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Effect of TiO_2 on thermal, structural and third-order nonlinear optical properties of Ca–La–B–O glass system

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ABSTRACT

A series of calcium lanthanum metaborate glasses in the composition (wt%) of $23.88CaO–28.33La_2O_3–47.79B_2O_3$ modified with TiO_2 up to 20 wt% are prepared by a melt quenching technique to study the influence of TiO_2 on their thermal, structural, linear and nonlinear optical properties. The differential thermal analysis (DTA) studies have demonstrated significant effects due to the presence of TiO_2 on the glass forming ability and crystallization situations. The glass with 15 wt% TiO_2 has achieved a eutectic composition and also exhibited a better glass forming ability among the glasses studied. The FT-IR spectra of these glasses show mainly vibration modes corresponding to stretching of BO_3 trigonal, BO_4 tetrahedral units and of B–O–B bending bonds. At higher concentrations of TiO_2, development of vibration band around 400 cm^{-1} has indicated the formation of TiO_6 structural units in the glass network. The red shift of optical absorption edge (UV cutoff) shows a monotonous decrease in direct and indirect optical band gap energies (E_{opt}) with an increase of TiO_2 content in the glasses based on their absorption spectra. The optical transparency of these glasses is found to be varied from 64 to 87% within the wavelength range 450–1100 nm depending on the TiO_2 content. Besides these studies, linear refractive indices, the nonlinear optical properties of these glasses have also been evaluated.

1. Introduction

The lanthanum borate glasses are considered as the new generation of optical glasses with a high refractive index and a relatively low mean dispersion for their use in the design and development of optical devices [1–4]. However, these systems could exhibit fragile glass forming oxide melts. An improvement in the glass forming ability has been observed with the addition of alkaline earth elements in the lanthanum borate glass system [1]. The alkaline earth lanthanum borate glasses demonstrate high refractive index, low dispersion, improved durability and high glass transition temperatures over lanthanum borate glasses demonstrating with low electrical conductivities. Furthermore, single-crystalline borates are reported to be very promising for ultra-violet (UV) applications due to their relatively high UV transparency, good nonlinear optical (NLO) efficiency, and high damage threshold for laser radiation. Kityk et al. have reported that lanthanum borate crystals show two-photon absorption (TPA) induced by a UV laser field and may be of great interest due to the UV-operated nonlinear absorption [5]. The devitrified glass with ferroelectric crystallites has potential applications such as second harmonic generation (SHG) and nonlinear optical applications [6]. These glasses show nonlinear optical properties with a considerable large third-order nonlinear susceptibility and fast response times enabling these glasses that are extensively used as the ultra-fast all optical switching devices in the field of optical communications [7,8].

The glasses consisting of hyperpolarizable ions such as Ti, Nb, Pb, Bi, etc. find potential scientific and technological importance due to their nonlinear properties. In general, the titanium plays a dual role in the glass structure: (i) as network former (NWF) in the form of tetrahedral TiO_4 or (ii) as network modifier (NWM) in the form of octahedral TiO_6 and rarely with a tetragonal pyramid structure of TiO_5. The addition of TiO_2 contributes to an enhancement in linear and nonlinear refractive indices of oxide glasses due to its lone pair electronic configuration [9,10]. The empty d-shells of titanium ions could strongly improve the nonlinear polarizabilities. Moreover, the d-orbital contribution to nonlinear polarizability would be high for bond lengths less than 2 Å and the estimated bond length of Ti–O is 1.96 Å [9,10]. Due to its higher optical nonlinearity, TiO_2 containing glass systems such as silicate, phosphate, borate and germinate have been undertaken for investigations towards their use in different photonic applications [11,12]. Interestingly, the multivalent nature of Ti (Ti^{3+} and Ti^{4+}) could affect the nonlinear properties of glass in two ways. The tetravalent titanium ions (Ti^{4+}) induce positive nonlinear refractive index, whereas Ti^{3+} induces negative nonlinear refractive index [11]. The negative nonlinear refractive

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Table 1
The chemical composition, density and specific volume of Ti-doped calcium lanthanum metaborate glasses.

