In this chapter we have studied second order susceptibility studies of ZnF$_2$–PbO–TeO$_2$: TiO$_2$ glass ceramics (after the samples were dc field poled at elevated temperatures) with 10 ns Er: glass laser (of wavelength 1540 nm with power densities up to 1.5 GW/cm$^2$) and photo-induced changes (variations in the refractive index with the probe wavelength). These studies have indicated that Pb$_5$Ti$_3$F$_{19}$ crystal phases do contribute to NLO effects in addition to PbTiO$_3$ and PbTeO$_3$ crystal phases.
4.1 Introduction

The understanding of the origin of optical susceptibilities in TeO$_2$ based glasses and glass ceramics stimulated by ultra-short laser pulses has gained momentum in the recent years. Such studies in fact help in examining the suitability of the materials for potential applications like three-dimensional photonic devices for integrated optics and other laser-operated devices (such as ultrafast optical switches, optical fiber modulators, power limiters, broad band optical amplifiers) [1, 2].

Transparent polar glass ceramics comprising nano/ microcrystallites that are capable of exhibiting piezo, pyro, ferroelectric and non-linear optical (NLO) properties have been in increasing demand and recognized to be potential multifunctional materials. Recently, transparent crystallized glasses (composites of crystalline and glassy phases), consisting of non-linear optical or ferroelectric crystals have received much attention and there have been many reports on the fabrication and characterization of such transparent crystallized glasses [3]. Transparency of glass-ceramics can be retained by controlling the crystallization of a glass precursor with appropriate chemical compositions and appropriate nucleating agent. The general conditions for retention of transparency of glass even after the crystallization include small refractive index difference between the crystalline and residual glass phases, a small birefringence of the crystallites and
smaller wavelength of the incident light when compared with that of size of crystallites. Investigations along these lines have been carried out on several glass systems including some silicate, fluoride or oxyfluoride matrices, polymers and thin films [4 – 8].

Among a variety of polar glass ceramics that were investigated for various physical properties, tellurium dioxide (TeO$_2$)-based glasses were promising for use in optically operated devices because of their refractive-index compatibility with those of well-known ferroelectric compounds [9]. Further it has been widely accepted that tellurite glasses are promising non-linear optical materials for their high third-order optical non-linear (TONL) susceptibility $\chi^{(3)}$ [10].

The characteristics of glass ceramic depend on the kind and quantity of the crystalline phase formed as well as on the residual glass composition. Hence, the selection of a suitable nucleating agent in the correct concentration and determination of the temperature and the time of nucleation and growth are important factors, in the design of desirable glass ceramic. Among various crystallizing agents, TiO$_2$ is expected to be more effective mineralizer especially in the glass systems like tellurite exhibiting high optical susceptibilities. Further the inclusion of Ti$^{4+}$ ions into the tellurite glass ceramic network is substantial advantage to use these materials for optically operated devices, since the empty or unfilled 3d-shells of Ti ions contribute more strongly to the non-linear polarizabilities that can be determined prevalingly by optical/electrical Kerr effect [11–14]. In the Ref. [15], it was found that partial crystallization of the glass-like
materials leads to substantial enhancement of the photo-induced SHG. Recently, our group has also reported the second-order non-linear optical effects of antimony borate glasses crystallized with CoO as nucleating agents [16]. From these studies, the optimal concentrations of the dopant ions/crystallizing agents for getting the maximum optically induced effects have been identified.

In this chapter we have studied second order susceptibility studies (after the samples were dc field poled at elevated temperatures), photo-induced changes (variations in the refractive index with the probe wavelength) and discussed the correlation between glass structure and non-linear optical (NLO) susceptibilities.

### 4.2 Brief review on non-linear optical properties of TeO$_2$ based glasses

Brief review of some recent studies on non-linear optical properties of different tellurite glass systems is presented below:

Castro-Beltrán et al [17] investigated third-order non-linear optical response and photoluminescence characterization of tellurite glasses with different alkali metal oxides as network modifiers by the standard Z-scan and the thermally managed Z-scan techniques under femtosecond pulse excitation at 800 nm. For different modifiers and intermediates, the non-linear refraction indices $n_2$ of these glasses varied in the range 1.31–2.81 ($\times 10^{-15}$ cm$^2$/W). It was found that $n_2$ increases as the ionic radius of both network modifiers and intermediates decreases. Furthermore, these measurements have shown that the contribution from thermo-optical effects to the non-linear refraction index is negligible for all of the studied glass compositions. In addition, the effect of modifiers and intermediates in the
formation of localized states in the vicinity of the optical band gap was also studied through photoluminescence experiments. These experiments revealed the presence of two emission bands (red and blue) originating from these localized states that can be populated after optical excitation and subsequent relaxation.

