps to provide more rapid and less arduous progress. Calculations in nonlinear optics have been claimed to lead to "a rethinking of paradigms now used to design molecules [5]. The theoretical results are useful to the device engineer as a guide for understanding the best material properties that can be achieved, to the chemist as a metric of the usefulness of a particular synthetic paradigm and to the physicist for an understanding of how complex material structures could be used to obtain as much out of a materials as is fundamentally possible". A great deal of synthetic work has been carried out and the NLO properties of novel molecules must be characterized.

All of these studies allow trends to be established as far as the chemical structure-NLO activity is concerned. On the basis of these studies some factors that affect β values have been proposed. For example, structural changes in the strength of electron donor and acceptor substituents and their conformations, the nature of the conjugated bonds and the length and aromaticity of π-systems have all been investigated. In an effort to the increase further the number of organic molecules that incorporate new electron-donating or electron-withdrawing groups, the incorporation of metal atoms through the use of coordination complexes has opened up new possibilities for the design of materials, both from the electronic and structural points of view (Fig. 2.2). These metal-containing compounds were expected to exhibit large molecular hyperpolarizabilities due to the transfer of electron density between the metal atom and the ligands, as well as to increase the design possibilities through the use of different central metal atoms with diverse

oxidation states, coordination geometries and ligands[5,6]. Furthermore, to the most commonly reported monodimensional A-π-D structures one can add 2D and 3D-systems to the variety of new molecules for NLO that chemists have explored
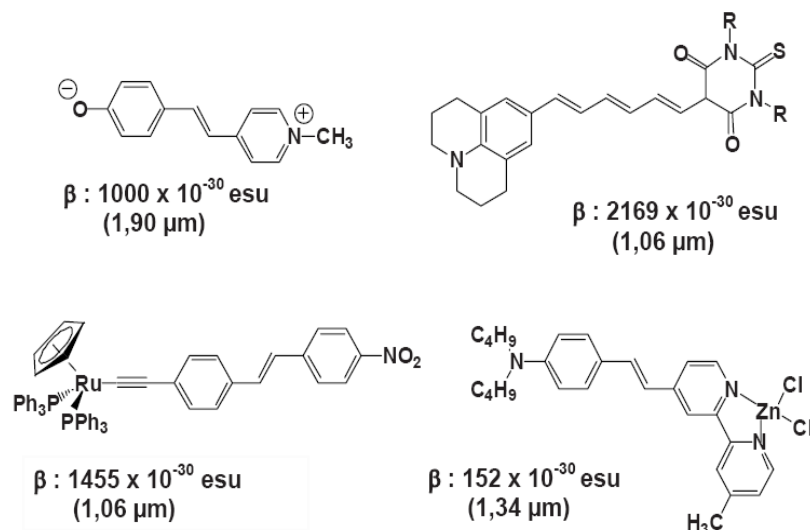
Fig. 2.2 *Chemical structures and first order hyperpolarizabilities of some representative 1D NLO-phores.*
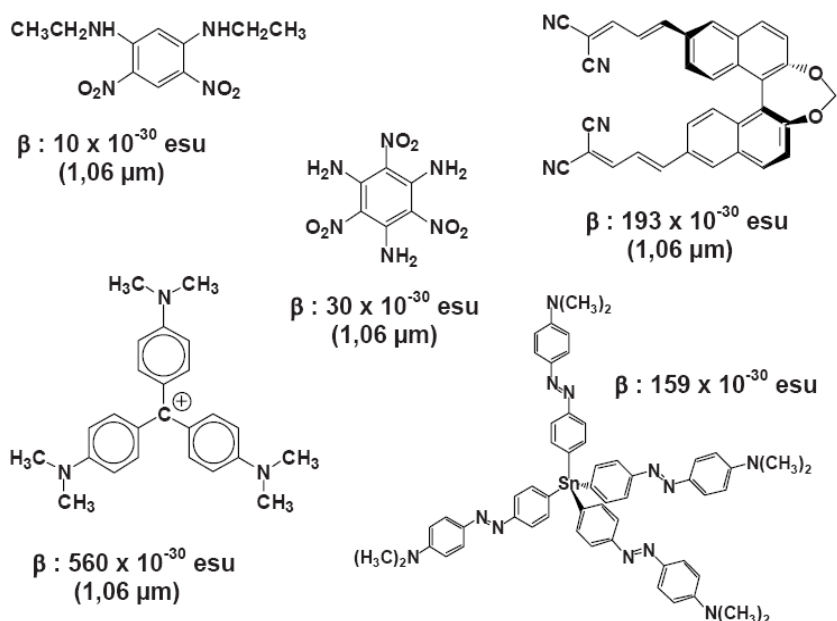
Fig. 2.3 *Chemical structures and first order hyperpolarizabilities of some representative 2D and octupolar NLO-phores.*

recently and which can be advantageously associated with other components of β tensor (Fig. 2.3).

Generally, this tensor has two irreducible components, one dipolar and other octupolar. It is therefore possible to design molecules where a nonzero β_{oct} is compatible with a zero dipole moment. In this respect, the development of experimental techniques such as HRS [6], which is used to measure the molecular parameter β for ionic and octupolar molecules, was very important.

2.2.2 Material Engineering

Applications based on NLO effects require materials rather than molecules. Thus, even though progress at the molecular level has offered very good starting points, a great deal of effort has been devoted to provide materials that allow these molecules to be processed in a suitable way for applications [5]. In the case of second order effects, a serious problem arises at the macroscopic level as molecules with large β values alone are not sufficient. According to equation (1.5), second order nonlinear optical phenomena only occur when $\chi^{(2)}$ has a value other than zero, so the molecular disposition within the material must be non-centrosymmetric.

This limitation, along with processing and thermal and chemical stability of the materials, has had a major influence on the advances and the strategies as far as material design are concerned. Different alternatives have been developed for the attainment of non-centrosymmetric order and alignment of the NLO-phores.

Single crystals are among the most attractive materials because of their typically large macroscopic nonlinearities, high packing densities, superior long-term orientational and photochemical stabilities and their optical quality. Inorganic single crystals are currently used in a variety of NLO photonic applications and, in a similar way, organic crystals were expected to be used in industry. However, considering that roughly 75% of nonchiral organic molecules crystallize centrosymmetrically, many NLO-phores that are active at the molecular level do

not show any nonlinear optical activity[11]. Thus, noncentrosymmetric orientation in the bulk is one of the most important issues for this approach (Fig. 2.4).
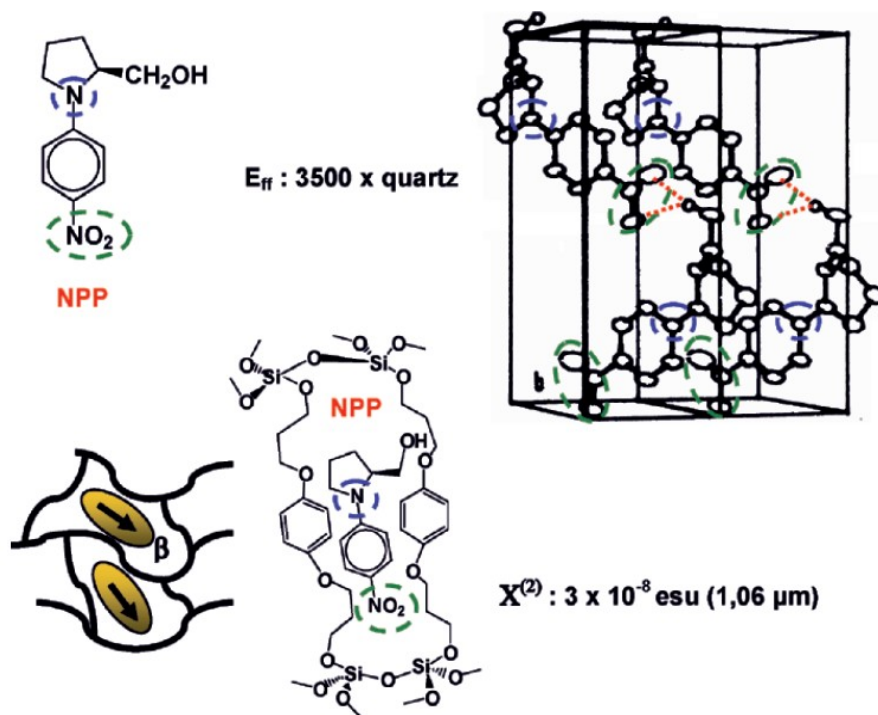
Fig. 2.4 *Different strategies followed to orient NNP (N-(4-nitrophenyl-(L)-prolinol) forsecond order nonlinear optical responses: single crystals (top), where molecules arearranged head to tail by intermolecular H-bonding and as intercalated materials (bottom).*

