The effect of the addition of CaF$_2$ and PbF$_2$ on boro-tellurite glasses doped with chromium ions

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Abstract
This article presents the impact of CaF$_2$ and PbF$_2$ on boro-tellurite glasses, together with preparation of glass, primary experimental techniques, modern technology and progress, particularly the development of transition metal ion doped boro-tellurite glasses for optical glass related applications. Physical and structural investigations on chromium doped boro-tellurite glasses have been studied as a function of metal fluorides. Several physical and optical parameters have been obtained and their results are explained clearly. High density and refractive index values were observed for lead fluoride doped boro-tellurite glasses which are the essential properties of the materials for applications in fiber optical communication. Electron Paramagnetic Resonance (EPR) spectrum have shown two resonance signals at low and high field regions. FTIR spectra revealed that the B–O–B vibrations are due to various BO$_3$ and BO$_4$ units and Te–O vibrations are from different TeO$_3$ and TeO$_4$ units. Deconvoluted Raman spectra being used to locate the band positions in the spectra. Raman spectra confirmed that the presence of stretching vibrations of Te–O–B links, B–O links in BO$_4$ units. The conversion of Te–O linkages to Te–F linkages by the addition of metal fluorides is observed from of Raman spectra.

1. Introduction

Glasses are generally used as optical fiber materials because of their unique optical properties. Wide spectral range with low loss limit in fluoride glasses made them suitable for optical fiber sensor applications. It is well established that the addition of metal fluorides to the glass matrix enhanced optical transparency and refractive index$^{[1–3]}$. TeO$_2$ as glass former has received more attention over the other glass formers such as phosphate, silicates, etc because of high index of refraction, better chemical durability, low melting point and very good non linear optical properties$^{[4–8]}$. The addition of metal halides like PbF$_2$, CdF$_2$, CaF$_2$ etc to the telluride based glasses have shifted the IR absorption edge towards the higher wavelength side and also reduced the OH absorption$^{[9, 10]}$. Lead oxide has of wide range of composition and PbO acts as modifier at low concentration and as former at high concentration. Even though PbO is toxic in nature, the addition of PbO enhances the refractive index and other optical parameters$^{[3, 10, 11]}$.

Nowadays, the investigations on borate and boro-tellurite glasses have got more attention because of their unique properties like flexibility in composition, durability, chemical resistance, transparency, low phonon energy, etc. Borate network is mainly consists of BO$_3$ and BO$_4$ units with boroxol rings formed by B–O–B links whereas tellurite glass made from TeO$_4$ trigonal bipyamids linked by Te–O–Te linkages$^{[6, 12–14]}$. Borotellurite glasses are the best host materials for transition metal (TM) ions such as Cu$^{2+}$, VO$^{2+}$, Mn$^{2+}$, Cr$^{3+}$ etc$^{[15–17]}$. The addition of TM ions into the glass network makes structural changes around the TM ions as they
are sensitive to the amorphous matrix. The existence of chromium in various oxidation states \((\text{Cr}^{2+}, \text{Cr}^{3+}, \text{Cr}^{4+}, \text{Cr}^{5+} \text{& Cr}^{6+})\) and molecular structure (chromate, dichromate, trichromate etc) makes more important to study compared to other TM ions. Out of all the oxidation states, \(\text{Cr}^{3+}\) is the most stable state, remaining states are unstable and \(\text{Cr}^{3+}\) ion doped glasses are specially used in tunable solid state lasers and high temperature sensors \cite{18–20}.

The alignment of the glass structure can be obtained by Fourier transform infrared (FTIR) and Raman spectroscopy. FTIR spectroscopy is well known spectroscopic experimental technique for the analysis of organic materials and certain inorganic compounds such as glasses to get information about the chemical bonding and molecular structure of materials. Raman spectroscopy is another spectroscopic technique which differs from the infrared spectroscopy by an indirect coupling of high-frequency radiation with vibrations of chemical bonds. Changes in the dipole moment gives FTIR spectra and changes in polarizability gives Raman bands \cite{21, 22}. Density measurement, UV-Visible, EPR, FTIR and Raman spectroscopy are the experimental techniques employed to extract the information about the structural and dynamic properties of materials and to observe the network changes around the TM ions. In the present study on boro-tellurite glasses, physical, FTIR and Raman studies were used to investigate the strength and structural changes occurring in the materials whereas UV-Visible and EPR studies were used to get the information about the environment around the TM ion.