Berkaïne et al [18] have computed second and third non-linear optical susceptibilities of two crystalline bulk tellurium oxide polymorphs: \( \alpha \)-TeO\(_2\) (the most stable crystalline bulk phase) and \( \beta \)-TeO\(_2\) (the crystalline phase that resembles the more to the glass phase). Third-order non-linear susceptibilities of the crystalline phases are two orders of magnitude larger than \( \alpha \)-SiO\(_2\) cristoballite, thus extending the experimental observations on glasses to the case of crystalline compounds. While the electronic lone pairs of Te were found contribute to those large values. These authors have reported that a full explanation of the anisotropy of the third-order susceptibility tensor requires a detailed analysis of the structure, in particular, the presence of helical chains that seems to be linked to cooperative non-local polarizability. Soulis et al [19] have studied second harmonic generation in TeO\(_2\)–Tl\(_2\)O–ZnO ternary system. In this study the second order non-linearity amplitude is found to be increasing as a function of the Tl\(_2\)O concentration, in the tested range. Hayakawa et al [20] have investigated third-order non-linear optical susceptibilities (\( \chi^{(3)} \)) of thallium-tellurite (Tl\(_2\)O–TeO\(_2\)) glasses doped separately with various metal oxides using a femtosecond Z-scan technique. In these studies the highest change in refractive index was obtained for M = Ti other than Pb and
Bi. The authors have attributed this to the formation of the TeO$_2$/TiO$_2$ glass structure without destruction of the initial three-dimensional network, accounting for a strong dielectric response intrinsic to pure TeO$_2$. Noguera and Suehara [21] have reported high non-linear optical properties in TeO$_2$-based glasses and they have also investigated modifier's influence on these properties study from the localized hyperpolarizability approach the analysis of the calculations on optimized structures showed that the effects of the second cation on the non-linear optical properties are significant and related to the geometric modification of the structural unit. They have also reported that the introduction of the second cation induces an increase of both linear polarizability and second hyperpolarizability, whereas experiments show the opposite. Further these authors have found that the second hyperpolarizability is much more affected by the introduction of the second cation.

Sigaev et al [22] have reported non-linear optical composites based on oxide glasses and ferroelectrics included TeO$_2$ glasses. Fujiwara et al [23] have investigated third-order optical non-linearities (χ$^{(3)}$) by femto-second Z-scan technique for various compositions of bismuth-tungsten- tellurite glasses. These studies have revealed that a small additive of BiO$_{1.5}$ (5 mol%) in WO$_3$–TeO$_2$ glass was capable of improving a real part of χ$^{(3)}$. However, an excess amount of BiO$_{1.5}$ is found to decrease the non-linearity, resulting from TeO$_4$–to–TeO$_{3+1}$ transformation with an increase in BiO$_{1.5}$. The authors have attempted to explain the improvement on a basis of a two-phase model for WO$_3$–TeO$_2$ glasses. Munoz-
Martin et al [24] have reported non-linear optical susceptibility of multicomponent tellurite (TeO$_2$–TiO$_2$–Nb$_2$O$_5$) thin film glasses. The authors have measured the dispersion of the real and imaginary parts of the linear refractive index of these glasses in the range from 300 to 1700 nm. The results indicated that the studied glass films possess high refractive index (n=2.01) and reduced absorption (k< $10^{-4}$) at $\lambda$ =1500 nm. The non-linear third order optical susceptibility ($\chi^{(3)}$) was determined at four different wavelengths (viz., 600, 800, 1200, and 1500 nm). The out-of-resonance ($\chi^{(3)}$) values (~ $10^{-12}$ esu) were found to be ten times higher than those of the bulk glass and $10^2$ times higher than that of silica. Compositional and structural analysis reveals an increase of both the Ti atomic content and the fraction of nonbridging oxygen bonds in the deposited films. Both factors lead to a higher hyperpolarizability of the film constituents that is proposed to be responsible for the high ($\chi^{(3)}$) value of the films.