Numerous authors have incorporated into their designs stereogenic centers or/and hydrogen bonded systems as "tools" to induce polar order. The former possibility guarantees crystallization in one of the non- centrosymmetric groups. On the other hand, non-covalent interactions are used to define the tridimensional structure of the crystal [8]. Alternatively, the use of strong coulombic interactions, for example by changing the counterions in organic salts, has also proven to be a simple and highly successful strategy to obtain materials with large $\chi^{(2)}$ values (Fig. 2.5). The use of single crystals does, however, have some limitations related to the size and mechanical stability and processing. As a result, many different approaches to overcome such drawbacks have been developed by researchers in

this field. Intercalated materials have been proposed to control the mobility and order of the NLO-phores within their cavities.
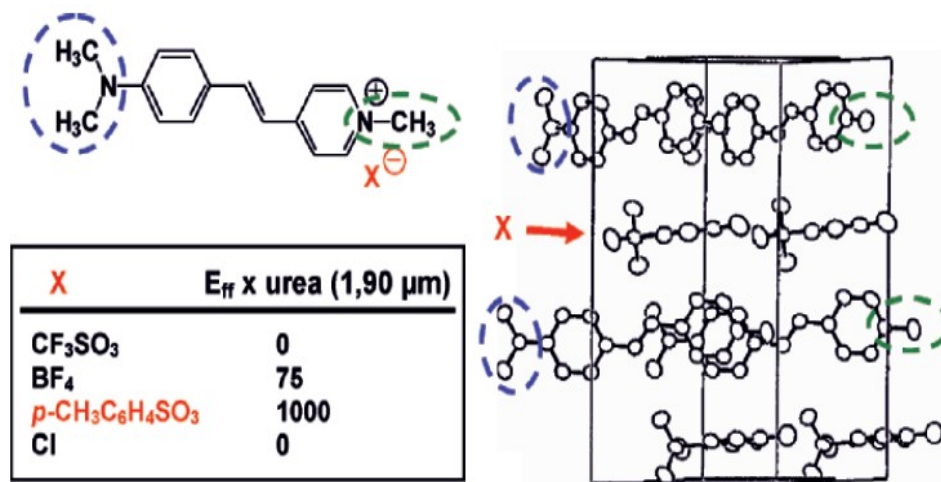

Fig. 2.5 *Packing drawing of DAST (N,N-dimethylamino-N´-methylstilbazolium ptoluenesulfonate)showing the non-centrosymmetric order within the single crystal andpowder second harmonic generation efficiencies for different salts based on the samecationic NLO-phore.*

With this aim in mind, matrices that are different in nature and morphology (e.g. zeolites, cyclodextrins, silicates, ..etc) have been investigated. In this respect the sol-gel methodology has opened very attractive possibilities. The increased interest in thin films in electronics, nonlinear optics and related new technologies has focussed interest on developing organic materials that have easily controlled film thickness and highly ordered micro- or nanostructures [3].

In this area the Langmuir–Blodgett technique is one of the most powerful ways to obtain films with uniformly oriented close packing and controlled thickness. As a result, the Langmuir–Blodgett technique has been identified as a very suitable approach to prepare non-centrosymmetric materials that give large NLO-parameters. Indeed, a number of classical D- π-A structures have been incorporated into designs that combine the hydrophobic-hydrophilic characteristics that allow the preparation of this type of film. Alternatively, promising results have

also been reported for non-covalent films prepared by PVD techniques. With the same general aim, a very closely related design strategy has been introduced and this involves building materials through covalent interactions (Fig. 2.6).
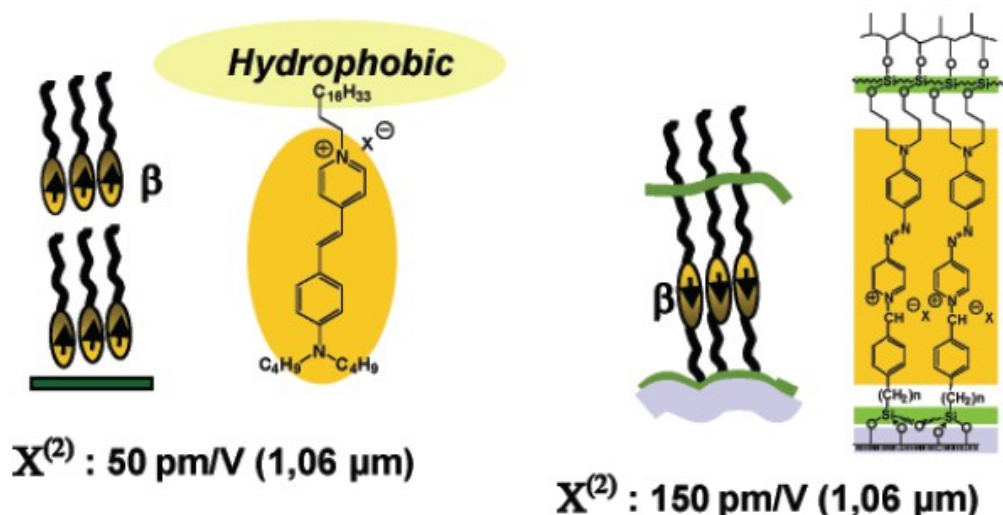

Fig. 2.6 *Different strategies followed to prepare thin films for second order nonlinear optical responses: Langmuir-Blodget films and covalent self-assembled multilayers.*

It is thought that this approach could overcome some limitations inherent in this type of non-covalent film. The application of an appropriate sequence of chemical reactions can create non-centrosymmetric self-assembled multilayers that give rise to NLO-materials with good mechanical properties and a high degree of order [9].

2.3 Organic Materials for Third Order NLO Applications

Third order nonlinear optical effects have been developed to a lesser extent than the second order systems, particularly as far as the design is concerned. The structural requirements at the microscopic level are not well understood and the number of studies in this line is significantly lower in comparison to those developed for second order materials. Third-order nonlinear optics imposes no symmetry requirements for the effects to occur. But in contrast to second-order nonlinear optical materials, there are few rational strategies for optimizing this kind of response for materials. Acentricity strongly enhances the third-order

nonlinear optical properties of molecules. The presence of conjugated systems connecting donor and acceptor structures favours this type of NLO response [2, 5].
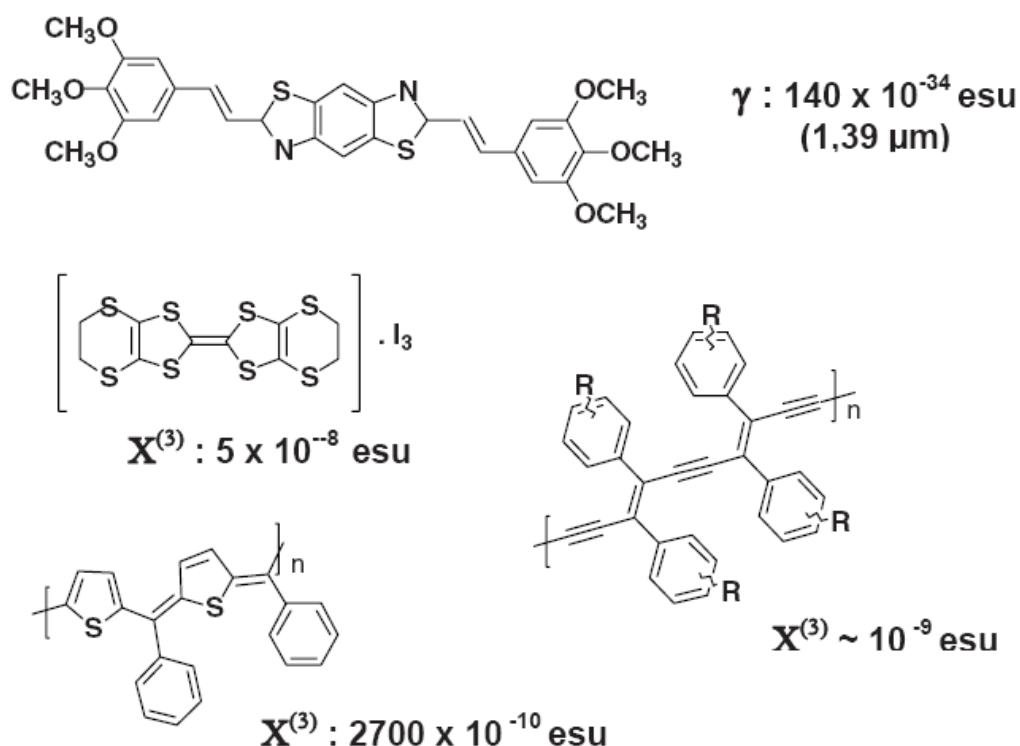
Fig. 2.7 *Chemical structures and non-linear responses of some representative NLO-phores designed for third-order responses.*

Furthermore, certain combinations of parameters also used for molecular electronic are welcome for these materials, even though no direct correlation between high conductivity and $\chi^{(3)}$ values has been observed. A range of very different compounds such as phthalocyanines, cyanines, tetrathiafulvalenes or fullerene-derivatives have been characterized as third order NLO- phores (Fig. 2.7).