2. Experimental

2.1. Glass preparation

Melt-quenching method is used to prepare the glasses with \(\text{xMF}_2-(10-x)\text{TeO}_2-30\text{PbO-59.8B}_2\text{O}_3-0.2\text{Cr}_2\text{O}_3\) (where \(M = \text{Pb} \& \text{Ca}, x = 0, 10 \& 20 \text{ mol}%)\) composition. Analar grade chemicals, boric acid \((\text{H}_3\text{BO}_3)\), tellurium oxide \((\text{TeO}_2)\), lead oxide \((\text{PbO})\), calcium fluoride \((\text{CaF}_2)\) lead fluoride \((\text{PbF}_2)\) and chromium oxide \((\text{Cr}_2\text{O}_3)\) were taken as the initial starting materials. The glass compositions with codes are presented in table 1. The chemicals of the glass compositions were taken in silica crucible and placed in an electrical furnace maintained at 900 °C for one hour. The melt in the furnace frequently stirred to get the homogeneity. The melt is then quenched on pre heated stainless steel plate and quenched glasses were annealed to remove the stress present in the samples.

2.2. Characterization

X-ray diffraction (XRD) spectra of the MPTBCR glasses were recorded in the range 10°–80° of 2\(\theta\) at room temperature (RT). The Archimedes principle is used to measure density values of MPTBCR samples. UV-Visible spectra were recorded on polished MPTBCR glass samples in absorption mode in the wave length range 200–900 nm using Shimadzu UV-1800 spectrometer at RT. BRUKER EPR spectrometer \((X\text{-band frequency 9.7 GHz})\) and modulating frequency of 100 kHz is used to record EPR spectra of the MPTBCR glasses at RT. The FTIR spectrum of the MPTBCR samples is scanned in the range 400–1600 cm\(^{-1}\) on Bruker FTIR spectrophotometer \((\text{accuracy in wave number accuracy is } \pm{0.01 \text{ cm}^{-1}})\). Photometric is 0.1% T and resolution is 0.5 cm\(^{-1}\) at RT. The micro Raman spectrum of MPTBCR glass samples were recorded in the range 200–1800 cm\(^{-1}\) at RT using Jobin Yvon Horibra LABRAM-HR Raman spectrometer.

3. Results and discussions

3.1. X-ray diffraction

XRD spectra of \(\text{xMF}_2-(10-x)\text{TeO}_2-30\text{PbO-59.8B}_2\text{O}_3-0.2\text{Cr}_2\text{O}_3\) (where \(M = \text{Pb} \& \text{Ca}, x = 0, 10 \& 20 \text{ mol}%)\) glasses is shown figure 1. No sharp peaks were observed in XRD spectra of MPTBCR glass system which confirms the non crystalline state of MPTBCR glasses.

Table 1. Glass compositions of the \(\text{xMF}_2-30\text{PbO-} (10-x)\text{TeO}_2-59.8\text{B}_2\text{O}_3-0.2\text{Cr}_2\text{O}_3\) (Where \(M = \text{Ca} \& \text{Pb}, x = 0, 5, 10 \text{ mole}%)\) glass system.

| Glass Code | CaF\(_2\) | PbF\(_2\) | PbO | TeO\(_2\) | B\(_2\)O\(_3\) | Cr\(_2\)O\(_3\) |
|------------|-----------|-----------|------|-----------|---------------|---------------|
| MPTBCR-0   | 0         | 0         | 30   | 10        | 59.8          | 0.2           |
| CPTBCR-1   | 5         | 0         | 30   | 5         | 59.8          | 0.2           |
| CPTBCR-2   | 10        | 0         | 30   | 0         | 59.8          | 0.2           |
| PPTBCR-1   | 0         | 5         | 30   | 5         | 59.8          | 0.2           |
| PPTBCR-2   | 0         | 10        | 30   | 0         | 59.8          | 0.2           |
3.2. Physical and optical properties

