CHAPTER - VIII

SUMMARY AND SUGGESTIONS FOR FUTURE WORK

Nonlinear Optical (NLO) phenomena are potentially useful in the context that they have the ability to alter the frequency of light and to amplify one source of light with another, switch it or alter its transmission characteristics through a medium, depending on its intensity. The common thread running through the applications is the need for a powerful, compact, rugged, inexpensive source of laser light in the blue-green region of the electromagnetic spectrum. The generation of coherent blue-green light through second harmonic generation (SHG) from near infra-red (NIR) laser is an important technological problem that has attracted much attention. Potential applications of this technology include high-density optical data storage, high resolution printing, spectroscopy inspection, biomedicine and others.

At the same time, with the advent of optical detectors and sensors which are used for scientific and industrial purposes, there is a need for using optical limiting devices that protect the photosensitive components from intense optical radiation. Such NLO materials are passive devices and are referred as intelligent or smart materials owing to sensing, processing and actuating functions that are inherent in them. The low threshold of these materials for nonlinear response is of much importance as they can be used for protecting the human eye from the enfeebling laser effects as the maximum permissible exposure for human eyes even with a laser pointer is \( \sim 2.5 \text{ mW/cm}^2 \) in the visible spectral region. For the past two decades, extensive research works have been carried out for identifying such materials.
Based on this, an attempt was made to study the synthesis and growth of single crystals of certain phenolate based organic and metal organic materials for nonlinear optical applications. In the present study a series of novel organic NLO materials (EDA-X, X= 2NP, 3NP, 4NP) such as Ethylenediamminium di(2-nitrophenolate) (EDA2NP), Ethylene diamminium di(3-nitrophenolate) (EDA3NP) and Ethylenediamminium di(4-nitrophenolate) (EDA4NP) were studied to understand the influence of position of the functional groups in the phenyl ring. Also to understand the contribution of Group I metal ion in bringing the NLO properties, another series of semi-organic NLO materials (M-PNP, M= Li, Na, K) such as Lithium p-nitrophenolate trihydrate (LPNP), Sodium p-nitrophenolate dihydrate (SPNP) and Potassium p-nitrophenolate monohydrate (PPNP) were studied. The fundamental characteristics such as structural, functional, thermal, optical and nonlinear optical properties have been examined. The second harmonic generation capability and optical limiting capacity were studied in detail.

The organic NLO materials of interest such as EDA2NP, EDA3NP and EDA4NP were synthesized successfully by proton transfer reaction using ethylenediamine and nitrophenol (ortho, meta and para) as starting materials respectively. Metal organic salts such as LPNP, SPNP and PPNP were synthesised by acid base reaction using alkali hydroxide with p-nitrophenol. Solubility of the synthesised materials in various solvents was determined by gravimetric method. All the materials exhibit positive solubility temperature gradient. From the solubility curve, ethanol (EDA2NP, EDA3NP and EDA4NP), methanol (SPNP, PPNP) and water (LPNP) were chosen as solvents for crystal growth. By adopting slow evaporation method, brownish yellow single crystals of EDA2NP, EDA3NP, EDA4NP and pale yellow single crystals of LPNP, SPNP and PPNP were grown at room temperature. The reason for choosing methanol as solvent for metal organic p-nitrophenol materials (SPNP, PPNP) is that although the materials are highly
soluble in water, the crystals lose their transparency in a couple days after crystallization. Although several attempts have been made to grow EDA3NP crystals, the single crystal is not stable due to its hygroscopic nature.

The elemental analysis and the confirmation of molecular formula of the prepared compounds were carried out by CHN and ICP-AES elemental analyses. The molecular formulas of the prepared compounds were found to be C_{14}H_{18}N_{4}O_{6} • H_{2}O for EDA2NP, EDA3NP and EDA4NP and Li• (C_{6}H_{4}NO_{3}) •3H_{2}O, Na• (C_{6}H_{4}NO_{3}) •2H_{2}O, K• (C_{6}H_{4}NO_{3}) •H_{2}O for LPNP, SPNP, PPNP respectively. In all the samples, the presence of water molecule was observed and this may be due to the nature of phenolate ion. The presence of inorganic element (Group I metal ion M=Li, Na, K) was identified by the ICP-AES analysis. The computed values from its molecular structure show a good agreement with the measured values.

