

## **An Investigation of Chalcone Derivatives as Organic Nonlinear Optical Materials**

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### **ABSTRACT**

*Non-linear optics deal with the materials where the polarization is proportional to the field and the susceptibility starts depending on the field. This occurs as a consequence of the modification of the optical properties of a material system by the presence of light. There are inorganic as well as organic materials show nonlinear optical effects. Suitability of materials for nonlinear phenomenon depends upon several factors like high SHG efficiency and figure of merit, optical transparency, surface morphology etc along with the architectural flexibility for molecular design, ease of synthesis, low production cost and ability to process into large size single crystals. Chalcones are a group of compounds widely distributed in plants. Chalcone derivatives offer a larger variety of structures, the possibility of high environmental stability, and a diversity of electronic properties by virtue of the substituent functional groups. The purpose of current paper is to investigate chalcone derivatives as organic nonlinear materials.*

**KEYWORDS-** *Nonlinear optics, NLO, nlo materials, Organic NLO materials, Chalcone derivativs, SHG, frequency doubling*

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### **I. INTRODUCTION**

Nonlinear optics is the study of the phenomena that occur as a consequence of the modification of the optical properties of a material system by the presence of light [1-6]. It deals with the interactions of applied electromagnetic fields in various materials to generate new electromagnetic field altered in phase, frequency, amplitude or other physical properties. Nonlinear optics is gaining attention due to its wide application in the area of laser technology, optical communication and data storage technology [7-9]. An NLO material is a compound in which a nonlinear polarization is invoked on application of an intense electric field. The intense electric field results from the external application of an intense laser-source. The nonlinear material is different from the other linear materials in several aspects. [10-13]

In linear materials, the response is always proportional to the stimulus. The induced polarization is proportional to the field and the susceptibility is independent of the field. In practice, this is always the case at low fields. However at high fields, the polarization is proportional to the field and hence the susceptibility starts depending on the field.

In non-linear optics, at high intensity, the graph representing the dependence of optical polarization on the light field amplitude has curvature and deviates from straight line. One of the obvious requirements for a non-linear crystal is that it should have excellent optical quality. This means that for new materials, for which single crystal specimens are not available, it is necessary to grow single crystal specimens of optical quality [14-15]. Thus in many cases the search for new and better NLO materials is very largely a crystal growing effort. It is realized that the requirements on optical quality for a useful NLO material are more stringent than even the most exciting requirements on optical quality for materials used in linear optics.

### **THEORETICAL EXPLANATION OF NONLINEAR OPTICS**

The explanation of nonlinear effects lies in the way in which a beam of light propagates through a solid. The nuclei and associated electrons of atoms in the solid forms an electric dipole. The electromagnetic radiation interacts with these dipoles causing them to oscillate which, by the classical laws of electromagnetism, results in the dipoles themselves acting as sources of electromagnetic radiation. If the amplitude of vibration is small, the intensity of the incident radiation increases the relationship between irradiance and amplitude of vibration becomes nonlinear resulting in the generation of harmonic in the frequency of radiation emitted by the oscillating dipoles. Thus, frequency doubling or second harmonic generation (SHG) and indeed higher order frequency effect occurs as the incident intensity is increased. In a nonlinear medium, the induced polarization is a nonlinear function of the applied field. A medium exhibiting SHG is a crystal composed of molecules with asymmetric charge distributions arranged in the crystal in such a way that a polar orientation is maintained throughout the crystal.

A linear dielectric medium is characterized by a linear relation between the polarization density and the electric field,  $P = \epsilon_0 \chi E$  where  $\epsilon_0$  is the permittivity of free space and  $\chi$  is the electric susceptibility of the

medium. A nonlinear dielectric medium, on the other hand, is characterized by a nonlinear relation between P and E, as illustrated in Figure 1