Nevertheless, the majority of work and interest in this area concerns conjugated polymers [9]. Examples are polydiacetylenes, poly-p-phenylenevinylene or polythiophenes. The polymer chains should pack as closely as possible to maximize the $\chi^{(3)}$ values. Alternatively, polyalkyl- silanes are non conjugated polymers that contain no π electrons in the polymer backbone, but $\chi^{(3)}$

values have been reported for some polysilanes. Since third-order effects do not require bulk order, all materials, including solids as crystalline materials, amorphous polymers, glassy materials or multilayer films, as well as liquid crystals can be used for this purpose.

On the other hand, cascaded second-order nonlinearities provide an attractive alternative to obtain third-order nonlinearities. Cascading is a process where lower-order effects are combined to contribute to a higher- order nonlinear response. Therefore the development of materials with large $\chi^{(2)}$ values are also pursuit for cubic nonlinear optics. In the last year interest in both the optical phenomena controlled by $\chi^{(3)}$ as well as the characterization and development of materials for third order NLO-responses have increased markedly and have attracted further interest in this field.

2.4 Perspectives for the future

A sustained level of fundamental research over the past ten years has left organic NLO well positioned to make a technological impact in a variety of disciplines. It would not be surprising if the initial applications that fueled the growth of the field around 20 years ago were to be eclipsed by a completely new set, enabled by our improved understanding of the detailed relationship between chemical structure and optical nonlinearity. In particular I expect to see: that electro-optic coefficients of 500 pm/V will likely be achieved in poled polymers and may enable numerous applications beyond electro-optic modulation including efficient terahertz frequency generation, that can facilitate imaging for medical and security applications; a resurgence of interest in the exploration of all-optical signal processing based upon third-order nonlinear optical materials; rapid development and application of two-photon microfabrication, pushing the limits of achievable resolution below 100 nm and greatly expanding upon the range of materials that can be fabricated; application of organic NLO materials for biomedical applications including imaging, sensing, treatment and tissue engineering; the combination of efficient organic NLO materials with nanostructured metal clusters to provide dramatically enhanced NLO effects

through surface plasmon effects; and the use of NLO materials in photonic crystals to provide tunability of their optical properties. Many of these applications will benefit from new highly nonlinear molecules and materials. An increased level of control over and understanding of, not only intramolecular effects, but also importantly intermolecular interactions will be essential in enabling these advances and, therefore, many challenges still face the chemical community in this field.

2.5 Summary

The organic materials exhibit extremely large nonlinear optical and electro-optic effects. The electronic nonlinearities are essentially based on the molecular units. They are important materials for the fast processing of information and for optical storage applications. Due to the important advantages of the organic materials, they will be widely used in the field of organic chemistry, materials science, physics and electrical engineering. This Chapter tries to have a quick look at their properties and some effects. There need certain good techniques in order to incorporate the organic materials into thin films which can be used for various applications. It will be discussed in the next chapter.

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Chapter 3

If you're not part of the solution, you're part of the precipitate.

~Henry J. Tillman

3 DEPOSITION TECHNIQUES FOR ORGANIC THIN FILMS

3.1 Introduction

So far, we have studied the basics of nonlinear optical property and organic NLO thin films. Thin films of organic materials with low molecular weight are received greater importance for their optoelectronic properties that making them suitable for photovoltaic and optoelectronic applications. In order to incorporate such materials into useful applications, one should need some versatile techniques to deposit the materials on the substrate. There are many deposition techniques for organic thin films, among them vacuum thermal deposition sometimes called physical vapour deposition and chemical solution deposition are being widely used [1]. Structure, morphology and properties of thin films are found to be dependent on deposition conditions and on the substrate used. Thin films are deposited mainly on transparent substrates made of glass or quartz, especially while optoelectronic or photovoltaic devices are concerned.

Thickness of the thin film is of great importance because thinner the film, stronger the influence of transition interface between the substrate and a film. In case of optoelectronic or photovoltaic applications, thickness of the film can influence optical or electrical parameters of the substrate [2, 6]. Thus, suitable deposition technique should be required. The aim of this chapter is to discuss the various techniques which are employed for thin film deposition.

3.2 Thin film deposition

Thin film deposition is the process of placing a thin layer of one substance on to another in order to modify the physical properties i.e., the increase of hardness, change in electrical conduction and the optical properties of underlying material, referred as substrates. "Thin" is a relative term, but most deposition

techniques control layer thickness within a few tens of nanometres [7]. In the case of organic thin films, the deposition techniques are broadly classified as:

1. Physical methods

2. Chemical methods

3.3 Physical methods

Physical methods involve atom – by – atom, molecule – by – molecule or ion deposition of various materials on solid substrate in vacuum systems. It uses mechanical or thermodynamic means to produce a thin film of solid. Since most engineering materials are held together by relatively high energies and chemical reactions are not used to store these energies, commercial physical deposition systems tend to require a low pressure vapour environment to function properly. Most of them are classified as Physical Vapour deposition [3].

The material to be deposited is placed in an energetic, entropic environment, so that particles of material escape from its surface. Facing this source is a cooler surface which draws energy from these particles as they arrive, allowing them to form a solid layer. The whole system is kept in a vacuum chamber, to allow the particles to travel as freely as possible. Since particles tend to follow a straight path, films deposited by physical means are commonly directional rather than conformal. For the deposition of organic materials, physical methods are generally classified as;
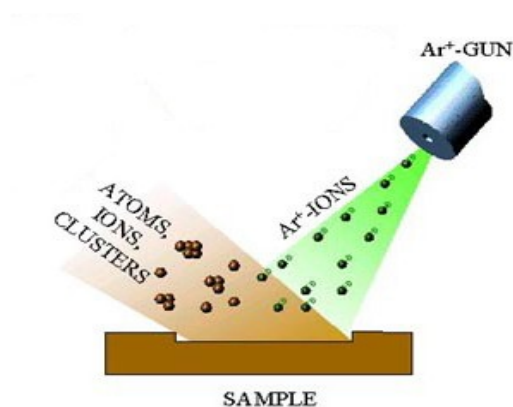
(i) Evaporation

(ii) Sputtering.

Vacuum evaporation techniques are simple and easy to control. Sputtering technique often employed to produce a vaporized beam is by remove the atoms or the molecules of material by bombarding its surface with high momentum ions of inert gases such as argon.

3.3.1 Sputtering

Sputtering relies on a plasma (usually a noble gas, such as argon) to knock material from a 'target' a few atoms at a time. The target can be kept at relatively low temperature. Since the process is not one of evaporation, making this one of the most flexible deposition techniques[4,5]. It is especially useful for compounds or mixture, where different components tend to evaporate at different rates. Sputtering can produce hard thin film coatings (less than 3 μm). Sputtering is now widely applied on cutting tools, forming tools, injection moulding tools and common tools such as punches and dies, to increase wear resistance and service life.

Fig 3.1. *Schematic of sputtering process*

3.3.2 Thermal Evaporation

Thermal evaporator uses an electric resistance heater to melt the material and raise its vapour pressure to a useful range. This is done in a high vacuum, both to allow the vapour to reach the substrate without reacting with or scattering against other gas-phase atoms in the chamber and to reduce the incorporation of impurities from the residual gas in the vacuum chamber. Obviously, only materials with a much higher vapour pressure than the heating element can be deposited without contamination of the film. Molecular beam epitaxy is a particular sophisticated form of thermal evaporation[6].
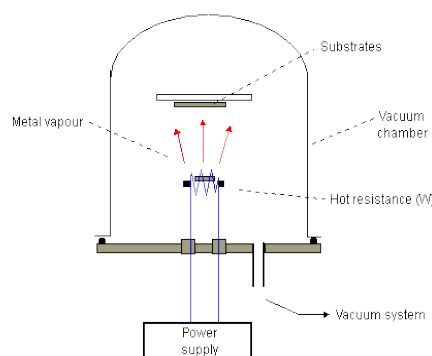
Fig. 3.2 *Schematic of thermal evaporation technique*

3.4 Chemical methods

Chemical methods are capable of producing thick, dense, ductile and good adhesive coatings on metals and non – metals such as glass and plastic. Contrasting to Physical deposition in the line of sight, chemical methods can coat all surfaces of the substrate. Here a fluid precursor undergoes a chemical change at a solid surface, leaving a solid layer. Since the fluid surrounds the solid object deposition happens on every surface with little regard to direction; thin films from chemical deposition techniques tend to be conformal, rather than directional[8,9]. Some important chemical methods that are widely used to deposit organic thin films are:
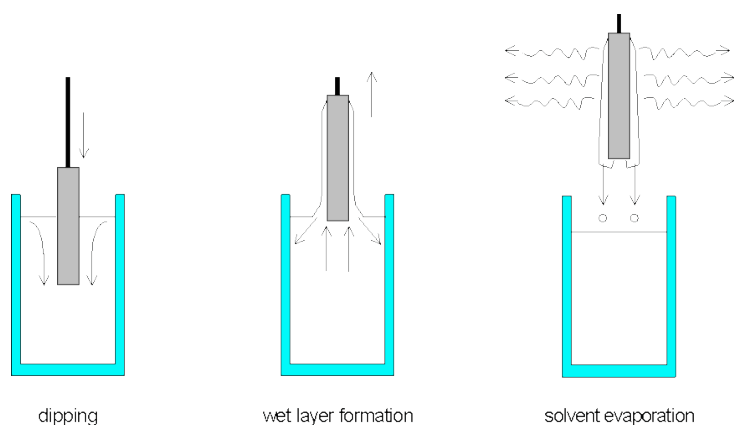
1. Dip coating

2. Drop casting

3. Spin coating

4. Chemical bath deposition

3.4.1 Dip coating

In dip-coating process, a substrate is dipped into a liquid coating solution and then is withdrawn from the solution at a controlled speed. Coating thickness generally increases with faster withdrawal speed. The thickness is determined by the balance of forces at the stagnation point on the liquid surface. A faster

withdrawal speed pulls more fluid up onto the surface of the substrate before it has time to flow back down into the solution.