The various cell parameters and crystal structural properties of the grown crystals were studied by single crystal and powder X-ray diffraction analyses. EDA2NP and EDA4NP crystallize in orthorhombic and monoclinic system with space group Pccn and C2/c having four molecules in the unit cell. LPNP and SPNP belong to monoclinic and orthorhombic system with a non-centrosymmetric space group Pa and Ima2 respectively. At the same time, PPNP crystal belongs to the monoclinic system with a centrosymmetic space group P2_{1}/c. The structural characterization of semiorganic materials clearly show that the role of metal ion (Group I metal ion M=Li, Na, K) is crucial in bringing the noncentrosymmetry. Thus elements with small ionic radii and large electro negativity will favour noncentrosymmetric condition. It is interesting to note that elements in the complexes that are more electronegative induce more delocalization of electrons, favouring the noncentrosymmetric structure. This is the reason why, PPNP is centrosymmetric while LPNP and SPNP are noncentrosymmetric as the electronegativity
of alkali metals Li (0.98), Na (0.93) and K (0.82) fall down as one move down the Group I. From the X-ray powder diffraction study, the lattice parameters were determined and these values are in good agreement with the single crystal XRD values.

The FTIR and Laser Raman spectrum reveal the various modes of vibrations of different molecular groups present in the materials. NMR analysis confirmed the molecular structure of the compound in general as well as the presence of ring, alkene and alkane groups were identified in particular. It can be noted from the FTIR spectra of EDA-X series that the intermolecular hydrogen bonding network formed between hydrogen atoms of ethylenediamine of a cation and oxygen atoms of adjacent phenolate anions play an important role to achieve the desire molecular design. In the $^1$H NMR spectra of EDA-X series, the signal splitting is caused by spin–spin coupling between adjacent nuclei. The $^{13}$C NMR spectrum of M-PNP series shows a chemical shift in the low field region (ipso carbon) and identifies the protonation site of metal nitrophenolate. The presence of metals was also confirmed by the FTIR absorption spectra in the lower region (400-500 cm$^{-1}$). A broad intermolecular hydrogen bonded O–H stretching of p-nitrophenol is shifted to the higher frequency which increases the polarizable nature of p-nitrophenol to a higher order and it easily forms a metal coordination compound.

Thermal stability of the grown single crystals was estimated from thermo gravimetric (TG) differential thermal analysis (DTA) and differential scanning calorimetry (DSC) analysis. In all the samples, the material suffers a small weight loss before 120 °C, and it is due to the liberation of traces of physically adsorbed water molecules. In the EDA-X series, as the position of nitro group varies in the nitrophenol, the decomposition temperature also varies. EDA2NP decomposes before it starts melting at 150 °C, while EDA3NP and EDA4NP have their melting temperatures at 88 °C and 144 °C respectively. Similarly in the M-PNP series, the crystallised water shows a weight
loss and an endotherm peak before 120 °C. All the materials show a major weight loss before 350 °C, due to decomposition p-nitrophenolate into fragments and their subsequent volatilization. Hence all the materials are not subjected to phase transition till their dehydration state, which reveals that they possesses favourable thermal stability and they can be used for device applications. As expected the semiorganic nitrophenolates are thermally more stable compared to their organic nitrophenolates.

The linear optical properties such as transmittance, absorbance, reflectance, linear refractive index and optical band gap of the materials were studied with UV-Vis-NIR spectrum in the range of 200 and 2000 nm. For all the materials the cut-off wavelength and optical window range were found to be around 450 nm and 450-1200 nm respectively. In general, the absorption peaks of benzene are mainly observed around 200 nm. However, when it comes to nitrophenol, which has a hydroxyl group, due to substituent of nitro group, the absorption peaks are strongly red shifted. All the materials show a strong absorbance in the UV and IR region. In the case of EDA-X series, with respect to the position of nitro group, the absorbance maxima position varies. The material was found to reflecting in the entire visible region and is less reflection both in the UV and IR region. Addition of metal ion (sodium) modifies the optical transparency of the original molecule (p-nitro phenol) and consequently introduces a bathochromic shift of 90/40 nm in the crystal transparency.

The linear refractive index of the material was estimated from the reflectance data of the sample. The linear refractive index of EDA2NP, EDA3NP, EDA4NP, LPNP, SPNP and PPNP at 532 nm was estimated to be 1.36, 1.37, 1.38, 1.38, 1.37 and 1.36 respectively. The laser induced surface damage threshold of LPNP, SPNP, PPNP single crystals using a Q-switched Nd:YAG laser (532 nm, 5 ns) was found to be 60, 52, 16 MW/cm² respectively. Hence higher the laser damage, higher is the heat capacity and
thermal conductivity. It means that the dispersion of heat induced by the absorption of laser radiation in the materials strongly depends on the thermal diffusivity which leads to the occurrence of damage in the crystals. Although much strong variation in the linear optical properties of the materials were not observed, the mechanical and thermal stability of the material was found to be improved due to the incorporation of metal ions.