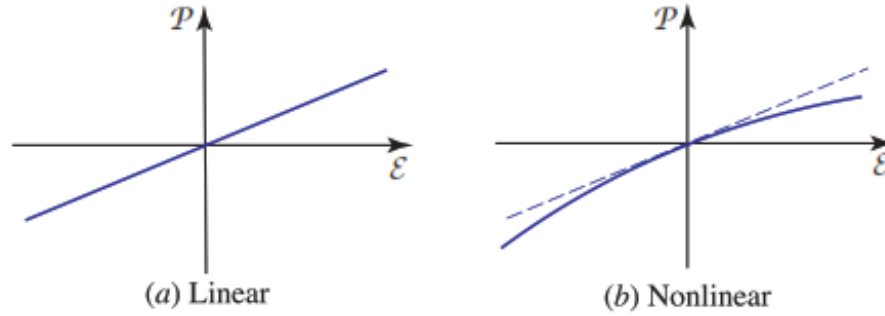


Figure 1: Illustration of linear and non-linear process

The nonlinearity may be of microscopic or macroscopic origin. The polarization density  $P = Np$  is a product of the individual dipole moment  $p$  induced by the applied electric field  $E$  and the number density of dipole moments  $N$ . The nonlinear behavior may reside either in  $p$  or in  $N$ .

The relation between  $P$  and  $E$  is linear when  $E$  is small, but becomes nonlinear when  $E$  acquires values comparable to inter-atomic electric fields, which are typically  $10^7$  to  $10^{10}$  V/cm. This may be understood in terms of a simple Lorentz model in which the dipole moment is  $P = -ex$ , where  $x$  is the displacement of a mass with charge  $e$  to which an electric force  $eE$  is applied. If the restoring elastic force is proportional to the displacement (i.e., if Hooke's law is satisfied), the equilibrium displacement  $x$  is proportional to  $E$ . In that case  $P$  is proportional to  $E$  and the medium is linear. However, if the restoring force is a nonlinear function of the displacement, the equilibrium displacement  $x$  and the polarization density  $P$  are nonlinear functions of  $E$  and, consequently, the medium is nonlinear. The situation is similar to the time dynamics of an anharmonic oscillator model describing a dielectric medium with the application of electric field. Another possible origin of a nonlinear response of an optical material to light is the dependence of the number density  $N$  on the optical field. An example is provided by a laser medium in which the number of atoms occupying the energy levels involved in the absorption and emission of light are dependent on the intensity of the light itself. Since externally applied optical electric fields are typically small in comparison with characteristic interatomic or crystalline fields, even when focused laser light is used, the nonlinearity is usually weak. The relation between  $P$  and  $E$  is then approximately linear for small  $E$ , deviating only slightly from linearity as  $E$  increases. Under these circumstances, the function that relates  $P$  to  $E$  can be expanded in a Taylor series about  $E = 0$ ,

$$P = a_1E + \frac{1}{2}a_2E^2 + \frac{1}{6}a_3E^3 + \dots \dots \dots (1)$$

The coefficients  $a_1$ ,  $a_2$  and  $a_3$  are the first, second, and third derivatives of  $P$  with respect to  $E$ , evaluated at  $E = 0$ . These coefficients are characteristic constants of the medium.

The first term, which is linear, dominates at small  $E$ . Clearly,  $a_1 = \epsilon_0\chi$ , where  $\chi$  is the linear susceptibility, which is related to the dielectric constant and the refractive index of the material by  $n^2 = \frac{\epsilon}{\epsilon_0} = 1 + \chi$ .

The second term represents a quadratic or second-order nonlinearity, the third term represents a third-order nonlinearity, and so on. It is customary to write above equation as