Glass type	Glass composition (wt%)				Density, d (g/cm^3)	Specific volume, V_m (cm^3/mol)
	CaO	La_2O_3	B_2O_3	TiO_2		
Ti-0	23.88	28.33	47.79	0	3.2150	25.9364
Ti-2.5	23.28	27.62	46.60	2.5	3.2261	25.8190
Ti-5.0	22.69	26.91	45.40	5.0	3.2463	25.6286
Ti-10	21.49	25.50	43.01	10	3.2727	25.3632
Ti-15	20.30	24.08	40.62	15	3.4446	24.0489
Ti-20	19.10	22.66	38.23	20	3.3338	24.7960

index imparts self-focusing phenomenon in the materials and its value always being higher than positive nonlinear refractive index at lower frequencies for a given material. Hence the materials possessing negative nonlinear refractive index could be worked at low input powers increasing the life of the device [13]. The existences of titanium in its trivalent or tetravalent states mainly depend on its concentration, also on the glass composition (for example, acidic composition favors Ti^{3+} state) and the method of glass preparation. Thus, by monitoring the composition of the glass and atmosphere influence during the melting, it becomes possible in tailoring overall nonlinear optical properties of the materials in a required way for the photonic applications by controlling Ti^{4+} and Ti^{3+} states [12].

Thus, considering the importance of the TiO_2, in the present work, it has been aimed to study the influence of TiO_2 addition on the thermal, structural and nonlinear optical properties of calcium lanthanum metaborate glass system through the measurements of DTA, FT-IR, refractive index and optical absorption spectra.

2. Experimental

The chemical compositions (in wt%) of all prepared glasses are given in Table 1. These glasses were prepared using the raw chemicals high purity (99.99%) H_3BO_3, $CaCO_3$, La_2O_3, and TiO_2 in pure platinum crucible at 1300 °C temperature by adopting the conventional melt quench technique followed by an annealing at 650 °C for 1 h. Subsequently, the annealed glass samples were cut to the desired sizes and were processed for carrying out further experiments. The amorphous nature of the prepared glasses was confirmed by X-ray diffractometry (XRD) on X'Pert, PANalytical, and field emission-scanning electron microscopy (FE-SEM) on Supra 35 VP of Carl Zeiss. X-ray diffraction analysis exhibited broad halos, which were typical for an amorphous nature and field emission-SEM images (which are not presented here) showed featureless matrix for all the samples. The three refractive indices ($n_{F'}$, n_e, $n_{C'}$) of glasses at different wavelengths ($\lambda_{F'}$ = 480 nm, λ_e = 546.1 nm and $\lambda_{C'}$ = 634.6 nm) were measured by a minimum deviation method on a Pulfrich Refractometer (Model PR-II) fitted with Hg, He, H_2 and Cd lamps as illuminating sources. The densities (d) of glasses were measured by following Archimedes' principle using water as buoyancy liquid on Metler Tollado balance fitted with a density measurement kit. The differential thermal analysis (DTA) of all glasses was performed in the temperature range of room temperature to 1200 °C on a Netzsch differential thermal analyzer model STA 409 at a heating rate of 10 K/min to obtain various thermal data.

The FT-IR transmission spectra of different glasses were measured using KBr pellet method on a Perkin-Elmer FTIR spectrophotometer model 1615 series with the resolution of 4 cm^{-1} in 2000–400 cm^{-1} wavenumber range. The optical absorption spectra in the wavelength range 200–1100 nm were measured for all glasses on a Perkin-Elmer UV-Vis spectrophotometer model Lambda 20.