The powdered single crystals were imposed for SHG test by Kurtz powder technique using a Q-switched Nd:YAG laser (1064 nm, 10 ns, 10 Hz). The relative powder SHG efficiency of the material (EDA2NP) was found to be 0.8 times that of KDP. The optical nonlinearity arises due to strong charge delocalization between the oxygen and the phenolic ring, which is confirmed from the FTIR analysis of the compound. Hence as mentioned earlier, the conjugated base, thus formed has increased the molecular hyperpolarizability due to better electron donating character of phenolate O⁻ (Hammett coefficient $\sigma = -0.81$) than that of phenolic OH (Hammett coefficient $\sigma = -0.38$). As the value of second order susceptibilities of the KDP crystals at 1064 nm is about 1 pm/V and the optical second order susceptibilities of EDA2NP is observed to be about 0.8 pm/V. It is to be emphasized that for organic materials the principal role begins to play as the electron-phonon anharmonicities as well as the intrinsic defect states defining the efficiency of interaction among the particular molecular fragments forming the crystals. The SHG efficiency results of the material EDA3NP show a signal output of 14 mV with input laser power of 5.5 mJ/pulse when compared to 44 mV of KDP. SHG efficiency of EDA3NP is 0.3 times that of KDP.

The SHG test reveals that SPNP, LPNP exhibits SHG and no SHG signal was observed for PPNP. In SPNP and LPNP, metal atom is ionically bonded with p-nitrophenol introducing the noncentrosymmetry, which is an essential criterion for SHG. The results are compared with the pulverized KDP and the relative powder SHG
efficiency was found to be 9.25 and 5 times greater than KDP for LPNP and SPNP respectively. It is worthwhile to note that a material with smaller ionic radii has larger polarizability and hence larger nonlinear polarization. Thus LPNP with lowest ionic radii alkali (Li = 0.76 Å) metal has higher SHG efficiency than other alkali nitrophenolates. The intensity of SHG output as a function of particle size was measured. The SHG output of SPNP increases with respect to the range of particle sizes, indicating the phase matchable character of SPNP. While for LPNP, SHG output decreases with increase in particle size, showing the non-phase matchable nature of LPNP.

The nonlinear parameters of the samples under cw laser illumination is determined by the well known closed Z-scan set up formulated by Sheik-Bahae [SBF model] et al., using a diode-pumped Nd: YAG (532 nm, 50 mW) laser. The nonlinear response is related to the thermally induced nonlinear effects because the cw laser normally produces heating effect and the defocusing nonlinearity is due to laser heating process. The peak followed by a valley normalized transmittance obtained from the closed-aperture Z-scan data, indicates that the sign of refraction nonlinearity is negative i.e. self-defocusing. Self- defocusing effect is due to local variation of refractive index with temperature. The open aperture Z-scan data shows a maxima for normalized transmittance at the principal focus (Z = 0) and hence the observed nonlinear absorption coefficient is due to saturable absorption nature of the value. The third-order NLO (TONLO) properties such as nonlinear refractive indices, the nonlinear absorption coefficients, and the third-order susceptibilities of the samples dissolved in ethanol are presented in Table 8.1 for comparison.
Table 8.1 Comparison of nonlinear optical properties of EDA-X series and M-PNP series

<table>
<thead>
<tr>
<th>Parameters</th>
<th>EDA2NP</th>
<th>EDA3NP</th>
<th>EDA4NP</th>
<th>LPNP</th>
<th>SPNP</th>
<th>PPNP</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nonlinear refractive index (n_2) x 10^{-8} cm^2/W</td>
<td>-3.04</td>
<td>- 3.99</td>
<td>-5.46</td>
<td>-5.11</td>
<td>-7.76</td>
<td>-8.85</td>
</tr>
<tr>
<td>Nonlinear absorption coefficient (β) x 10^{-3} cm/W</td>
<td>-6.04</td>
<td>-6.11</td>
<td>-6.48</td>
<td>-7.41</td>
<td>-8.33</td>
<td>-9.27</td>
</tr>
<tr>
<td>Real part of third-order susceptibility [Re(χ^3)] x 10^{-6} esu</td>
<td>1.45</td>
<td>1.89</td>
<td>2.64</td>
<td>2.47</td>
<td>3.70</td>
<td>4.18</td>
</tr>
<tr>
<td>Imaginary part of third-order susceptibility [Im(χ^3)] x 10^{-6} esu</td>
<td>1.22</td>
<td>1.23</td>
<td>1.33</td>
<td>1.52</td>
<td>1.68</td>
<td>1.86</td>
</tr>
<tr>
<td>Third-order nonlinear optical susceptibility (χ^3) x 10^{-6} esu</td>
<td>1.89</td>
<td>2.25</td>
<td>2.96</td>
<td>2.90</td>
<td>4.06</td>
<td>4.58</td>
</tr>
<tr>
<td>Limiting Thershold (mW)</td>
<td>33</td>
<td>36</td>
<td>33</td>
<td>23</td>
<td>25</td>
<td>26</td>
</tr>
<tr>
<td>Clamping Value (mW)</td>
<td>6.6</td>
<td>7.91</td>
<td>8.5</td>
<td>3.9</td>
<td>4.4</td>
<td>5.1</td>
</tr>
</tbody>
</table>