$$P = \epsilon_0\chi E + 2dE^2 + 4\chi^{(3)}E^3 + \dots \dots \dots (2)$$

Equation 2 provides the essential mathematical characterization of a nonlinear optical medium. Material dispersion, inhomogeneity and anisotropy have not been taken into account for the sake of simplicity and to enable us to focus on the essential features of nonlinear optical behavior. In centrosymmetric media, which have inversion symmetry so that the properties of the medium are not altered by the transformation  $r \rightarrow -r$ , the  $P$ - $E$  function must have odd symmetry, so that the reversal of  $E$  results in the reversal of  $P$  without any other change. The second-order nonlinear coefficient  $d$  must then vanish, and the lowest order nonlinearity is of third order. Typical values of the second-order nonlinear coefficient  $d$  for dielectric crystals, semiconductors, and organic materials used in photonics applications lie in the range  $d = 10^{-24} - 10^{-21}$  (cm/V<sup>2</sup> in MKS units). Typical values of the third-order nonlinear coefficient  $\chi^{(3)}$  for glasses, crystals, semiconductors, semiconductor-doped glasses, and organic materials of interest in photonics are in the vicinity of  $\chi^{(3)} = 10^{-34} - 10^{-29}$  (cm/V<sup>3</sup> in MKS units).

**Table 1: Optical effects of nonlinear materials**

Susceptibility	Effects	Application
$\chi^{(1)}(\omega = \omega)$	Refraction	Lenses, Optical fibers
$\chi^{(2)}(2\omega = \omega + \omega)$	Frequency doubling	Second harmonic generation
$\chi^{(2)}(\omega_c = \omega_a + \omega_b)$	Frequency mixing	Frequency up converters, Optical parametric oscillators, Spectroscopy
$\chi^{(2)}(\omega = \omega + 0)$	Electro-optic effect	Q-Switching, Modulators, Beam deflectors
$\chi^{(3)}(3\omega = \omega + \omega + \omega)$	Frequency tripling	Third harmonic generation, Spectroscopy
$\chi^{(3)}(\omega = \omega + 0 + 0)$	DC Kerr Effect	Variable Phase retarder
$\chi^{(3)}(\omega_a = \omega_a + \omega_b - \omega_b)$	AC Kerr Effect, Optical Kerr Effect, Raman scattering, Brillouin scattering	Fast switching, Time resolved experiments, Generation of different wavelengths
$\chi^{(3)}(\omega = \omega + \omega - \omega)$	Intensity dependent refractive index, Self focusing, Phase conjugation	Optical limiters, optical bi-stability, Real time holography

Above equation can also be represented as

$$P = \epsilon_0(\chi E + \chi^{(2)}E^2 + \chi^{(3)}E^3 \dots \dots \dots) \quad (3)$$

where  $\chi(2)$ ,  $\chi(3)$  ... are the nonlinear susceptibilities of the medium give rise to certain optical effects.  $\chi(1)$  is the linear term responsible for material's linear optical properties like, refractive index, dispersion, birefringence and absorption.  $\chi(2)$  is the quadratic term which describes second harmonic generation in non-centrosymmetric materials.  $\chi(3)$  is the cubic term responsible for third harmonic generation, stimulated Raman scattering, phase conjugation and optical bi-stability. Hence, the induced polarization is capable of multiplying the fundamental frequency to second, third and even higher harmonics. Various susceptibility functions and frequency arguments with their applications in various fields are given in Table 1.

### NONLINEAR OPTICAL MATERIALS

NLO materials play a major role in nonlinear optics and in particular they have a great impact on information technology and industrial applications. In the last decade, however, this effort has also brought its fruits in applied aspects of nonlinear optics. This can be essentially traced to the improvement of the performances of the NLO materials. The understanding of the nonlinear polarization mechanisms and their relation to the structural characteristics of the materials has been considerably improved. The new development of techniques for the fabrication and growth of artificial materials has dramatically contributed to this evolution. Optical solitons, optical switching and memory by NLO effects, which depend on light intensity, are expected to result in the realization of crucial optical devices in optical fiber communication (OFC) and optical computing which make the maximum use of light characteristics such as parallel and spatial processing capabilities and high speed [16,17]. The goal is to find and develop materials presenting large nonlinearities and satisfying at the same time all the technological requirements for applications such as wide transparency range, fast response, high damage threshold but also processability, adaptability and interfacing with other materials [18-21].

There are different ways to classify NLO materials. The criteria can be the order of nonlinearity, the nature of the NLO interaction involved, or some characteristics of the materials. The corresponding nomenclatures are nth order, passive or active (non-resonant or resonant), organic or inorganic, crystalline or amorphous NLO materials.