Sabadel et al [25] have reported non-linear optical characterization of pseudo ternary TeO$_2$–TiO$_2$–BaO glasses using Z scan technique. These authors have obtained the highest non-linear absorption values for titanium tellurite glasses and this they have discussed based on the optical response of different tellurite structural units in the glass network. Dos Santos et al [26] have evaluated the third-order non-linear optical properties of TeO$_2$–ZnO–Na$_2$O (TZN) glasses codoped with BaO, Nb$_2$O$_5$, and La$_2$O$_3$ by thermally managed eclipse Z -scan The results for the sign and magnitude of the non-linearity were obtained using a
combination of the eclipse Z-scan with thermal non-linearity managed Z-scan, whereas the Kerr shutter technique was employed to obtain the electronic time response of the non-linearity. In these studies the authors have performed all the measurements with 76 MHz repetition rate 150 fs pulses at 800 nm. The results showed a fast response (<200 fs) and a non-linear refractive index varying from 1.5 to $3.5 \times 10^{-15} \text{cm}^2/\text{W}$, depending upon glass composition. The observed non-linearity was found to be electronic origin in nature. Xu et al [27] have studied third-order optical non-linear (TONL) properties of TeO$_2$–Bi$_2$O$_3$–BaO system by the Z-scan method at a wavelength of 800 nm with femtosecond laser pulses. The results showed that glass former Te$^{4+}$ ions exhibited positive influences on the TONL and glass modifiers Ba$^{2+}$ ions behaved similarly; low concentrated Bi$^{3+}$ ions as glass modifiers were found to weakened the non-linearities, but an excess amount of Bi$^{3+}$ behaved oppositely. Te–O$_{eq}$ bonds were found to promote the TONL susceptibility $\chi^{(3)}$. Hayakawa et al [28] have studied the third-order non-linear optical susceptibilities $\chi^{(3)}$ of tellurite(TeO$_2$)-based ternary glasses viz., MO–Nb$_2$O$_5$–TeO$_2$ (M = Zn, Mg, Ca, Sr, Ba) by Z-scan measurement using Ti:Sapphire femtosecond laser pulses. The non-linear susceptibilities $\chi^{(3)}$ of these tellurite glasses were found to increase as the stretching Raman band of Te$^{IV}$–O$_{ax}$ in TeO$_4$ (trigonal bipyramids (tbp)), while the stretching band of Te$^{III}$–O in TeO$_3$ (trigonal pyramid (tp)) decreased. From these results the authors have concluded that the amount of TeO$_4$ (tbp) units was deeply related to the value of $\chi^{(3)}$. These
results have also indicated higher $\chi^{(3)}$ values with decreasing $\text{Te}_{eq}^{IV-O_{ax}-\text{Te}^{IV}}$ Raman band. Desirena et al [29] have measured third-order non-linear optical susceptibility ($\chi^{(3)}$) of $\text{R}_2\text{O}–\text{MO}–\text{TeO}_2$ glasses as function of alkali metals, as network modifiers and network intermediates. The analysis of the results has indicated that both components $\text{R}_2\text{O}$ and $\text{MO}$, have great influence on ($\chi^{(3)}$) values. Hayakawa et al [30] have investigated the third-order non-linear optical susceptibilities, ($\chi^{(3)}$) of tellurite glasses with $\text{MO}–\text{Nb}_2\text{O}_5–\text{TeO}_2$ system ($\text{M} = \text{Zn}$, $\text{Mg}$, $\text{Ca}$, $\text{Sr}$, $\text{Ba}$) by Z-scan measurement using Ti:Sapphire femtosecond laser pulses. The relationship between the non-linear optical properties and the glass structures were estimated by Raman spectroscopy.

4.3 Experimental set-up

The method of measuring of second order optical susceptibility consists of recording the power of the output spectrally separated second-harmonic wave generated (SHG) intensity for the dc-polied sample as a function of applied electrostatic field at elevated temperatures. The beam of 10 ns pulsed $\text{Er}^{3+}$ glass laser with wavelength 1540 nm was focused onto the poled region of the sample up to diameter up to 1-2 mm. The non linear optical effects (controlled by the output SHG signal) were recorded after the achievement of maximal sample’s polarization which corresponds to the applied electrostatic strength of 4 kV/cm
Fig. 4.1 Principal Set-up used for second harmonic generation measurement.

with simultaneous sample’s heating up to 400 °C. The incident beam of the 10 ns Er\(^{3+}\): glass laser (of wavelength 1540 nm with power densities varying successively up to 1.5 GW/cm\(^2\) per pulse and frequency repetition about 10 Hz) was used as fundamental laser beam. After 3-4 min of such treatment the dc-induced signal of the SHG started procuring intensity and got saturated within several minutes and finally the output SHG value was recorded. As a reference samples we have used crystals of BiB\(_3\)O\(_6\) with the known values of second order suscpetibilities. The sketch of the apparatus used for measuring the SHG is given in Fig. 4.1.