3. Results and discussion

Fig. 1 depicts the DTA curves of calcium lanthanum borate glasses with varied TiO_2 additions. The DTA thermograms can be divided into three regions for the sake of a clear understanding. The first part corresponds to glass transition region with an endothermic peak, the second region relates to the crystallization process with exotherm(s) and finally the third part represents the melting phenomena exhibiting endotherm(s). The glass transition (T_g) and the crystallization onset (T_x) temperatures were estimated from the intersections of the slopes to the curves at first endothermic and exothermic peaks, respectively as indicated by the arrows on the DTA curves in Fig. 1. The melting temperature (T_m) is defined as the

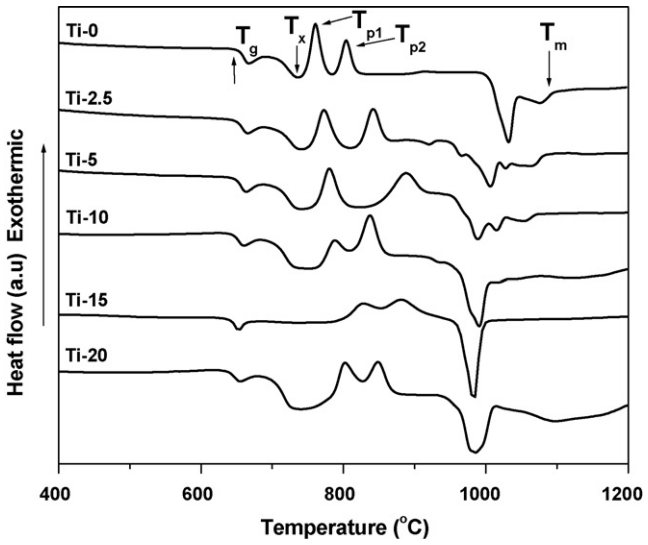

Fig. 1. DTA curves of TiO_2 doped calcium lanthanum metaborate glasses.

peak temperature of the final endothermic signal. The DTA curves of all glasses show distinct T_g followed by two crystallization peaks (T_{p1} and T_{p2}), which indicate their amorphous nature. From the data determined from differential thermal analysis, the glass forming ability (GFA) was estimated through three well-known parameters [14–16]:

$$\text{Glass stability factor,} \quad \Delta T = T_x - T_g \tag{1}$$

$$\text{Reduced glass transition temperature,} \quad T_{rg} = \frac{T_g}{T_m} \tag{2}$$

$$\text{Hruby parameter,} \quad K_{gl} = \left[\frac{T_x - T_g}{T_m - T_p}\right] \tag{3}$$

The derived values of thermal parameters were summarized in Table 2. From this table it is observed that, the T_g decreases as the TiO_2 content is increased up to 15 wt% followed by an increase of T_x making the supercooled liquid region wider, thereby increasing the glass stability factor (ΔT_x). However, the increase in T_x is more pronounced than the decrease in T_g. This small decrease in T_g with the increase in TiO_2 content till 15 wt% TiO_2 addition, could be explained by the fact that with increasing TiO_2, number of nonbridging oxygen increases which makes the glass structure less rigid. The Hruby parameter is usually taken as a measure of glass stability against devitrification on heating of the glass, as the derivation of this parameter (Eq. (3)) involves the relative positions of glass transition temperature (T_g), crystallization (T_x, T_p) and melting temperature (T_m) peaks in DTA thermograms. Therefore, the high values of Hruby parameter illustrate the good glass forming ability of any glass system. In the present Ti-modified glass series, the values of reduced glass transition temperature (T_{rg}) and Hruby parameter (K_{gl}) increased as the TiO_2 is increased till 15 wt% and diminished as the TiO_2 is increased further to 20 wt% demonstrat-

Table 2
The different thermal properties of Ti-doped calcium lanthanum metaborate glasses.

Glass	T_g (°C)	T_x (°C)	T_{p1} (°C)	T_{p2} (°C)	T_m (°C)	ΔT_x (°C)	T_{rg}	K_{gl}
Ti-0	654	736	761	804	1076	82	0.687	0.260
Ti-2.5	651	741	772	841	1063	90	0.692	0.310
Ti-5	650	741	782	885	1053	91	0.696	0.333
Ti-10	646	753	789	838	1043	107	0.698	0.421
Ti-15	641	775	830	880	1003	134	0.716	0.775
Ti-20	640	740	801	848	1097	100	0.666	0.339