The thickness is primarily affected by fluid viscosity, fluid density and surface tension. Dip-coating, while excellent for producing high-quality, uniform coatings, requires precise control and a clean environment [9]. The applied coating may remain wet for several minutes until the solvent evaporates. This process can be accelerated by heated drying. In addition, the coating may be cured by a variety of means including conventional thermal, UV or IR techniques depending on the coating solution formulation. Once a layer is cured, another layer may be applied on top of it with another dip-coating / curing process.


dipping   wet layer formation   solvent evaporation

Fig. 3.3 *Schematic diagram of the Dip-Coating Process*

3.4.2 Drop casting

Drop casting is a process in which the solution to be deposited is placed on the substrates as drops. Depending upon the density of the solution it can spread over the substrate. Due to the volatile nature of the solvent, it is vaporized and the crystalline form of the material is deposited on the substrate. This process is simple and very effective tool to produce the organic thin films. One of the main disadvantages of this method is the film formed is very thicker one. On the other hand, this method can be used to check the crystallinity nature of the material, before using ink jet or other advanced technique [10].

3.4.3 Spin coating

Spin coating is currently the predominant technique employed to produce uniform thin films of photosensitive organic materials with thickness of the order of micrometers to nanometres. Spin coating process for a colloidal suspension exhibit four distinct stages of development, the first two happening rapidly and the second two occurring over a much longer time period. In the first stage, a colloidal fluid is deposited as a droplet onto a fixed substrate. In the second stage, the liquid droplet spreads out to form a film that rotates at nearly the same rate as the substrate. In the third stage, this film spreads outward and thins, controlled primarily by centrifugal force and viscous shear force. In the fourth stage, the film becomes sufficiently thin that evaporation dominates. The transition from the third to fourth stage depends on the volatility and other material properties of the coating liquid. For colloidal suspensions, the film thickens during this fourth stage can reduce to the same order as the particle size, at which point capillary forces at the liquid-gas interface can have a significant effect on particle aggregation. In some applications, the evaporation transport in the fourth stage is aided by high temperature heating and imposition of special atmospheric conditions to control film and particle development and chemical composition [11]. Several processing parameters involved in the spinning process are: dispense volume, final spin speed, final film thickness, solution viscosity, solution concentration, spin time, etc. Using the different parameters, film thickness and radius of spreading are calculated. The film forming process is primarily driven by two independent parameters, viscosity and spin speed. The range of the film thickness easily achieved from the spin coating is 1-200 micrometers.
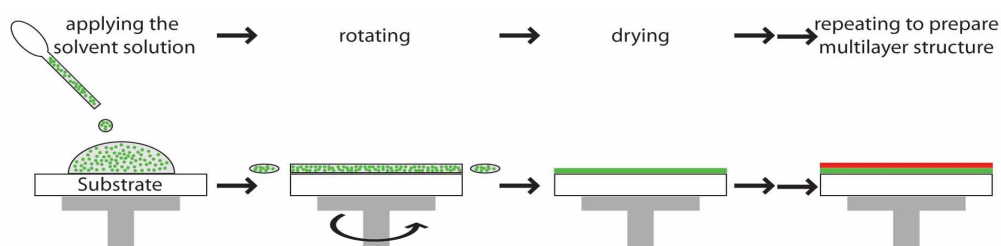
Fig. 3.4 *Schematic diagram of the spin -Coating Process*

3.4.4 Chemical bath deposition

There is a considerable interest in the deposition of organo – metalic and organic materials by methods which involve relatively low capital expenses and are technically undemanding on the experimentalist. One process to meet these criteria is chemical bath deposition. Since we used this technique in our present work to deposit the thin films of Benzimidazole brief of description experimental set up and deposition of films using this technique will be discussed in the next chapter.

3.4.4.1 Mechanism of chemical bath deposition (CBD)

The mechanism of CBD can be divided into two different process:

(i) Formation of required compound by ionic reactions involving free anions

(ii) Decomposition of metal complexes (in case of Organo – metalic materials).

These two categories can be further divided into two: (i) Formation of isolated single molecules that forms cluster and eventually form a crystal or particle (ii) Mediation of a solid phase, usually the metal hydroxide [12].

A starting point for discussing the mechanism of CBD is to consider a simple precipitation reaction. If H_2S is added to an aqueous solution of a Cd salt, yellow CdS precipitates out immediately. H_2S precipitates the sulphide of most cations (the alkaline and alkaline earth sulphides are soluble in water); this is the basis of the well-known inorganic analytical scheme. Such a precipitation will not, however, result in a film on substrate or on the walls of the reaction vessel (actually, it may do so to a very slight extent but this film would be extremely thin). To form a visible film of CdS, conditions must be chosen so that bulk precipitation is prevented or at least slowed down drastically.

3.4.4.2 Nucleation

Depending on the deposition mechanism, the nucleation which can occur in CBD is classified into two types:

(a) Homogeneous nucleation

(b) Heterogeneous nucleation

3.4.4.3 Crystal growth

Once stable nuclei have formed, there are several ways in which they can increase in size. When the gaps are completely bridged by the nuclei, films will be continuous. However, it often happens that void space may still remain unbridged. In ideal film there should not be any gap in the aggregate mass. Thermal treatment for sufficiently long time will cause migration of diffusion of atoms leading to a stable phase. This is known as aging of films.

3.4.4.4 Particle size distribution

If nucleation occurs in a very short time, whereas growth occurs separately, often over a much longer time but without further nucleation, then the size distribution is likely to be narrow, since all the original nuclei should be of similar size and grow at the same rate. The opposite case, where nucleation and growth occur simultaneously, usually results in a wide size distribution. In CBD, where the reaction is slow, it might be expected that nucleation and growth will always occur together, resulting in a relatively wide size distribution [12].

3.4.4.5 Forces between particles and surfaces

Once nanoparticles have been formed, whether in an early state of growth or in a more or less final size, their fate depends on the forces between the individual particles and between particles and solid surfaces in the solution. While particles initially approach each other by transport in solution due to Brownian motion, convection or sedimentation, when close enough, interparticle forces will determine their final state. If the dominant forces are repulsive, the particles will

remain separate in colloidal form. If attractive, they will aggregate and eventually precipitate. In addition, they may adsorb onto a solid surface (the substrate or walls of the vessel in which the reaction is carried out).

For CBD, both attractive particle – surface and particle – particle forces are required for film formation. In all the stages of the CBD process, except for a very few studies that of adhesion of the film to the substrate is probably the least understood. In order to understand these sticking phenomena, the understanding of various forces involved in CBD process such as repulsive and attractive forces is needed. The two dominant forces involved in CBD process are Van der Walls forces and Electrostatic forces.

3.6 Summary

In this chapter, we provided the various techniques which are widely employed for the deposition of organic thin films. Also, we discussed the mechanism involved in chemical bath deposition. Deposition of Benzimidazole thin films using chemical bath deposition will be discussed in the next chapter.

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Chapter 4

The most exciting phrase to hear in science, the one that heralds the most discoveries, is not "Eureka!" (I found it!) but "That's funny..."

~ **Isaac Asimov**

4   Deposition of Benzimidazole thin films

4.1 Introduction

The extraordinary potential of certain classes of organic molecules for nonlinear optical applications has long been recognized and several groups of worldwide have devoted significant resources to develop new classes of potential organic materials over the past few decades . Organic molecules consisting of strong donor-acceptor groups separated by a π- electron bond system are attractive candidates for a variety of opto-electronic applications due to their exceptionally large hyperpolarizabilities. Benzimidazole (BMZ) is one of such a potential candidate for nonlinear optical processes and scintillation detector and other related applications. BMZ crystallizes in the orthorhombic crystal system which has significant absorption in the near infrared region and moderate hardness [6].