The study of the dispersion of the induced non-linearity of the samples was carried out with dc field treatment and also by optical poling and with simultaneous registration of the \(\Delta n\) by Senarmont method (Fig. 4.2). For this
purpose a probe beam possessing varying wavelength (emitted from tungsten-halogen lamp and spectrally separated by spectrophotometer Specord 80 M) is allowed to incident upon the sample after polarization by a polarizer. The effective phase retardation due to electrically induced effect of the out coming beam is changed by the quarter wave-plate and the analyzer with nonius regite the angle corresponding to the minimum light transmission by the photo-detector. The set-up allows measuring the birefringence with accuracy up to $10^{-5}$. The saturation of the birefringence was achieved after 3-5 min. of treatment by dc field at 4 kV/cm and fixed temperature 400 °C.

![Experimental setup used for measuring birefringence (Δn)](image)

**Fig. 4.2** Experimental setup used for measuring birefringence (Δn)

It should be emphasized here that no macroscopic crack formation could be visualized in these samples after this treatment. The wavelength of the probe beam was varied from 450 to 720 nm. Spectrophotometer (SP) emits the varying wavelengths in the spectra range 450 to 720 nm. The light beam is polarized by
polarizer P. The pulsed light from Er glass laser operating at 1540 nm is doubled by frequency by KTP crystal and varying by the angle of this crystal we have the different ratios of 1.54 µm to 0.77 µm wavelengths. The λ/4 phase plate is changed by electro optical effect the effective phase retardation. And the analyzer with the rotator, the angle corresponding to the minimum light transmission by the photo detector P.D. which is necessary for the light induced birefringence registration. The set-up allows to measure the induced changes in ‘n’ with precision up to 10⁻⁵.

4.4 Results and Discussion

Fig. 4.3 represents the comparison plot of second-order susceptibility versus concentration of TiO₂ for ZnF₂–PbO–TeO₂ glasses and glass ceramic samples. The comparision points out higher values of susceptibility for the crystallized samples. The figure indicate substantial increase of the second-order optical susceptibility (χ(2)) with the increase of TiO₂ content up to 1.0 wt%. When the concentration of TiO₂ is increased from 1.0 to 1.5 wt%, a considerable decrease of second-order susceptibility is observed. For further rise of TiO₂ content the susceptibility is observed to increase. Fig. 4.4 presents feature of electrically-induced birefringence (Δn) with the probe wavelength for the glass ceramics (mixed with different concentrations of TiO₂. It is observed that the value of induced Δn is decreased with increase in probe wavelength with
exhibiting a maximum at about 570 nm for the samples containing any concentration of TiO$_2$. It may be noted here that the birefringence for the pre-

![Graph](image)

**Fig. 4.3** Variation of second order susceptibility with the concentration of TiO$_2$ in ZnF$_2$–PbO–TeO$_2$ glasses and glass ceramics.

crystallized samples could not be recorded because $\Delta n$ for these samples is below the detection level ($< 10^{-5}$). Further, we have identified that the variation of $\Delta n$ with the concentration of TiO$_2$ is similar to that of second order susceptibility (Fig. 4.4).
Fig. 4.4 Variation of change in refractive index of ZnF$_2$–PbO–TeO$_2$–TiO$_2$ glass ceramics with wavelength recorded at room temperature.