As mentioned earlier, it is well known that the nonlinearity of the samples of interest basically originates from the organic part, nitrophenol and the stability is varied with respect to the position of nitro group and inorganic metal (Group I) part. Although the molecular structure appears to be the same in EDA-X series, the variation in nitro group position in the phenyl ring has brought the variation in nonlinearity. This is because the delocalization due to π electron cloud movement in the phenyl ring increases the
polarization and hence the samples have varying nonlinear response. Among the EDA-X series, EDA4NP possess a larger third-order nonlinear optical susceptibility than EDA2NP and EDA3NP. In case of M-PNP series, as one move down to the Group I from lithium to potassium, third-order nonlinear optical susceptibility increases. Thus PPNP has maximum third-order nonlinear optical susceptibility followed by SPNP, LPNP. Thus it can be inferred that metals with larger ionic radii and smaller electronegativity has enhanced optical susceptibility which is the most essential criteria for optical limiting applications. Hence, PPNP is more suitable for third order NLO applications such as optical limiters.

The transmitted output intensity was found to vary linearly with incident input intensities at very low input intensities but it starts to deviate at high incident intensities. With further increment of the input power, the transmitted intensity reaches a plateau and is saturated at a point defined as the limiting amplitude: i.e. the maximum output intensity, showing obvious limiting property. Thus at low incident powers, the output varies according to Beer’s law and beyond a limiting thershold, it becomes nonlinear. The optical limiting threshold and the corresponding output clamping value are presented in the table. For EDA-X series the optical limiting threshold was clamped between 33 – 36 mW and the corresponding output is clamped between 6.6 - 8.5 mW. While for M-PNP series the optical limiting threshold was clamped between 23 - 26 mW and the corresponding output is clamped between 3.9 - 5.1 mW.

In the present investigation, EDA2NP, EDA3NP, LPNP, SPNP were identified to be second harmonic generation active nonlinear optical materials. In particular, SPNP with five times efficiency that of KDP and phase matchable property can be used as a potential candidate for generation of short wavelength laser (Green) using the Q-switched Nd:YAG (1064 nm) laser. Although SHG efficiency of LPNP is found to be 9.25 times
that of KDP, due to the non-phase matchable capability, it cannot be effectively used for short wavelength generation. All these materials of interest show saturable absorption behaviour and self-defocusing nature. Hence these materials, dissolved in ethanol can be used as optical limiter for low-power cw lasers, as liquid media have certain specific advantages over solid media as limiters in terms of dissipation of high incident intensities through solvent heating and bubbling. As exposures to laser beams of even a few mW for a shorter duration of about 0.25s can cause permanent damage to the human eye, M-PNP series can be a potential candidate for low power optical limiting application in the 532 nm regime.

Hence, it can be concluded that nitrophenol is identified to be an excellent NLO chromophore for frequency doubling and optical limiting applications. Metal complexes nitrophenol are found to be more attractive than the organic derivatives of nitrophenol. Choosing the position of the nitrogroup in the phenyl ring and the ionic radii of metals are crucial parameters in bringing the nonlinearity of the material. Para nitrophenols are identified to be excellent chromophores for attaining the metal derivatives.

Apart from these studies, an attempt can be made to solve the hygroscopic problem of EDA3NP by changing the solvent/growth parameters/alternative methods like slow cooling. Phase matching angle of EDA2NP, EDA3NP, LPNP and SPNP may be measured to explore their suitability for nonlinear applications. Size of EDA2NP and EDA4NP crystals need to be improved in order to study the characteristics of device applications. The metal organic crystals were grown by conventional solution growth method. The unidirectional growth method can be adopted for the growth of metal organic crystals and the properties of the crystals grown from both methods can also be compared.
The concept of understanding the elements behaviour can be complete and more authentic when complexes based on the left out element of Group I (Rb, Cs, Fr) is taken into account. Also the work can be further extended on other positions of nitrophenols (ortho and meta). In such consideration, the model that has been framed will be complete for nitrophenol based systems. In succeeding ethylenediamminium nitrophenol part, the concept can be still challenging when propylenediamine is taken for consideration. As all the materials are highly transparent, the limiting behavior based on pulsed lasers will yield more interesting results for high speed optoelectronic applications. Research attempts on the limiting behaviour as a function of wavelength, particularly in UV regime, will yield more interesting results. Hence all such research attempts are left as path ways for the future work.