4.2 Material Profile

Benzimidazole is a heterocyclic aromatic organic compound. This bicyclic compound consists of the fusion of benzene and imidazole. The most prominent benzimidazole compound in nature is N-ribosyl-dimethylbenzimidazole which serves as an axial ligand for cobalt in vitamin B12. Benzimidazole, in an extension of the well-elaborated imidazole system, has been used as carbon skeletons for N-heterocyclic carbenes. The NHCs are usually used as ligands for transition metal complexes. They are often prepared by deprotonating an N,N'-disubstituted benzimidazolium salt at the 2-position with a base [5].

Structure of benzimidazole:
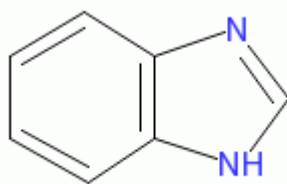
Benzimidazole

Product identification:

IUPAC name   1H-benzimidazole

CAS No.   51-17-2

Properties:

Molecular formula $C_7H_6N_2$

Physical state   slightly beige powder

Molar mass $118.14 \text{ g mol}^{-1}$

Melting point   170–172 °C

Boiling point   360 °C

Solubility   Slightly soluble in water. Soluble in cold water and organic solvents

Crystallographic data of BMZ:

❖   Orthorhombic crystal system

❖   Non-centrosymmetric structure

❖   Space group of Pna21

❖   Cell dimensions are

a = 6.7922 (29) Å,

b = 6.8937 (40) Å,

c = 13.3878 (56) Å

4.3 Deposition of the benzimidazole films

4.3.1 Substrate cleaning

The need for high quality thin films has become one of the most critical issues in the deposition technology. Its importance has increased further for ULSI structures which demand very low defect densities. As a result, the silicon surface preparation prior to deposition has acquired a large impact on device yield and performance. Because of this, the wafer surface termination has become an important issue [1, 3]. In this work several cleaning procedures were employed in order to get thin and uniform films.

4.3.2 Cleaning procedures for glass substrate

The chart below shows the various step processed during the cleaning of substrates.
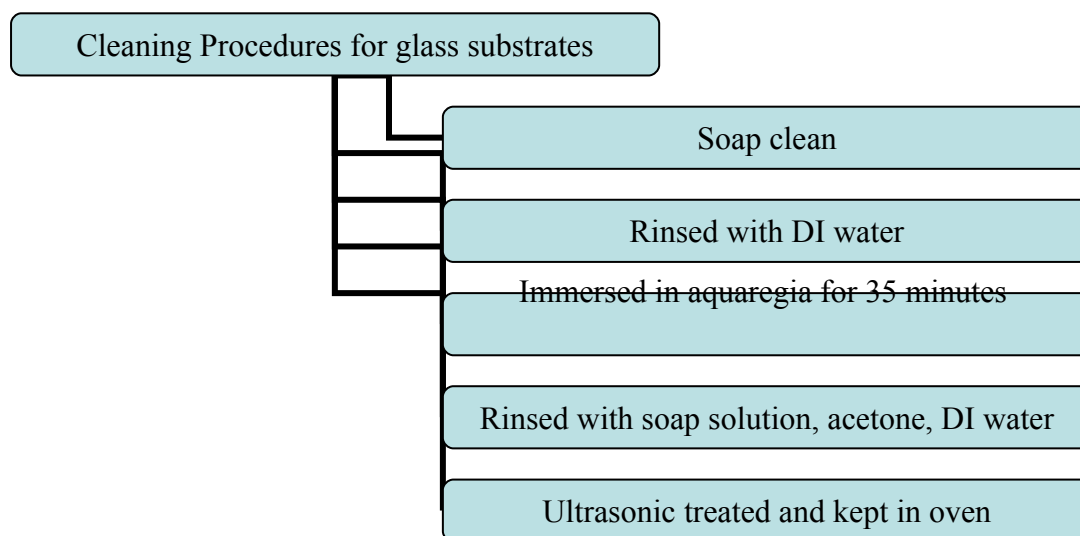
Soap clean:

Most slides and glass substrates can be effectively cleaned with soapy water. Thus, a bath of soapy water was prepared. Lint-free wipe and cotton swab were used to gently rub the surface in order to clean off from dirt and residues. Then, the substrates were thoroughly rinsed in DI water [2].

Aqua regia:

Since the benzimidazole molecules are comparatively small in size, the etching of the substrate play wide role in the deposition of film. In order to achieve good etching the substrates were treated with aqua regia. Set up time for this process is about 5 minutes. This process takes 35 minutes to complete. Aqua regia ("Royal etch") is a HCl-HNO$_3$ (3:1) etchant used to etch many metals, including gold [4]. An Aqua regia mixture was prepared in a glass container by the following recipe.

150 ml hydrochloric acid (HCl)

50 ml nitric acid (HNO$_3$)

Acid was poured in the container followed by addition of nitric acid. Glass substrates were soaked for 30 minutes into the bath of aqua regia mixture. After that the substrates were rinsed in soap solution, water, acetone and DI water. Ultrasonic treatment was carried in the ultrasonic bath. Finally, the substrates were kept in the hot oven in order to dry the surface.

4.3.3 Experimental set up

Chemical Bath deposition refers to the deposition of films on a solid substrate from a reaction occurring in a solution (almost always aqueous). In CBD, the trick is to control the rate of these reactions (by adjusting either rotation speed of the substrate or the temperature of the solution) so that they occur slowly enough to allow the compound of interest either to form gradually on the substrate or to diffuse these and adhere either to the substrate itself (at the early stages of deposition) or to the growing film, rather than aggregate into larger particles in solution and precipitate out.

The picture shows the experimental set up used in this work. In which the substrate is rotated by using a motor of 0.5 rpm speed, the speed can be controlled by a voltage controller. The solution can be heated by a heater from the bottom of

the solution beaker. The temperature was measured by using a digital thermometer.
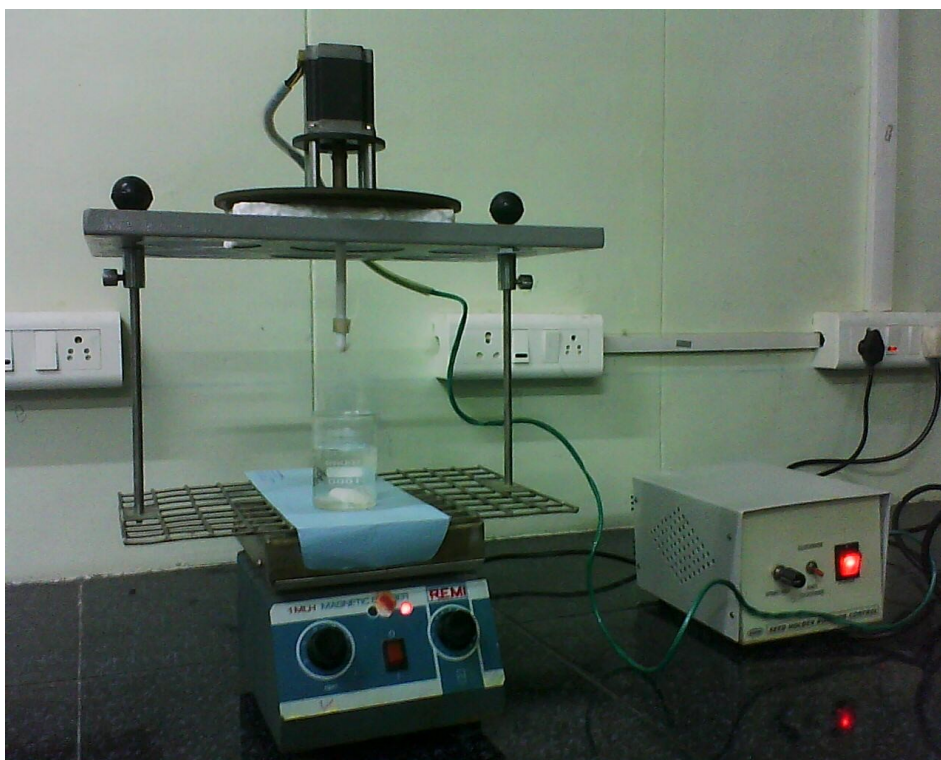
Fig. 4.1 *Experimental arrangement for the deposition of Benzimidazole thin films*

4.3.4 Deposition of Benzimidazole thin films

Benzimidazole thin films were deposited using homemade chemical bath deposition technique. The precursor solution was prepared with different molar concentration of Benzimidazole in ethanol. The microscopic glass substrate was immersed into the solution beaker which is on the heated metal plate. The substrate was rotated at a speed of 0.5 rpm. BMZ thin films were deposited for different experimental conditions by varying the molar concentration as 0.1, 0.2, 0.5 and by varying the solution temperature as 40, 50, 60 °C respectively. The deposition time was about 1 hour. It is observed from the results, 0.2 molar concentration and 60°C are the optimized experimental condition for obtaining the good quality thin films.