Many organic and inorganic materials are highly polarizable and thus are good candidates for study. However, the net polarization of a material depends on its symmetry properties, with respect to the orientation of the impinging fields. It can be shown that the odd order terms in equation are orientation independent, but the even terms vanish in a centro-symmetric environment. Thus materials for second order NLO must be orientationally noncentrosymmetric. But no such restriction applies to third order materials.

### Material Requirements of NLO

In the initial stages, material scientists working on novel nonlinear optical materials had given importance only to the optical nonlinearity, without worrying much about the other properties. However, it was understood later that high conversion efficiency alone was not sufficient for any device fabrication. Other intrinsic and extrinsic parameters should also be specified for comparison of different nonlinear optical crystals. The elastic constants and mechanical properties like fracture toughness and micro hardness can be specified. The physico-chemical properties that are worth considering for the presence of ferroelectric phase transitions which may lead to domain formation, compositional inhomogeneity, melting point and resistance to moisture. Thermal expansion of the crystals can play considerable role in laser damage threshold especially in high average power applications [22-26].

Second order NLO materials have wide variety of applications in frequency doubling, parametric amplification, parametric oscillation, frequency up conversion, difference frequency generation etc. It is a challenging task to arrange the molecules in a non-centrosymmetric structure with molecules arranged in head-to-tail fashion. To have such an arrangement of molecules in crystal structure one requires a very sound knowledge of crystal engineering to design molecules for SHG applications as well as combination of chemical intuition and theoretical understanding of intermolecular hydrogen bonding forces.

Third order NLO materials finds applications in optical switching, optical data processing, optical communications, optical logic gates, nonlinear spectroscopy, coherent UV-light generation, optical limiting, passive laser mode-locking, waveguide switches and modulators. For generating UV-light through third harmonic generation (THG) one requires optical transparency of the materials in that region [27-28].

For optical switches, the molecules should show ultra fast NLO response while for optical limiting applications a material should have low optical absorption at low intensities of laser light and high optical absorption at high intensities of laser light. The inorganic materials are largely used to generate the frequencies of coherent light which are in the UV region. The major advantage of these materials is the transparency that allows one to obtain a coherent UV radiation by THG. In general, an ideal NLO material should possess the following characteristics:

- ✓ Ease of synthesis and low production cost
- ✓ Architectural flexibility for molecular design
- ✓ Ability to process into large size single crystals / thin films
- ✓ Ability to tune the surface morphology
- ✓ High SHG efficiency and figure of merit
- ✓ Wide optical transparency
- ✓ High thermal stability
- ✓ High mechanical strength
- ✓ Phase-match in the entire transparency range
- ✓ Ultra fast response
- ✓ High laser damage resistance

The entire set of above requirements is not yet fulfilled by any of the single crystals developed so far. Therefore, there is a need to search for new materials that can simultaneously fulfill most of the above requirements.

**Table 2: Factors for selecting a NLO crystal**

<b>Laser Parameters</b>	<b>Crystal Parameters</b>
Lasing wavelength(s)	Transmittance of Crystal
NLO Process	Phase-Matching Type and Angle
Power or Energy	Damage Threshold, effective nonlinear optical coefficient
Divergence	Acceptance Angel
Bandwidth	Spectral Acceptance
Beam Size	Crystal Size, Walk-Off Angle
Pulse Width	Group Velocity Mismatching
Repetition Rate	Damage Threshold
Environment	Temperature Acceptance, Moisture

### **Inorganic Materials**

These are covalent and ionic bulk materials where the optical nonlinearity is a bulk effect. The examples of this type of materials are inorganic systems, semi conductors and inorganic photorefractive crystals. InSb has one of the largest known  $\chi^{(2)}$ , but being a semiconductor, it is highly absorbing in the visible region of the spectrum and is therefore not useful for many applications. LiNbO<sub>3</sub> is the most extensively studied material for device applications involving the linear electro-optic effect, but it suffers from degradative photorefractive effects which restrict its use in various applications. Potassium dihydrogen phosphate (KDP) has been used widely for phase matched SHG of high-powered near-IR lasers.