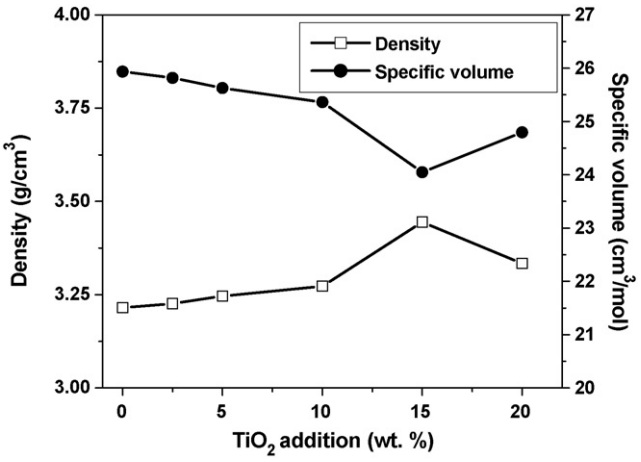

Fig. 2. Density and specific volume values with a varied TiO_2 content in calcium lanthanum metaborate glasses.

ing that, the sample containing 15 wt% TiO_2 (sample Ti-15) possess best glass forming ability.

Another interesting observation could be made from Fig. 1 regarding the melting event of these glasses with the variation of TiO_2 content. The melting event for samples without TiO_2 addition (sample Ti-0) showed a typical off-eutectic nature with two endothermic melting peaks. Whereas, the samples Ti-2.5 and Ti-5 exhibited three melting peaks and in the case of sample Ti-10, the endothermic peak pertaining to melting event has not displayed multipeaks but still it appeared with small kinks which indicates the composition is of near eutectic. While in the sample Ti-15, it demonstrated the achievement of a eutectic behavior having with single endotherm peak. When TiO_2 content is increased further to 20 wt% (sample Ti-20), again two endothermic peaks are observed which confirm the eutectic composition. It has been shown that the best glass forming in any system could be found around the eutectic composition [17]. Thus, these observations corroborate the best glass forming ability of sample Ti-15 determined from three empirical parameters.

Fig. 2 shows the variation of density (d) and specific volume (V_M) of these glasses as a function of TiO_2 content. It is clear from this figure that, with increasing TiO_2, density increases and specific volume decreases till 15 wt% TiO_2 addition. This may be attributed to the contraction of the glass structure and shortening of B–O bonds with the inclusion of TiO_2 in the glass network. Abdel-Baki et al. [18] have observed a similar effect of TiO_2 in silicate glasses. Generally, in most of the oxide glasses with an addition of any particular oxide into the glass structure, density follows the same trend as that of T_g [19,20]. However, the reverse trend is also observed in few glasses where glass transition temperature decreased with the increase in glass density [21]. In the present glass series also the glass transition temperature has decreased while the glass density increased with the addition of TiO_2 content. At the same time, there is an increase in density followed by a decrease in specific volume up to 15 wt% of TiO_2 and for further increase to 20 wt%, density decreased with an increase in specific volume. However, the sample Ti-20 exhibited higher density (3.3338 g/cm^3) than the sample Ti-10 of density 3.2727 g/cm^3. This slight decrease in the density of the sample Ti-20 compared to the sample Ti-15 may be attributed to the volume expansion due to the formation of octahedral TiO_6 structural unit in the glass network. This could further be confirmed through FT-IR measurements of the glasses.