Density is the intrinsic property of a glassy material which plays a prominent role in explaining the structural studies of glasses since it is affected by interstitial spaces, crosslink density etc. \[23, 24\]. Figure 2 shows the variation of density with metal fluorides in MPTBCR glasses. The density of metal free glass (MPTBCR-0) is 5.26 gm cc\(^{-1}\) which is greater than CaF\(_2\) added CPTBCR glasses. PbF\(_2\) contained glasses have furthermore densities than MPTBCR-0 and CPTBCR glasses. The order of density of glasses as follows \(\text{PPTBCR} > \text{MPTBCR-0} > \text{CPTBCR}\). The variation in density may be explained on the basis of crystal density and molecular weights of metal fluoride and TeO\(_2\). The order of crystal density and molecular weights of metal fluoride and TeO\(_2\) follow the relation CaF\(_2\) < TeO\(_2\) < PbF\(_2\). Therefore, the replacement of TeO\(_2\) with CaF\(_2\) in CPTBCR glasses causes decrease in the density values since the crystal density and the molecular weight of CaF\(_2\) relatively lesser than TeO\(_2\). The replacement of TeO\(_2\) with PbF\(_2\) in PPTBCR glasses causes the increase in density values because the crystal density and the molecular weight of PbF\(_2\) relatively greater than TeO\(_2\). The decrease in the density of CPTBCR glasses may also be due to the creation of BO\(_3\) units and the increase in the density of PPTBCR glasses due to the creation of BO\(_3\) units. The increase in density values of PPTBCR glasses may find applications in radiation shielding materials.

Figure 3 shows optical absorption spectra of \(x\text{MF}_2 -30\text{PbO} - (10-x)\text{TeO}_2 - 59.8\text{B}_2\text{O}_3 - 0.2\text{Cr}_2\text{O}_3\) (where \(M = \text{Pb} \& \text{Ca}, x = 0, 10 \& 20 \text{ mole\%}\)) glasses. From the optical absorption spectra, Urbach energy (\(\Delta E\)), the optical band gap (\(E_g\)) and Racah parameters have been obtained \[25–29\]. Urbach energy values are obtained.
from the Urbach plot (figure 4). Urbach energy value of MPTBCR-0 glass sample is (0.982) quite high; these values are decreasing with the addition of metal fluorides. $\Delta E$ values of PbF$_2$ incorporated glasses found relatively less than the CaF$_2$ added glasses. From these results, one can conclude that MPTBCR-0 glass have more disorder in the glass network than CPTBCR and PPTBCR glass samples. Optical band gap values are evaluated from Tauc plots (figure 5). Obtained band gap values are decreased from 3.394 eV (MPTBCR-0) to 3.027 eV (CPTBCR-2) when TeO$_2$ is replaced with CaF$_2$ and 3.394 eV (MPTBCR-0) to 2.660 eV (PPTBCR-2) when TeO$_2$ is replaced with PbF$_2$.

Using the optical band gap and molar volume values, refractive index, molar refraction and molar electronic polarizability values has been calculated [30–32]. The refractive index value for MPTBCR-0 glass sample is 2.299 is less than the CPTBCR and PPTBCR glass samples. The addition of CaF$_2$ enhancing the refractive index value to 2.389 and incorporation of PbF$_2$ further enhanced the value to 2.429. All the physical, optical parameter values have been presented in table 2.

Racah parameter B reveals the inter electron repulsion in the d-shell and $D_0/B$ gives the crystal field information [33, 34]. The B values of MPTBCR-0 and CPTBCR glasses are greater than $B_{\text{free}}$ value (918 cm$^{-1}$) whereas for PPTBCR glasses the value is less than $B_{\text{free}}$. From the table 3, it is clear that the B value is decreasing with the addition of metal fluorides, but the decrease is found to be more with PbF$_2$ compared to CaF$_2$ containing glasses. This can be attributed to the boron network is shielding the d-shell electrons in PPTBCR glasses only. The $D_0/B$ value for all the samples is less than 2.3 except for PPTBCR-2 glass sample which has greater $D_0/B$ value (3.30). It is also observed that the $D_0/B$ value is increasing with the addition of metal.
fluorides and the increase is found to be more in PPTBCR glasses. From these results, one can conclude that the CPTBCR glasses are in the weak crystal field and PPTBCR samples changing from weak crystal fields to strong crystal field on the addition of PbF₂ to boro-tellurite glasses.