In early days of the development of second order NLO materials, most of the materials studied for the NLO applications were inorganic crystals such as quartz, potassium dihydrogen phosphate (KDP), lithium niobate (LiNbO<sub>3</sub>), and its analogues, potassium titanyl phosphate (KTP) and its analogues, Beta Barium Borate and semiconductors such as cadmium sulfide, selenium, and tellurium. Many of these materials have been successfully used in commercial frequency doublers, mixers and parametric generators to provide coherent laser radiation with high frequency conversion efficiency in the new region of the spectrum inaccessible by other nonlinear crystal conventional sources. After that various borate crystals including  $\beta$ -BaB<sub>2</sub>O<sub>4</sub> (BBO), LiB<sub>3</sub>O<sub>5</sub> (LBO), Sr<sub>2</sub>B<sub>2</sub>Be<sub>2</sub>O<sub>7</sub> (SBBO), BiB<sub>3</sub>O<sub>6</sub> (BiBO) and the latest Ca<sub>4</sub>LnO(BO<sub>3</sub>)<sub>3</sub> (CLnOB, where Ln = Gd,

La, Y) have been reported as promising NLO crystals. The family of various borate crystals thus plays a very important role in the field of nonlinear optics

Single crystals of inorganic materials were found to have moderate SHG efficiency, wide transparency, chemical inertness, thermal and mechanical stability, high laser damage threshold, and they were adopted for developing NLO devices. The classical inorganic materials often used for frequency doubling applications are potassium dihydrogen phosphate (KDP), ammonium dihydrogen phosphate (ADP), deuterated potassium dihydrogen phosphate (DKDP), cesium lithium borate (CLBO) and potassium niobate (KN). Inorganic crystals are ionic bonded, hence it is easier to synthesize. However, inorganic crystals encountered a 'trade-off' problem between response time and magnitude of optical nonlinearity. High temperature oxide materials are studied for device application like piezoelectric, ferroelectric and electro-optics. To date, only few inorganic solids, such as LiNbO<sub>3</sub> and KH<sub>2</sub>PO<sub>4</sub>, have traditionally been the NLO materials of choice

### **Organic nonlinear optical materials**

Organic materials are molecular materials that consist of chemically bonded molecular units interacting in the bulk media through weak van der Waal interactions. Organic materials are emerging as an alternative to inorganic materials because of their low cost, ease of fabrication and integration into devices, and intrinsic tailorability which allows one to fine tune the chemical structure and properties for a given NLO process. The organic materials possess low dielectric constants, inherent synthetic flexibility, high optical damage thresholds, and large NLO response over a broad frequency range comparable to those of inorganic materials. The NLO property of these molecule-based materials is governed by the NLO characteristics of the constituent individual molecular chromophores. It is observed that chromophores containing donor (D) and acceptor (A) substituent linked through an intervening  $\pi$ -backbone shows larger NLO response [29-35].

Conjugated D-A substituted organic molecules exhibit noticeable NLO and electro-optical effects. Such materials can be used to double or triple the frequency of laser light and are of considerable interest for the high-speed processing of data, which is essential for numerous modern technologies like optical computing and optical telecommunication systems. Generally D-A substituted compounds, where D and A are separated by an aromatic spacer group, represents the basis for all organic NLO compounds.

The conjugated  $\pi$  electron system provides a pathway for the entire length of conjugation under the perturbation of an external electric field. Fictionalization of both ends of the  $\pi$  conjugated system with appropriate electron donor and acceptor groups can increase the asymmetric electronic distribution in either or both the ground and excited states, thus leading to an increased optical non-linearity. When acceptor and donor moieties are placed at terminal position of conjugated backbone, both linear and nonlinear optical properties have increased significantly which involves correlated and high delocalized  $\pi$  electron states. The magnitudes of molecular polarizability and hyperpolarizability coefficients are found to increase super linearly with an increase in conjugation length between the donor and the acceptor. The strength of donor and acceptor groups and order of their stacking along the backbone plays important roles in determining the magnitude of nonlinear optical efficiency. The optical nonlinearity of organic molecules can be enhanced by adding strong electron donating and withdrawing entities as well as optimizing the distance between D and A. This generates a highly polarizable charge transfer compound with an asymmetric electron distribution. Charge separation produces internal electric fields, which locally alter the refractive index through the second-order optical nonlinearity.