4.4 Summary

In this chapter, the deposition of Benzimidazole thin films by Chemical bath deposition was discussed. The solution was prepared by using ethanol as

solvent. The films were coated for different experimental conditions. The coated films were subjected to various characterization techniques. This will be discussed in the next chapter.

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Chapter 5

The important thing in science is not so much to obtain

new facts as to discover new ways of thinking about them.

~ William Lawrence Bragg

5   Results and discussion

5.1 Introduction

The Benzimidazole thin films were coated by chemical bath deposition technique at different experimental conditions. The grown benzimidazole thin films were confirmed by powder XRD analysis. The thickness of the coated film was calculated by mass gravimetric method. The optical transmission properties of the films were examined between 300 and 1100 nm using Lambda 35 UV–Vis spectrophotometer. The third order NLO property of the BMZ film was confirmed by He-Ne laser using Z – scan technique. The detailed discussions of the obtained results are presented in the following sections.

5.2 Thickness of the sample

Thickness measurement is the most important parameter for the thin films, since it largely determines the film property. In the present work the thickness of the BMZ thin film coated from CBD was measured using mass gravimetric method. From this method film thickness can be calculated by the equation,

$$t = \frac{M}{\rho A}$$

- - - (5.1)

Where, M is the mass of the sample,

ρ is the density of the material,

A is the area of the sample.

Mass (M) of the material deposited on a known area (A) was determined from the weight of substrate of known size before and after deposition. By employing the values to the above equation the mean thickness for all the films was found to be ~ 400 μm.

5.3 Structural studies

Powder XRD studies were carried out to demonstrate the crystallinity of the thin film coated from CBD using XPERT-PRO powder diffractometer. The X-ray powder data were collected using a position-sensitive detector (PSD) with an angular range of 2.12°. The step size was 0.0500° and the nominal detector resolution is ± 0.02. The radiation of CuKα (λ=1.54060 Å) was used as source. The observed 2θ values were given in the input of the Checkcell software package and the lattice parameters are calculated and compared with the literature [1, 2]. It is observed that the benzimidazole crystal films belong to orthorhombic crystal system with a space group P21na. The powder XRD patterns of Benzimidazole thin films coated from CBD with optimized coated conditions are shown in the Fig. 5.1

It is evident from the XRD analysis that the solution temperature has no influence in the crystallinity of the BMZ film. The mean crystallite size (Grain size) D was calculated from the (110) diffraction peak using Shearer's formula

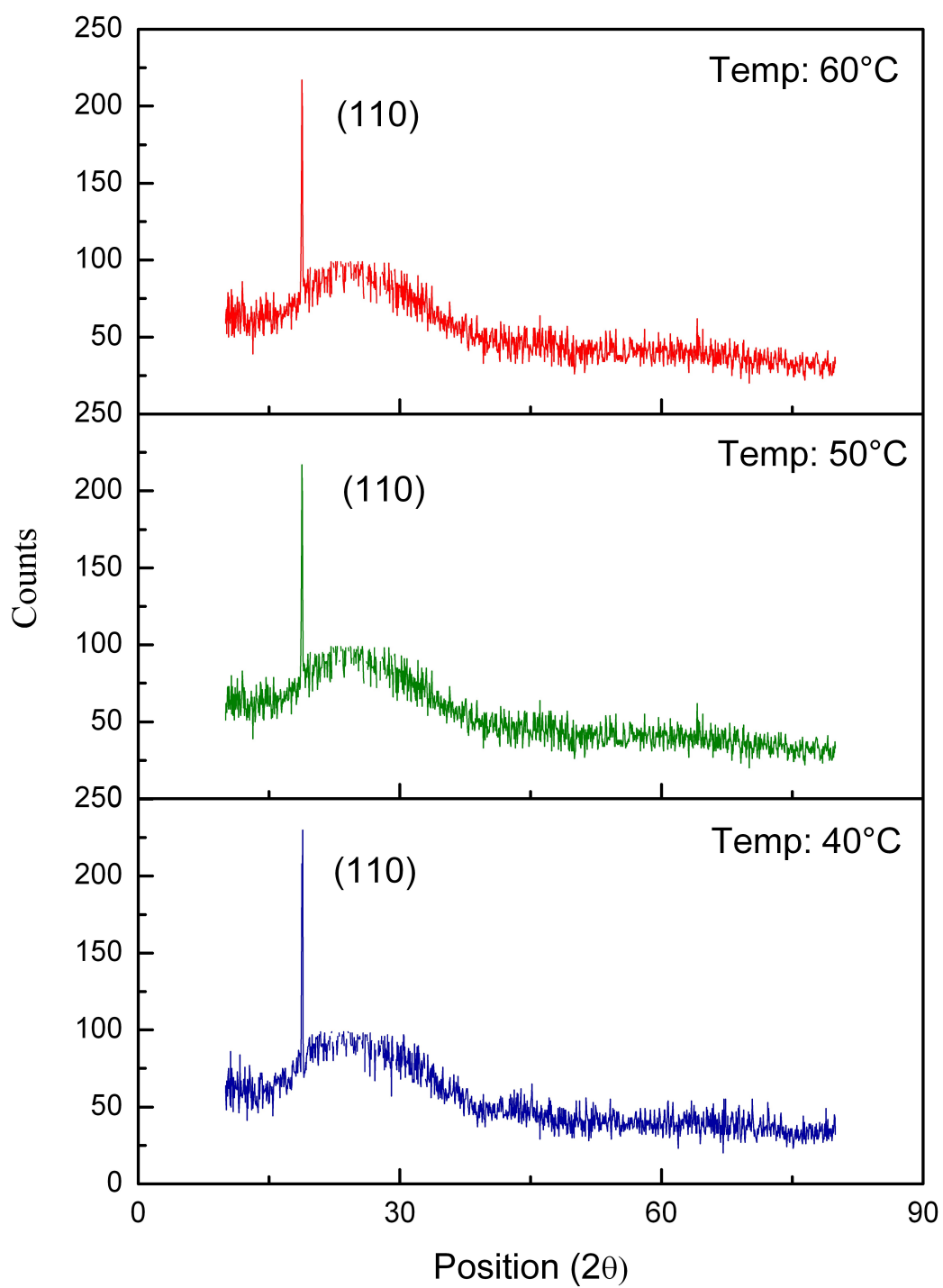$$D = \frac{K\lambda}{\beta \cos \theta} \qquad\qquad \text{- - - (5.2)}$$

Where, λ is wave length of the X – ray (for CuKα, λ=1.54060 Å),

K=0.9,

θ is the diffraction angle (from 2θ=18.7773) and

β is the FWHM (0.1310)

using the formula (5.2) the average grain size was determined as D=63.8 nm.

Fig. 5.1 *XRD patterns of benzimidazole films coated at (a) 40°C (b) 50°C (c) 60°C*

5.4 Optical studies

The UV–Vis analysis was made between 200 and 1200 nm, which covers near-ultraviolet (200–400 nm), visible (400–800 nm) and then far-infrared (800–1200 nm) regions. The plot of transmittance % vs. wavelength (nm) and is shown in the Fig 5.2(a). The absorbance is not registered until the wavelength 300nm is reached from 1100 nm. The nearly sharp fall in transmittance at 328 nm suggests that nearly similar distribution of energies among all molecules of the benzimidazole film, which otherwise will yield a gradual decrease in transmittance from the longer wavelength to 300 nm. Transmittance % increases with increasing solution temperature. Decreasing of absorption in the region between 400 and 1100 nm is an advantage as it is the key requirement for the materials having NLO properties [3, 5].
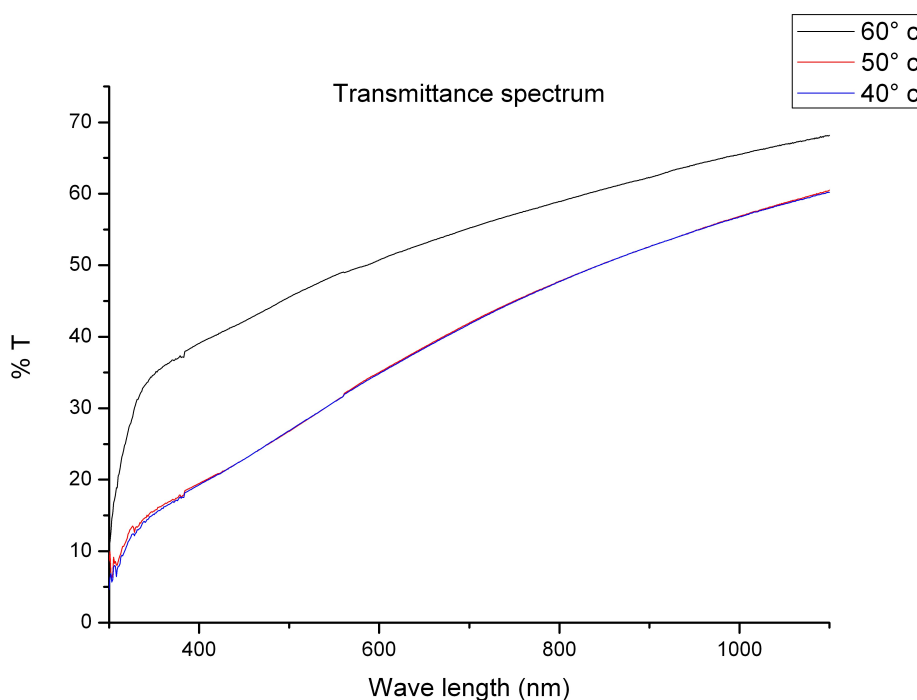