The FT-IR transmission spectra of all TiO_2 doped glasses are presented in Fig. 3 and from which it is noticed that the bands at 1385, 1177–754 and 669 cm^{-1} correspond to B–O bond stretching vibration modes of trigonal BO_3 units, tetrahedral BO_4 units and bending of B–O–B bonds, respectively [7]. In all the spectra, the distinct bands due to Ti–O bands of TiO_4 and TiO_6 have not been well resolved may be because, the bands corresponding to the vibration modes of TiO_4 (740 cm^{-1}) [22] and symmetric Ti–O–Ti stretching vibration of TiO_6 (650 cm^{-1}) [22,23] could be superimposed with the much broader absorption band due to the bending vibration modes of B–O–B bonds. On critical observation of Fig. 3, it could be noticed that the width of the band at 669 cm^{-1} has increased with the increase in TiO_2 content and the increase is more prominent in the sample containing 20 wt% TiO_2. This observation substantiates the fact that Ti–O–Ti stretching vibration band is overlaid with the bending vibration modes of B–O–B bonds. It can also be comprehended from Fig. 3 that there is a tendency of gradual formation of an additional band at around 400 cm^{-1} with the increase in TiO_2 content in the glass composition which is becoming more pronounced in sample Ti-20 where as it is absent in sample Ti-0. However, the full band could not be detected due to the limitation in the measurement range (400 cm^{-1}) of the instrument. This band corresponds to the vibration of Ti–O bond of the TiO_6 unit [24].

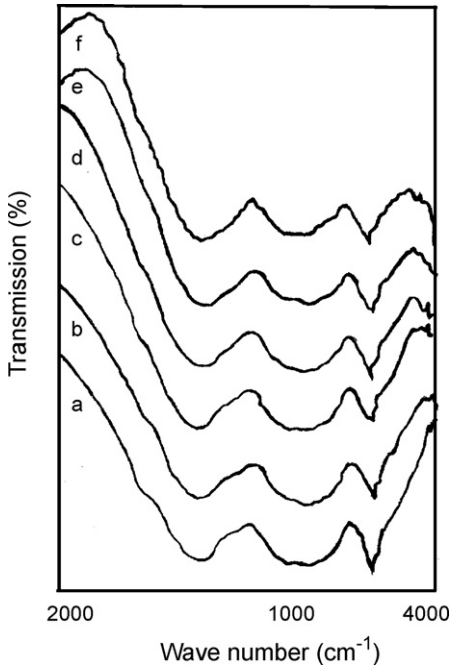

Fig. 3. FT-IR transmission spectra of calcium lanthanum metaborate glasses doped with (a) 0 wt%, (b) 2.5 wt%, (c) 5 wt%, (d) 10 wt%, (e) 15 wt%, and (f) 20 wt% TiO_2.

The optical absorption spectra of the calcium lanthanum borate glass samples with different amount of TiO_2 are shown in Fig. 4. It is clear from the figure that, with the increase of TiO_2 content in the glass composition, there is a shift in the ultra-violet (UV) cut-off towards the longer wavelength. The abrupt rise of absorption at the UV region signifies the optical band gap, which is due to the fundamental absorption phenomena of host glass matrix. The electronic transitions across the conduction and valance bands within the material are the cause for the occurrence of this fundamental absorption edge in the materials. Hence, the examination of UV absorption edge could provide the information about the electronic band structure of the materials. Especially in the case of amorphous solids, formation of the localized density of states within the band tails occur due to the presence of characteristic structural disorder causing the changes in optical or electronic transport processes, thereby influencing the physical and optical properties [25]. Due to the formation of localized states, the absorption edge of amorphous materials contain two regions, one is "Tauc region" where the tran-

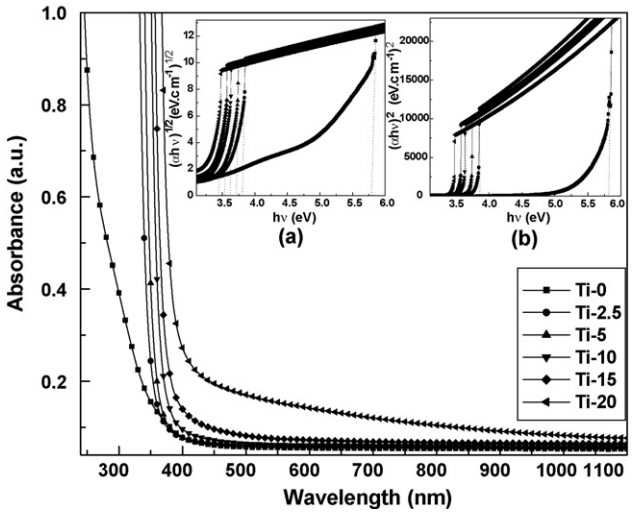

Fig. 4. Absorption spectra of different Ti-doped calcium lanthanum metaborate glasses. Determination of optical energy band gap has been shown in the inset for (a) indirect transition and (b) direct transition.