A typical SHG active molecule is shown in Figure 2. The groups listed on the left side of the  $\pi$ -conjugation bridge are electron donors and those listed on the right side are electron acceptor groups.



**Figure 2: Structure of a typical SHG active molecule.**

The combination of electron donor / acceptor works only when they have non-centrosymmetric crystal structure. Generally, the materials which possess inversion symmetry do not show SHG efficiency. As a consequence the crystallographic non-centrosymmetry requirement rejects many of the materials from being SHG active. Therefore, it is more important to introduce non-centrosymmetry in materials to make them SHG active. The D- $\pi$ -A molecular systems show large NLO responses because of the delocalized nature of the  $\pi$ -electrons resulting in low-energy excitons with high oscillator strength. However, these dipolar molecules tend

to pack in an anti-parallel arrangement in the crystal structure and usually crystallize in centrosymmetric class and therefore the SHG response in these systems becomes zero. The best examples for dipolar organic NLO system are nitroaniline derivatives. Zyss et al. reported the first hyperpolarizability of p-nitro aniline (PNA).

In spite of theoretical efforts, there is still no reliable way to predict first or even second order hyperpolarizabilities of organic DA compounds. There is great demand for non-centrosymmetric molecular crystals with large second order nonlinearities and with wide transparency range between the highest vibrational and lowest electronic transitions. The latter requirement is very restrictive to organic molecules and excludes the majority of them for further consideration in nonlinear optics. Among the remaining ones, a large proportion is also excluded because they cannot form stable non-centrosymmetric crystals. This is mainly because asymmetric molecules most frequently carry a dipole moment in their ground electronic state and in order to reduce the dipole-dipole interaction, which is dominant over the van der Waals in the lattice, a head to tail anti-parallel configuration will be favored when forming the crystal most frequently resulting in centrosymmetric crystalline structures and consequently vanishing  $\chi^{(2)}$  unless certain precautions are taken to prevent this from happening.

In case of organic crystals, two requirements are satisfied:

- They are made of highly polarizable molecules or the so-called conjugated molecules, where highly delocalized  $\pi$ -electrons can easily move between electron donor and electron acceptor groups on opposite sides of the molecule, inducing a molecular charge transfer,
- The molecules are adequately packed to build up a non-centrosymmetric crystal structure that provides non-vanishing second-order nonlinear coefficients.

A vast majority of organic NLO crystals have their absorption in the blue light region and some of them have their cut-off wavelength exceeding 450 nm. This indicates the possibility of reduced conversion efficiency of second order harmonic generation due to self-absorption of materials while using a semiconductor laser with 800 nm band. Ideally, the perfect organic material would be one which has a high efficiency, a very low absorption edge cut-off (to allow access into the UV), a high damage threshold and finally has favorable crystal growth properties. The enhancement in nonlinearity of organic materials in comparison to inorganic materials arises due to the existence of  $\pi$  electrons in the organic materials. Large second-order optical nonlinearity originates from organic conjugated molecules having an electron acceptor group at one end a donor group at the opposite end.

## II. CONCLUSION

Chalcones are a group of compounds widely distributed in plants. Naturally occurring chalcone and their synthetic analogs are capable of showing second and third order non-linear optical properties. Chalcone derivatives offer a larger variety of structures, the possibility of high environmental stability, and a diversity of electronic properties by virtue of the substituent functional groups. Chalcone possesses particular  $\pi$ -conjugated systems linking with donor (D) and an acceptor (A) group show large NLO response due to an increasing charge transfer possibility between the  $\pi$ -conjugated aromatic rings. Intramolecular charge transfer (ICT) is the characteristics of these molecules. In consequence of this, the large dipole moments, polarizability and molecular hyperpolarizabilities are associated with these molecules. Hence, the chalcone and their derivatives are found to be very useful material for the applications where the NLO properties play a vital role.

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