### 3.3. Electron paramagnetic resonance

The EPR spectra of materials are generally elucidated by using spin Hamiltonian. Unpaired electrons in Cr³⁺ ion with effective spin and nuclear spin S = 3/2 causes to the ⁷F ground state. According to crystal field theory, Cr³⁺ ions will take the positions in octahedral sites in all the inorganic materials which may due to their six fold coordination with strong field stabilization energy. Weak distortion in the ligand field or swift distortions in molecular vibrations causing the parity forbidden d-d transitions. Two Kramers doublets (Ms = ±3/2 and Ms = ±1/2) are attributed to axial distortion in octahedral symmetry and their spin degeneracy is lifted by applying Zeeman field. The transitions between Kramers doublet on the application of Zeeman field leads to raise in the resonance signals.
The EPR spectra can be analysed by using spin-Hamiltonian [35].

\[ \mathcal{H} = \beta H g S + I.A.S + S.D.S \]

Distortions in the local environment around Cr\(^{3+}\) ions related to the short range order in glasses affect the EPR spectra. In addition to this, a broad line spectra obtained by erratic alignment of field symmetry axis belong to the magnetic field. The broadened spectra, the distinct quality of amorphous materials, shows that the Cr\(^{3+}\) ions take the positions of distorted octahedral sites. According to the earlier literature survey, Babu et al (2019) [36], Kiran et al (2011) [37], Saad et al (2018) [38], Changwei et al (2018) [39], Hassan (2013) [40], Narendrudu et al (2017) [41] etc studied the glasses with various compositions doped with chromium ions. They observed two resonance signals at \(\sim 4.3\) and 1.97. The resonance signal at \(\sim 4.3\) is assigned to isolated Cr\(^{3+}\) ions in the strong crystal field with rhombic sites and exchange coupled pairs of Cr\(^{3+}\) ions contributed the signal at \(\sim 1.97\) in high field region.

EPR spectra of \(x\)MF\(_2\)–30PbO–(10–\(x\))TeO\(_2\)–59.8B\(_2\)O\(_3\)–0.2Cr\(_2\)O\(_3\) (where M = Pb & Ca, \(x = 0, 5, 10\) mol%) glass samples are shown in the figure 6. EPR spectra show two resonance signals at \(g \approx 4.24\) in the low field side and \(g \approx 1.97\) in the high field side. The g values for high and low field regions have been presented in table 4.

The effective g value in the low field region \(g \approx 4.2\) is due to isolated Cr\(^{3+}\) ions in octahedrally distorted positions whereas effective \(g \approx 1.97\) value in the high field region is attributed to exchange coupled pairs of Cr\(^{3+}\) ions (anti ferromagnetic Cr\(^{3+}\)–Cr\(^{3+}\)). According to Weil et al the number of spins participating in the resonance by taking the formula with reference to CuSO\(_4\)5H\(_2\)O [42]

\[ N = \frac{A_x (\text{Scan})^2 G_{m\text{rad}}(H_m\text{rad})^2 (g_{\text{rad}})^2 [S(S + 1)]_{\text{rad}} (P_{\text{rad}})^2}{A_x (\text{Scan}_{\text{rad}})^2 G_x (H_m)^2 (g_x)^2 [S(S + 1)]_{x} (P_x)^2} \]