sitions between extended valance and conduction bands take place, and the other is "Urbach region" which comprises of electronic transitions between localized band tails and extended conduction band. In the Tauc region, the absorption coefficient could be obtained from the relation [26]:

$$\alpha(\nu) = \frac{\alpha_0(h\nu - E_g)^n}{h\nu} \quad (4)$$

where E_g is the optical band gap energy and the exponent n takes the values ½ or 2 for allowed direct or indirect transitions, respectively and 3/2 or 3 for forbidden direct or indirect transitions, respectively, where α_0 is a constant. By plotting $(\alpha h\nu)^{1/2}$ and $(\alpha h\nu)^2$ as a function of photon energy $(h\nu)$, we can find the optical energy band gap for indirect and direct transitions. The respective values of the band gap energies can be obtained by extrapolating the linear portion of the plot for $(\alpha h\nu)^{1/2} = 0$ for indirect transitions and $(\alpha h\nu)^2 = 0$ for direct transitions as shown in inset of Fig. 4. It is observed that the direct band gap is larger than the corresponding indirect band gap. The values of direct and indirect band gap are shown in Table 3 for different glass samples. It is observed that the band gap decreases with the increase in the content of TiO_2. This may be due to the change in the average bond energy of the network brought about from the addition of TiO_2 in the glass [27]. When titanium ions enter into the glass network, Ti–O bonds replace some of the B–O bonds. As the energy of Ti–O (315 kJ/mol) is smaller than the bond energy of B–O having 449 kJ/mol, and as the band gap is sensitive to the bond energies, the decrease in average bond energy of the system and resulted in the decrease in the band gap energy accompanied by a shift in the absorption cutoff towards

Table 3
Optical band gap energy (E_{opt}) for direct and indirect transitions and Urbach energy (E_u) of Ti-doped calcium lanthanum metaborate glasses.

Glass type	E_{opt} (eV)		Urbach energy E_u (eV) (±0.01)
	Indirect transitions (±0.02)	Direct transitions (±0.01)	
Ti-0	5.79	5.81	0.59
Ti-2.5	3.81	3.86	0.11
Ti-5.0	3.71	3.74	0.10
Ti-10	3.61	3.65	0.10
Ti-15	3.54	3.58	0.10
Ti-20	3.44	3.47	0.09

Table 4
Measured linear refractive indices (n_e, $n_{F'}$, $n_{C'}$) and certain important nonlinear optical properties of Ti-doped calcium lanthanum metaborate glasses.

Properties	Glass types					
	Ti-0	Ti-2.5	Ti-5.0	Ti-10	Ti-15	Ti-20
n_e (±0.001)	1.668	1.682	1.698	1.729	1.775	1.799
$n_{F'}$ (±0.001)	1.674	1.689	1.705	1.738	1.786	1.815
$n_{C'}$ (±0.001)	1.662	1.676	1.691	1.721	1.765	1.785
$(n_{F'} - n_{C'})$	0.012	0.013	0.014	0.017	0.021	0.030
ν_e	55.67	52.46	49.86	42.88	36.90	26.63
n_2 ($\times 10^{-13}$ esu)	2.1917	2.4847	2.7768	3.7856	5.3034	9.1142
γ ($\times 10^{-16}$ cm^2/W)	5.5039	6.1878	6.8501	9.1712	12.5153	21.2214
$\chi^{(3)}_{1111}$ ($\times 10^{-14}$ esu)	0.9697	1.1086	1.2507	1.7362	2.4970	4.3490

the longer wavelength. This shift of band edge towards the visible region of the spectrum absorbing violet and weakening the blue with the increase of TiO_2 content imparts strong yellow color tint to the glasses. In the Urbach region of the energy band gap, the absorption coefficient (α) varies following the relation [28]:

$$\alpha(\nu) = \beta.e^{(h\nu/E_U)} \quad (5)$$

Here β is the proportionality constant, ν is the frequency of radiation and E_U is the Urbach energy, which characterizes the width or the extent of band tails of the localized states. The Urbach energy of the present glass series has been estimated by taking the inverse of the slope of linear portion of the curve between $\ln \alpha(\nu)$ and photon energy $(h\nu)$ according to Eq. (5) and are presented in Table 3. It is interesting to observe that there is a decrease in the Urbach energy of the TiO_2 doped glasses compared to undoped glasses. This can be attributed to the strong modification of the glass structure together with an enhanced density and with a reduction of the degree of disorder in the TiO_2 doped glasses.

Interestingly, no absorption peak has been noticed in the absorption spectra of all these TiO_2 modified calcium lanthanum metaborate glasses. It has been reported that absorption bands around 500, 540 and 660 nm are found and those are due to the $^2T_{2g} \rightarrow {}^2E_g$, $^2B_{2g} \rightarrow {}^2B_{1g}$, $^2B_{2g} \rightarrow {}^2A_{1g}$ transitions of Ti^{3+} ions in the octahedral sites, respectively [18]. Normally, under ordinary conditions of melting, it is difficult to get Ti^{3+} in glasses as Ti ion tends to achieve its higher valence state (Ti^{4+}). The Ti^{4+} ion does not show any absorption in the visible range of the spectrum as it has an electronic configuration $3d^0$. Thus it can be concluded that Ti ions in these glasses are present as Ti^{4+} ions. However, it has been reported that stabilization of Ti^{3+} is possible for some glasses with acidic composition such as phosphate or borosilicate glasses [29]. The optical transparency of these glasses is found to be varied in the range between 64 and 87% with the increase in TiO_2 content from 0 to 20 wt%. The glasses with TiO_2 up to 15 wt% show transparency above 80% and the one with 20 wt% having brown tinge exhibits about 64% optical transparency in the wavelength range of 450–1100 nm.

The measured linear refractive indices of different Ti-doped calcium lanthanum metaborate glasses at n_e (546.1 nm), $n_{F'}$ (480.0 nm), $n_{C'}$ (643.8 nm) are presented in Table 4. The refractive indices of these glasses at different wavelengths have been evaluated from the well-known Cauchy dispersion relation [18] and the results are presented in Table 4. The fitted dispersion curve is shown in Fig. 5. It is evident from Fig. 5 and Table 4 that with an increase in TiO_2 content, refractive indices and dispersion are found to be increasing. Another important optical quality defining factor known as Abbe number (ν_e) of all Ti-doped calcium lanthanum metaborate glasses have been computed along side their nonlinear refractive index (n_2) and also other related parameters such as nonlinear refractive index coefficient (γ) and third-order nonlinear susceptibility ($\chi^3{}_{1111}$) using relevant empirical expressions [10,30–32].

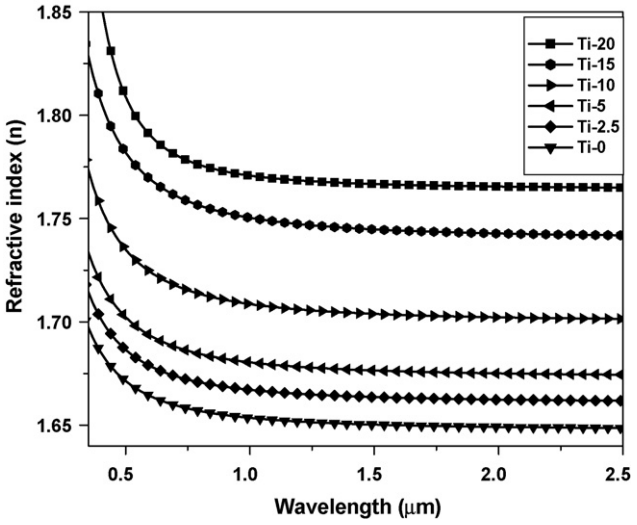

Fig. 5. The dispersion curves for different Ti-doped calcium lanthanum metaborate glasses.

