CHAPTER 8
Conclusions & Future Perspectives

8.1 Conclusions

The high intensities available from fs laser pulses makes the interaction of a fs pulse with the material it propagates through an interesting study, as the pulse itself affects and is affected by the material it propagates through in dramatic ways. Interactions representative of both of these classes form the subject of this thesis. Figure 8.1 shows the pictorial organization of the overview of the studies presented in this thesis.

Fig. 8.1: Overview of the studies presented in this thesis

8.1.1 Supercontinuum generation (SCG) in KDP:

In spite of voluminous literature available on the generation and application of SCG in various media, a more detailed scrutiny in this exciting field of research lead us to investigate in more detail the following aspects of SCG: (a) Several experimental studies revealed that for a particular medium there is a limit to the spectral extent of the attainable SCG with a high-frequency cutoff insensitive to pulse energy; (b) With the general assumption that polarization of the generated SC follows the incident pulse, it has been shown that at high input...
powers the SCG gets depolarized due to the formation of low density plasma. However, no report till date has ever dealt with the control of polarization properties of the SCG and hence research in this direction was relevant; and (c) Not much literature is available that discuss the role of media in exercising any control over SCG. Such a control is essential for fundamental understanding and improved SCG source generation.

In the thesis we addressed the above issues by our detailed studies of SCG in quadratic nonlinear media. Potassium Di-hydrogen Phosphate (KDP) crystal is studied as a potential SCG media. The intrinsic $\chi^{(3)}$ anisotropy of KDP was considered to achieve the desired control over SCG in KDP at different crystal orientations. Initial SCG studies were performed in a $z$-cut KDP crystal generated along its c-axis and all the general characteristics of SCG were observed. As an effort to study the SCG at other orientations of KDP we tried to generate SCG along the phase matching direction to achieve sum frequency generation and observed an enhancement in the bandwidth of the generated SC. The tunability in the blue region of the spectrum with angle due to wave-mixing between various frequencies present in the SCG and the residual fundamental was demonstrated. An enhanced bandwidth of supercontinuum spanning from 350 nm to 1300 nm was achieved. In addition, by employing arrangement of differently oriented crystals we demonstrated the generation of a spectrally flat SC.

As an effort to achieve desired control over the polarization properties of SCG at high input fundamental peak powers we performed a systematic study of depolarization of SC across its spectral range as a function of the femtosecond laser pump intensity for an anisotropic crystalline condensed medium, KDP crystal, and compare our results with commonly used supercontinuum generation materials namely BK-7 glass and BaF$_2$. Our results showed that at higher input power depolarization in the continuum increases for BK-7, BaF$_2$ and along the direction of the optic axis KDP crystal. However in case of KDP crystal we observe that the depolarization properties are strongly dependent on (i) the plane of polarization of incident light and (ii) the orientation of the crystal with respect
to the incident light. Our studies also confirmed that one can achieve SCG in a KDP crystal that maintains the same state of input polarization even at high input intensities when proper orientation of the crystal is used.

The motivation of pursuing SCG studies in KDP crystal was because the angular dependence of SCG in quadratic nonlinear media could help in one of the toughest challenges SCG experiments demand: *To control and generate the continuum with rich content in the spectral region we want with desirable optical properties.* The results presented above thus confirm our assertion making nonlinear crystalline media a promising candidate for SCG applications.

### 8.1.2 Enhanced third order nonlinearities at air-dielectric interfaces:

Breaking the inversion symmetry at any interface between two media causes structural asymmetry and local field variations across the interface. This leads to discontinuity in the normal component of the electric field and an induced nonlinear polarization containing high-order nonlinear susceptibility tensors. Several earlier theoretical and experimental studies focused on second harmonic generation (SHG) at the surfaces of different materials. Though third order NLO process are allowed in all materials independent of the symmetry property of the medium surface third order susceptibilities $\chi^{(3)}_{\text{surface}}$ were given lesser consideration because of its weaker magnitude requiring high intensities. This aspect of $\chi^{(3)}_{\text{surface}}$ was rarely addressed both theoretically and experimentally.

In this thesis we addressed this issue with simple experimental demonstration of the effect of interface contribution to the overall nonlinear third-order susceptibility tensor. We chose a typical non collinear four-wave mixing (FWM) geometry and generated FWM signal from the two interfaces of a 1-mm thick fused silica sample with air using two 800 nm, 100 fs pulses. We devised a theoretical formulation that explicitly separates the contribution of $\chi^{(3)}_{\text{surface}}$ at interface and bulk to the induced nonlinear polarization. Thus even if one the overall nonlinear field generated in the bulk is negligible, one should consider
substantial contribution from the field generated at the interface. By recording the FWM spectra at the two interfaces and the center of the slide we find that there is enhanced FWM at the two interfaces with the FWM at sTa more intense than aTs and no FWM at the center of the slide. More interestingly, owing to the spectral modification of the intense fs pulse after propagation through a dispersive medium, we observe that there is maximum peak shift of ~1.5 nm in the FWM generated at the two interfaces.