Where the symbols have their usual meaning. The number of spins in the MPTBCR glass samples is varying non linearly with metal fluoride concentration.
substitution of CaF2 network with the addition of metal vibrations. The present work is concentrated only on the structural changes in the borate and the boro-tellurite units [11–12]. Raman spectra of xMF2−30PbO−(10−x)TeO2−59.8B2O3−0.2Cr2O3 (where M = Ca and Pb; x = 0, 5, 10 mole%) glass samples are recorded in the range 200–1600 cm−1. The wave numbers below 600 cm−1 are well known, many researchers are reported that are arised due to metal cation vibrations. The present work is concentrated only on the structural changes in the borate and the boro-tellurite network with the addition of metal fluorides. FTIR spectra of MPTBCR glasses have shown the band positions at ∼700 cm−1, ∼870–950 cm−1, 1100 cm−1, 1300 cm−1, 1350 cm−1 and 1700 cm−1. The band at 710 cm−1 represents the presence of Te–O vibrations in TeO4 units and B–O–B bond-bending vibrations from pentaborate group or bending vibrations of BO3 triangles [12, 44]. And this band intensity is decreasing with the substitution of CaF2/PbF2 with TeO2. The deep band at 870–920 cm−1 and 920–1000 cm−1 are due to stretching vibrations of non bridging oxygen (NBO) of BO4 units and B–O vibrations of BO4 tetrahedra respectively [11, 45, 46]. In CPTBCR glasses, the replacement of TeO2 with CaF2 is shifting the band at wave number 920 cm−1 towards the higher wave number side which may be due to the creation of BO4 units. The replacement of TeO2 with PbF2 in PPTBCR glass system is shifting the band towards lower wave number side may be due to the creation of BO4 units. The creation of BO4 units decrease the density value of the CPTBCR glass sample and creation of BO4 units enhances the density of the PPTBCR glass sample. The band found around 1100 cm−1 is attributed to B–Osym stretching vibrations in BO4 units from various borate groups [11, 47] and shifting of this band towards lower wave number side in CPTBCR/PPTBCR glasses may be due to the creation of bridging fluorine’s in the glass network. A band at 1310 cm−1 is observed only in the MPTBCR-0 glass sample in which metal fluoride is absent and it is not observed in CPTBCR and PPTBCR glass samples in which metal fluoride is present. This band is attributed to asymmetric vibrations of B–O bonds on BO3 units. The deep band at 1400 cm−1 is due to asymmetric stretching relaxation of B–O bonds of trigonal BO3 units [12, 47].

3.4. FTIR spectra

FTIR spectra reveals the presence of various efficient modes of vibrations in bonds like bending, deforming and stretching vibrations in different structural groups, which constitutes the glass network. FTIR spectra of xMF2−(10−x)TeO2−30PbO−59.8B2O3−0.2Cr2O3 (where M = Pb & Ca, x = 0, 10 & 20 mol%) glass samples are shown in the figure 7. FTIR spectra of MPTBCR glass system recorded in the range 600–1600 cm−1. The wave numbers below 600 cm−1 are well known, many researchers are reported that are arised due to metal cation vibrations. The present work is concentrated only on the structural changes in the borate and the boro-tellurite network with the addition of metal fluorides. FTIR spectra of MPTBCR glasses have shown the band positions at ∼700 cm−1, ∼870–950 cm−1, 1100 cm−1, 1300 cm−1, 1350 cm−1 and 1700 cm−1. The band at 710 cm−1 represents the presence of Te–O vibrations in TeO4 units and B–O–B bond-bending vibrations from pentaborate group or bending vibrations of BO3 triangles [12, 44]. And this band intensity is decreasing with the substitution of CaF2/PbF2 with TeO2. The deep band at 870–920 cm−1 and 920–1000 cm−1 are due to stretching vibrations of non bridging oxygen (NBO) of BO4 units and B–O vibrations of BO4 tetrahedra respectively [11, 45, 46]. In CPTBCR glasses, the replacement of TeO2 with CaF2 is shifting the band at wave number 920 cm−1 towards the higher wave number side which may be due to the creation of BO3 units. The replacement of TeO2 with PbF2 in PPTBCR glass system is shifting the band towards lower wave number side may be due to the creation of BO4 units. The creation of BO4 units decrease the density value of the CPTBCR glass sample and creation of BO4 units enhances the density of the PPTBCR glass sample. The band found around 1100 cm−1 is attributed to B–Osym stretching vibrations in BO4 units from various borate groups [11, 47] and shifting of this band towards lower wave number side in CPTBCR/PPTBCR glasses may be due to the creation of bridging fluorine’s in the glass network. A band at 1310 cm−1 is observed only in the MPTBCR-0 glass sample in which metal fluoride is absent and it is not observed in CPTBCR and PPTBCR glass samples in which metal fluoride is present. This band is attributed to asymmetric vibrations of B–O bonds on BO3 units. The deep band at 1400 cm−1 is due to asymmetric stretching relaxation of B–O bonds of trigonal BO3 units [12, 47].