According to the Boling's equation [31], the third-order nonlinear optical susceptibility, χ^3, of the material is dependent on both the linear refractive index and the second-order index of refraction. As the glass being an isotropic dielectric material, the even order nonlinear optical susceptibility ($\chi^{(2)}$) becomes zero but the third-order nonlinear optical susceptibility ($\chi^{(3)}$) plays an important role in bringing about various significant nonlinear optical effects.

The computed nonlinear optical (NLO) properties are summarized in Table 4. It can be observed that with the increase in TiO_2 content in glass composition, both linear and nonlinear refractive indices and related nonlinear properties have been enhanced significantly. The increase in linear and nonlinear refractive indices can be attributed to the hyperpolarizability of Ti ions. There is an increase in the number of nonbridging oxygen ions with the increase in TiO_2 content in the glass, which can also enhance the linear and nonlinear refractive indices. However, these properties are dominated by the concentration of the ions of transition element (e.g. Ti) rather than by the number of nonbridging oxygen [10]. It has been observed in FT-IR studies that at lower concentration of TiO_2, TiO_4 structural units are mainly present in the network. With the increase in TiO_2, there is a gradual increase of formation of, TiO_6 structural units. The glass with 20 wt% TiO_2, TiO_6 structure appears to dominate the glass network. In both the cases, Ti ions remain as Ti^{4+} state within this composition range. Ti^{4+} metal ions have an empty d-shell and a lone pair of electrons either in TiO_4 network former or TiO_6 network modifier. This could be a possible reason for high polarizability of Ti ions, which are found to be clearly reflected from the linear and nonlinear properties of various glasses. The calculated nonlinear properties like nonlinear refractive index (n_2), nonlinear refractive index coefficient (γ), and third-order nonlinear susceptibility ($\chi^{(3)}$) are higher than previously reported TiO_2 doped silicate glasses [33]. The calculated nonlinear refractive index (n_2) is one order higher than fluoride, silicate, phosphate and borosilicate glasses as reported by Vogel et al. [10]. Furthermore, the third-order nonlinear susceptibility ($\chi^{(3)}$) is higher than niobium doped telluride glasses [34] or fluoride glasses [10]. Thus, this observation demonstrates the potentiality of TiO_2 doped calcium lanthanum borate glasses for their use in various nonlinear optical device applications.

4. Conclusions

The effect of TiO_2 addition (up to 20 wt%) on thermal, structural, linear and nonlinear optical properties of calcium lanthanum metaborate glasses of composition (wt%) $23.88CaO–28.33La_2O_3–47.79B_2O_3$ has been systematically studied. From the DTA studies, it has been found that the glass with 15 wt% TiO_2 has been in a eutectic composition and it has also revealed better glass forming ability parameters among the glasses studied. The FT-IR spectra of these glasses have exhibited vibration modes due to stretching of BO_3 trigonal, BO_4 tetrahedral units and of B–O–B bending bonds. At higher concentrations of TiO_2, the vibration band around 400 cm^{-1} thus confirms the formation of TiO_6 structural units. With the increase of TiO_2 content in the glass composition, ultra-violet (UV) cut off wavelength shifts towards a longer wavelength. There exists a monotonous decrease in optical absorption edge (UV cutoff), also for direct and indirect band gap energies (E_g) with an increase of TiO_2 content in the glasses because of the changes in the average bond energies of the networks. Interestingly, the Urbach tail energy is found to be decreasing with TiO_2 addition, therefore indicating a reduction in band structure disorders. The absence of an absorption peak confirms the presence of titanium in tetravalent state (Ti^{4+}) only in the glass network. With an increase of TiO_2 content in glass composition, both linear and nonlinear refractive indices and also other related nonlinear properties have significantly been found to be enhanced due to the hyperpolarizability of Ti ions. The nonlinear optical properties estimated from linear refractive indices of these titanium-doped glasses are found to be on a par with several glasses reported for NLO applications, hence indicating their potentiality and suitability as NLO materials.

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