8.1.3 Multi-photon absorption studies in organic molecules:

With high intensities associated with fs pulses multi-photon (n>2) absorption has been widely studied. Phthalocyanines have received particular attention in the context of optical nonlinearities because of their large π electron delocalization, planar structure, and high thermal stability with applications in optical processing devices, practical optical limiters, and biomedical applications. In organic materials, three-photon absorption (3PA) typically occurs at longer wavelengths in the near infrared region (NIR) introducing advantages including minimization of the scattered light losses and reduction of undesirable linear absorption. However, we discovered that there are sporadic reports on organic molecules exhibiting 3PA in the significant wavelength region of 750–850 nm corresponding to the output of commercially available femtosecond Ti:Sapphire source. Though nonlinear optical properties of variety of phthalocyanines have been investigated till date there are further opportunities and avenues to explore novel structures with superior figures of merit.

We addressed these issues by our systematic studies on nonlinear optical properties of a new class of phthalocyanines, 2(3), 9(10), 16(17), 23(24) tetra tert-butyl phthalocyanine and 2(3), 9(10),16(17), 23(24) tetra tert-butyl Zinc phthalocyanines. From the fs open aperture z-scan data we conclude that these molecules exhibit three-photon absorption (3PA) behavior. The measured 3PA coefficients (α₃) were independent of input intensity and the magnitudes were ~0.000091 cm³/GW² and ~0.000095 cm³/GW² for pc1 and pc2 respectively. This
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is, to best of our knowledge, first report on the 3PA behavior of phthalocyanines.

Our study concludes that these alkyl phthalocyanines are prospective candidates for multi-photon applications in the fs regime. A moderate nonlinearity the fs pumping was observed from the closed aperture z-scan data. The sign of nonlinearity for fs pulses were negative in nature. We measured large off-resonant second hyperpolarizabilities (\(\gamma\)) for these molecules with ultrafast NLO response. The measured values of \(\gamma\) were \((4.27 \pm 0.43) \times 10^{-31}\) esu and \((4.32 \pm 0.43) \times 10^{-31}\) esu for pc1 and pc2, respectively. The merit factors for photonic switching applications were estimated. For one-photon absorption as the dominant loss mechanism we estimated \(W\) to be \(\sim 37.9\) and \(\sim 25.6\) for pc1 and pc2, respectively. For three-photon absorption as the dominant loss mechanism we estimated \(V\) parameter as 0.57 and 0.59 for pc1 and pc2, respectively, for an input intensity of 230 GW/cm\(^2\).

8.2 Future perspectives

In terms of SCG studies, the availability of various types of fs laser pulse sources means substantial experimental results in various types of material media. However the theoretical explanations of most of the observed phenomenon always lag behind. This is mostly due to the complexity in the number of NLO processes that interplay in different permutations that make the exact quantification of each contribution very difficult. Most of the theoretical results available in literature deal with SCG in isotropic media. The results presented in this thesis deal for the first time with anisotropic crystal with quadratic nonlinearity. The theoretical formalism for these media therefore gets more complicated as one should take into consideration NLO processes that originate due to \(\chi^{(3)}\) as well as \(\chi^{(2)}\) at high intensities. As all the results presented in this thesis are from an experimental point of view a rigorous theoretical formalism of these results would be an extremely challenging task having enormous ramifications in the overall understanding of various aspects of the SCG phenomenon. Further, one can also attempt to study the coherence properties of
the SCG from a nonlinear crystal media, the results of which may lead of wholesome characterization of SCG. The characterization of temporal and spectral phase of SCG pulses is also an important issue one can attempt to address.

Though a rigorous theoretical formalism for $\chi^{(2)}_s$ (at surface) is available in literature no such mention can be found in case of $\chi^{(2)}_s$. This thesis attempted to develop a basic formalism from a heuristic point of view to demonstrate the observed enhanced four-wave mixing signal due to $\chi^{(2)}_s$ from an air-fused silica interface. However a more rigorous formalism can be derived to bring out the exact nature of $\chi^{(2)}_s$ tensor and its ratio relative to $\chi^{(3)}_{bulk}$. A severe drawback of the experimental arrangement used in this work is its inability to quantify the signal from interfaces and bulk. One can think of various novel ways of such quantification. One proposition in this aspect is to choose suitable media with high $\chi^{(3)}_{bulk}$ that shows FWM signal from bulk and then determine the ration of signal strength obtained from bulk to interface giving an easy estimate of the enhancement of $\chi^{(3)}$ at interfaces.

The multiphoton absorption (MPA) in organic molecules is still an area where there is continuous search for new materials with better 3PA cross-sections for various applications. The work presented in the thesis can be easily extending in determining MPA cross-sections in various molecular systems like porphyrins, polydiacetylenes etc.