The coupling of this acentric field with the third order susceptibility, $\chi^3$, gives rise to effective second-order susceptibility through the Eq.

$$\chi^{(2)} = 3\chi^{(3)}E_{dc}. \quad (4.1)$$
The induced polarizability is an effective optical second order non-linear coefficient $\chi^{(2)}$. This one is commonly believed to arise from the symmetry breaking recorded dc-electric field acting on the third-order non-linear susceptibility as per the Eq. (4.1). In the present investigation we have observed the highest value of $\chi^{(2)}$ for the sample TC$_{10}$; incidentally we have observed the lowest optical band gap for the same sample (Table 3.3). From the XRD data and even from ESR data we have observed that a major portion of titanium ions exists in Ti$^{3+}$ state and form Pb$_5$Ti$_3$F$_{19}$ crystal phase (Chapter – 3). The concentration of Pb$_5$Ti$_3$F$_{19}$ crystal phase is observed to the highest for the sample TC$_{10}$. The structure consists of infinite chains of eclipsed corner-sharing TiF$_6$ octahedra as well as individual octahedrons as reported in earlier chapter. Distortions from regularity in the independent TiF$_6$ octahedral phase result in the development of appreciable electric dipoles in these crystal phases that contribute to NLO effects. Hence such phases seemed to be facilitating for the growth of $\chi^{(2)}$ value and are responsible for higher values of $\chi^{(2)}$ observed for the sample TC$_{10}$. However, the highest value of $\chi^{(2)}$ observed for the sample TC$_{20}$ indicates the concentrations of conventional ferroelectric crystal phases viz., PbTiO$_3$ and PbTeO$_3$ dominate over that of Pb$_5$Ti$_3$F$_{19}$ crystal phase and contribute to $\chi^{(2)}$.

DC field-induced birefringence ($\Delta n$) with the probe wavelength of the glass ceramics (mixed with different concentrations of TiO$_2$) is decreased with increase in probe wavelength with exhibiting a maximum at about 570 nm ZnF$_2$–
PbO–TeO$_2$ glass ceramics samples containing any concentration of TiO$_2$. For the sake of understanding, in Fig. 4.5, we have plotted combined variation of $\Delta n$ and the optical absorption spectra recorded in the same wavelength region for the sample TC$_{10}$. The figure clearly confirms that there is a correlation between $^2\text{B}_{2g} \rightarrow ^2\text{B}_{1g}$ transition of Ti$^{3+}$ ion and the maximal value of $\Delta n$. This observation suggests that diffraction due to induced grating can be attributed to changes in the absorptive part (imaginary part) of the refractive index.

**Fig. 4.5** A correlation graph between optical absorption and induced birefringence for the glass ceramic sample TC$_{10}$. 
The relation between measured value of absorption coefficient $\Delta \alpha$ at the peak in the absorption spectrum and the changes in the real part of the refractive index $\Delta n'(\omega)$ (determined using a weak probe beam of variable frequency $\omega$ in the presence of a strong pump at the appropriate frequency) is represented by the conventional Kramers-Kronig (KK) relation as

$$\Delta n'(\omega, I) = \frac{C}{\pi} P \int_0^\infty \frac{\Delta \alpha' (\omega', I)}{\omega'^2 - \omega^2} d\omega'$$  \hspace{1cm} (4.2)

Here, $P$ refers to Cauchy’s principal value and $C$ is the velocity of light and $\Delta \alpha = \frac{1}{LN_i} \log(I_0/I)$ with $N_i$ being the titanium ion concentration (in wt %), $L$ the optical path length (thickness) in cm and log(I$_0$/I) the optical density at the peak position. The peaking of $\Delta n$ at ~570 nm in the presence of a pump, as per the Eq. (4.2), can therefore be attributed to the building up of maximum population by the pump at $^2B_1$ level. The fall of absorption observed above this wavelength is a result of saturation.
4.5 Conclusions

Second order susceptibility studies (after the samples were dc field treated at elevated temperatures) with 10 ns Er: glass laser (of wavelength 1540 nm with power densities up to 1.5 GW/cm$^2$) and also birefringence studies have indicated that Pb$_5$Ti$_3$F$_{19}$ crystal phases do contribute to NLO effects in addition to PbTiO$_3$ and PbTeO$_3$ crystal phases. The highest value of second order susceptibility and also $\Delta n$ with the concentration of TiO$_2$ observed for glass ceramic sample TC$_{10}$ is understood as due to the presence of largest concentration of Pb$_5$Ti$_3$F$_{19}$ crystal phases that contribute more to the NLO effects. The upward kink observed at about 570 nm in the variation of $\Delta n$ with the incident wavelength is correlated with the $^2B_2g \rightarrow ^2B_1g$ optical absorption transition of Ti$^{3+}$ ions.
References