Fig. 5.2(a) *Transmittance spectrum of benzimidazole.*
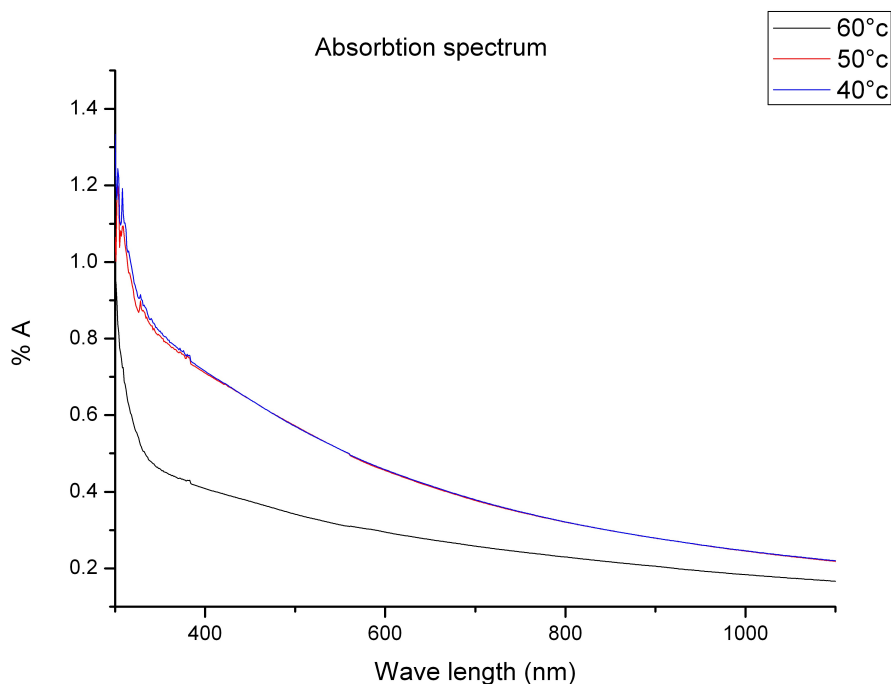
Fig. 5.2(b) *Absorbance spectrum of benzimidazole.*

Band gap calculation:

Optical-absorption studies provide an easy method for the investigation of optically induced electronic transitions and furnish ideas about the band structure as well as the energy gap in crystalline and non-crystalline materials. In the present study, the optical behavior was examined between 300 to 1100 nm using UV–Vis spectrum. The Tauc's graph between the product of absorption coefficient and the incident photon energy $(\alpha h \nu)^2$ with the photon energy $h\nu$ at room temperature shows a linear behavior that can be considered as evidence of the direct transition. The optical energy band gap (E_g) is estimated by extrapolation of the linear portion of the curve to a point $(\alpha h \nu)^2 = 0$. Using this method, we found that optical energy band gap of the film varies from 3.70 to 3.84 eV. Increasing solution temperature leads to increasing band width. The observed value is greater than that of the other organic NLO materials. The high value of energy band gap shows its suitability for photonic and optoelectronic applications [6, 7].
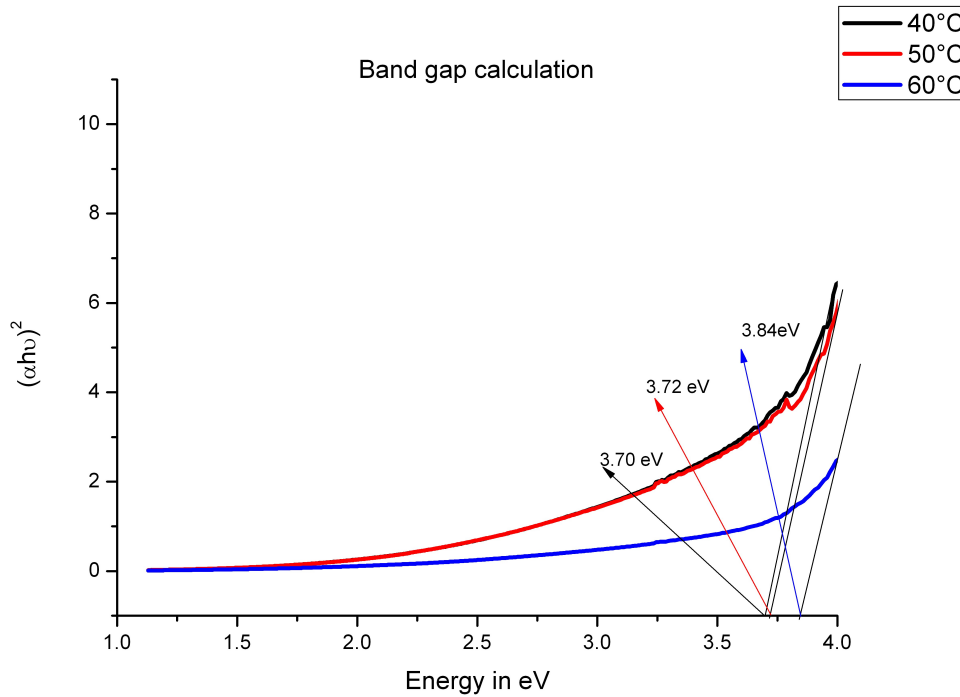
Fig 5.3 *Plot of (αhυ)² vs. photon energy of Benzimidazole*

5.6 Third order nonlinear susceptibility

5.6.1 Z – scan measurements

The single-beam Z-scan is a well-known technique for measuring an absolute magnitude of the third order nonlinear refraction coefficient of the investigated substance. It allows the simultaneous measurement of both the third order nonlinear refractive index and nonlinear absorption coefficient. The basic idea behind the Z-scan technique is the self-focusing or self-defocusing [4, 5]. The study of nonlinear refraction by the Z-scan method is based on the intensity dependence of the investigated thin sample along a focused Gaussian laser beam. The sample causes additional focusing due to the positive nonlinear refraction or the defocusing due to a negative refraction.

A Gaussian beam is focused by a spherical lens onto the sample and the variation in the beam profile is observed at the far field as the sample is taken through the focus of the lens. The beam propagation direction is taken as the *Z* direction and the sample is moved along that direction, and, hence this technique is

known as the Z-scan technique. By properly monitoring the transmittance change through a small aperture placed at the far field position (closed aperture), one is able to determine the amplitude of the phase shift. By moving the sample through the focus and without placing an aperture at the detector (open aperture), one can measure the intensity dependent absorption as the change of the transmittance through the sample. When both methods (closed and open ones) are used for the measurements, the ratio of the signals determines the nonlinear refraction in the sample.

Since the BMZ has a reasonable absorption at 632 nm, the Z-scan experiments were performed using a CW laser beam of a (SHG) He-Ne at 632.8 nm [7]. A lens of focal length 12 cm was used to focus the laser beam on the sample. The spot size of the laser beam at the focus was calculated and it was found to be 42.62 μm. The corresponding Rayleigh length which is related to the laser parameters used was calculated as 9.0170 mm. This satisfies the critical condition $Z_R>>L$ (where Z_R is the Rayleigh length and L is the sample thickness). Thus, the sample thickness of 0.004 mm was less than the Rayleigh length, it could be treated as a thin medium. The schematic diagram of the experimental setup used is shown in Fig. 5.4. The transmission of the beam through an aperture placed in the far field was measured using a photo detector fed to the digital power meter. For an open aperture Z scan, a lens to collect the entire laser beam transmitted through the sample replaced the aperture. The experiments were performed at room temperature.
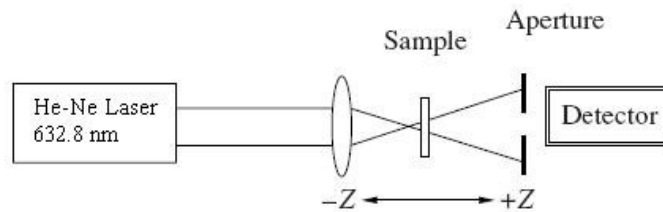
Fig. 5.4 *Schematic diagram of Z – Scan setup*

5.6.2 Results

The third-order nonlinear refractive index and the nonlinear absorption coefficient were evaluated for BMZ thin film from the optimized experimental condition (0.2 M, 60°C) by the Z-scan measurements. Figure 5.5 shows the Z-scan of a benzimidazole (BMZ) film. The enhanced transmission near the focus is suggestive of the two photon absorption at a high intensity. The focusing effect shown in Fig. 5.5a is due to the thermal nonlinearity resulting from the absorption of radiation at 632.8 nm. A spatial distribution of the temperature in the crystal surface is produced due to the localized absorption of a tightly focused beam propagating through the absorbing sample (crystal) medium. Hence, a spatial variation of the refractive index is produced, which acts as a thermal lens resulting in the phase distortion of the propagating beam.

The difference between peak and valley transmission (ΔT_{p-v}) can be written in terms of the on-axis phase shift $|\Delta\phi_0|$ at the focus as

$$(\Delta T_{p-v}) = 0.406 \, (1-S)^{0.25}|\Delta\phi_0|$$

where S is the aperture linear transmittance and can be calculated using the relation

$$S = 1-\exp\left(-2r^2_a/w^2_a\right).$$

Here, r_a is the aperture radius and w_a is the beam radius at the aperture. The nonlinear refractive index is given by the relation

$$n_2 = \frac{\Delta\phi_0}{KI_0 L_{eff}}$$

where $K = 2\pi/\lambda$ (λ is laser wavelength), I_0 is the intensity of the laser beam at the focus (Z = 0), $L_{eff} = [1-\exp(-\alpha L)]/\alpha$ is the effective thickness of the sample, α is the linear absorption coefficient, and L is the thickness of the sample.
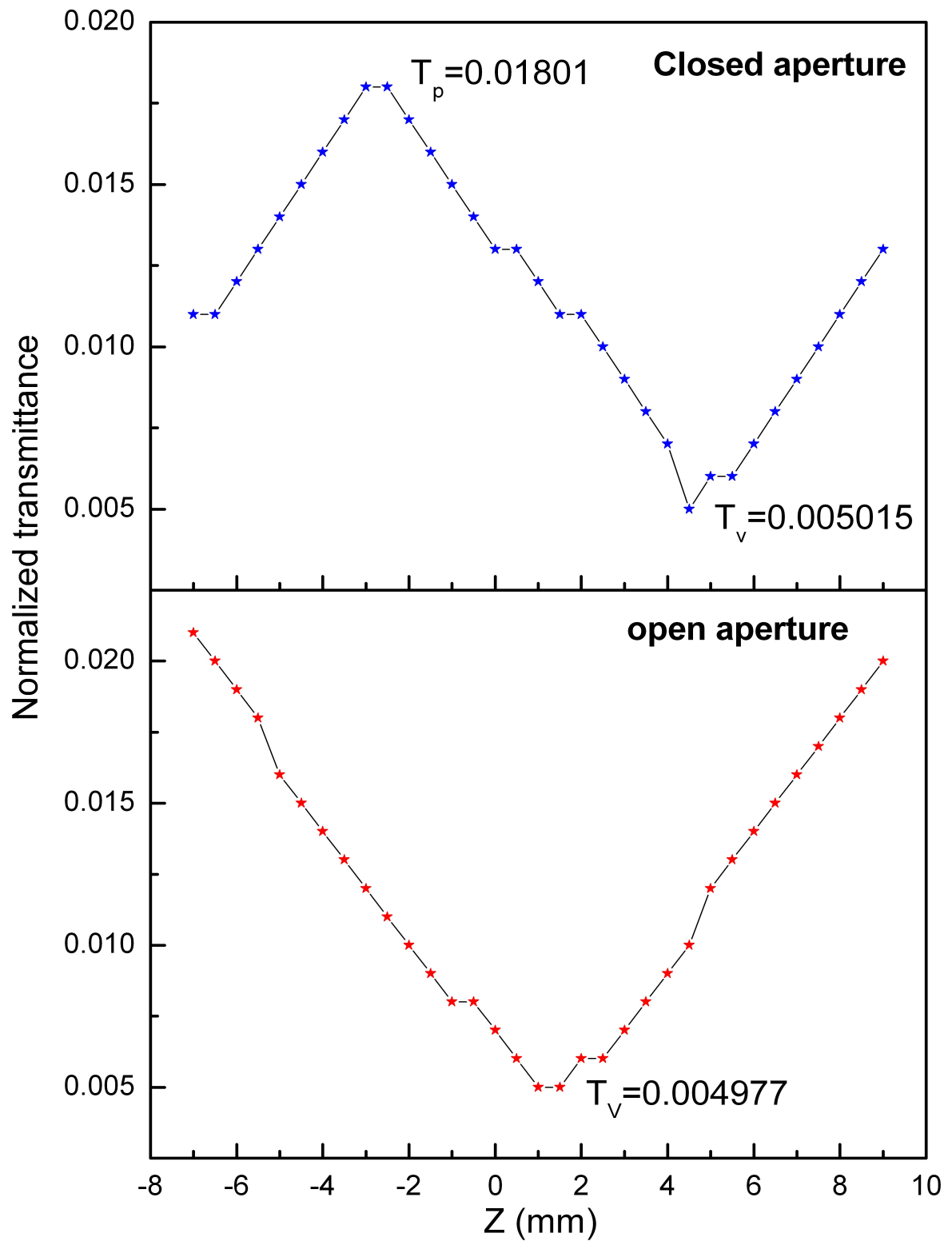
Fig. 5.5 (a) *Open aperture Z – Scan of BMZ* **(b)** *Closed aperture Z – Scan of BMZ*

From the open aperture Z – scan values, the nonlinear absorption coefficient can be estimated using the relation

$$\beta = \frac{2\sqrt{2}\Delta T}{I_0 L_{eff}}$$

where ΔT is the one-peak value at the open aperture Z – scan curve. The β value will be negative for the saturable absorption and positive for two-photon absorption. The real and imaginary parts of the third-order nonlinear optical susceptibity $\chi^{(3)}$ are defined as

$$\text{Re } \chi^{(3)} \text{ (esu)} = 10^{-4} \frac{\varepsilon_0 C^2 n_0^2 n_2}{\pi} \text{ (cm}^2/\text{W)}$$

$$\text{Im } \chi^{(3)} \text{ (esu)} = 10^{-2} \frac{\varepsilon_0 C^2 n_0^2 \lambda \beta}{4\pi^2} \text{ (cm}^2/\text{W)}$$

where ε_0 is the vacuum permittivity, n_0 is the linear refractive index of the sample, and C is the velocity of light in vacuum.

Table. 5.1 summarises the measurement details and results of the Z – scan measurements for benzimidazole thin films. The calculated value of the nonlinear refractive index n_2 for BNZ is (2.3764 X 10^{-10}) cm^2/W, nonlinear absorption coefficient (β) is (2.084) cm/W and third-order nonlinear susceptibility $\chi^{(3)}$ is 7.048 X 10^{-8} esu. The nonlinear absorption can be ascribed to two-photon absorption process and the nonlinear refraction leads to focusing in the film.

Table. 5.1 *Measurement details and the results of the Z-scan measurement*

Laser beam wavelength (λ)	632.8 nm
Lens focal length (*f*)	12 cm
Optical path distance (*Z*)	211 cm
Spot-size diameter in front of the aperture ω_0	42.629 μm
Aperture radius r_a	0.5 mm for open &
	0.25 mm for closed
Incident intensity at the focus at ($Z = 0$)	3.505 KW/ cm^2
Effective thickness L_{eff} of the sample	3.8 mm
Linear absorption coefficient (α)	2.58 X 10^5
Linear refractive index (n_0)	1.607
Nonlinear refractive index (*n*2)	2.376 X 10^{-10} cm^2/W
Nonlinear absorption coefficient (β)	2.084 cm/W
Real part of the third-order susceptibility [Re(χ^3)]	1.55 X 10^{-8} esu
Imaginary part of the thirdorder susceptibility [Im(χ^3)]	6.874 X 10^{-8} esu
Third-order nonlinear optical susceptibility (χ3)	7.048 X 10^{-8} esu

5.6 Summary

The deposited BMZ thin films were studied by various characterization studies. From the mass gravimetric method the thickness of the films were found

to be ~ 400 μm. From the XRD pattern it is found that the film possesses orthogonal crystal structure and the average grain size was calculated. The optical transmittance of benzimidazole thin film increases with increasing solution temperature. Optical band gap value of the material is found to be varied from 3.7 to 3.84 ev with respect to the solution temperature. Third-order nonlinear optical properties of the benzimidazole thin films were studied by the Z-scan technique using a He-Ne laser at 632.8 nm.

The measured nonlinear refractive index (n_2), nonlinear absorption coefficient (β) and third-order susceptibility (χ^3) were 2.3764 X 10^{-10} cm^2/W, 2.084 cm/W, 7.048 X 10^{-8} esu respectively. It is evident from the β value; the nonlinear absorption is due to the two-photon absorption process, while the nonlinear refraction leads to the self-focusing. Thus, it is found that the Benzimidazole thin films are new entrant for third order nonlinear optical applications.

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