3.5. Raman spectra

Raman spectra of xMF2−(10−x)TeO2−30PbO−59.8B2O3−0.2Cr2O3 (where M = Pb & Ca, x = 0, 10 & 20 mol%) glass samples are recorded in the range 200–1600 cm−1 and is shown figure 8. Deconvoluted spectrum (figure 9) has drawn to extract the hidden band positions in the Raman spectra. The major Raman bands observed at ∼356 cm−1, ∼753 cm−1, ∼1091 cm−1 and ∼1344 cm−1 in all the glass samples. The Raman band near 356 cm−1 is due to symmetric stretching vibrations of Te–O–Te linkages [14]. When the metal halide...
in the form of PbF$_2$ is added, an extra band at 838 cm$^{-1}$ is observed and the intensity of the band is increased from MPTBCR-0 to PPTBCR glass sample. In PPTBCR-2 glass sample the intensity of 838 cm$^{-1}$ band became maximum and the 753 cm$^{-1}$ band seems to be diminished. Generally the band at 753 cm$^{-1}$ is attributed to the stretching vibrations of Te–O bonds on TeO$_3$ and TeO$_4$ groups [14, 48]. The appearance of the band 838 cm$^{-1}$ along with 753 cm$^{-1}$ in PPTBCR-1 glass sample might be due to the addition of PbF$_2$ at the expense of TeO$_2$. The addition of metal fluoride might be creating Te–F bonds along with Te–O bonds. Therefore, the band at 838 cm$^{-1}$ can be attributed to Te–F bond vibrations. The disappearance of 753 cm$^{-1}$ band and presence of 838 cm$^{-1}$ in PPTBCR-2 glass sample can be attributed to Te–F bond vibrations only. Similar results were observed in the CPTBCR samples, but the increase in intensity of the band at 838 cm$^{-1}$ is relatively much less when compared to PPTBCR glass samples. In CPTBCR glass sample it is seen that 753 cm$^{-1}$ band is present and it is diminished in CPTBCR-2 glass sample while 838 cm$^{-1}$ band is found in both the samples. Another new band at 977 cm$^{-1}$ is grown in CPTBCR glass samples and its intensity increased with the increase of CaF$_2$ content. This new band at 977 cm$^{-1}$ in CPTBCR glasses is due to pentaborate and tetraborate groups. The bands at ~1100 cm$^{-1}$ are due to diborate and pyroborate groups. The band at ~1350 cm$^{-1}$ is due to BO$_3$O$^-$ triangles linked to B$_2$O$_3$ units [49–53].

**Figure 8.** Raman spectra of xMF$_2$–30PbO–(10-x)TeO$_2$–59.8B$_2$O$_3$–0.2Cr$_2$O$_3$ (Where M = Ca and Pb; x = 0, 5, 10 mole%) glass system.

**Figure 9.** Deconvoluted Raman spectra of MPTBCR-0 glass sample.
4. Conclusions

The glass samples with the compositional formula \( xMFe_2-(10-x)TeO_2-30PbO-59.8B_2O_3-0.2Cr_2O_3 \) (where \( M = Pb & Ca, x = 0, 10 \) & 20 mol\%) were prepared using melt quenching method. The Prepared MPTBCR glass samples were analyzed using physical, optical, EPR, FTIR and Raman measurements. The density values were decreased with the addition of calcium fluoride whereas the values were increased with the addition of lead fluoride. The variation in density values were explained on the basis of the relative crystal densities of tellurium oxide, calcium fluoride and lead oxide. The optical band gap and Urbach energy values were found to be decreased with incorporation of metal fluorides and the decrease is found more in PbF2 doped glasses. Refractive index values for MPTBCR glasses were increased with the addition of metal fluorides and lead fluoride doped glasses found to be more compared to other glasses. Therefore, even though the lead is toxic nature, due to their high index of refraction and high density, lead based glasses; find applications in fiber optic communication and radiation shielding materials. EPR spectra shown two resonance signals at low field (\( g = 4.17 \)) and high field (\( g = 2.0 \)) regions. The observed signals are attributed to isolated \( Cr^{3+} \) ions in the distorted octahedral sites for g value in the low field region \( g \approx 4.2 \) and exchange coupled pairs of \( Cr^{3+} \) ions for the effective g value at \( \approx 1.97 \) in the high field region. FTIR spectra revealed the creation BO3 units by the replacement of TeO2 with CaF2 and creation of BO4 units on replacement of TeO2 with PbF2. FTIR spectra also revealed that the glass structure of MPTBCR glasses mainly composed with TeO3, TeO2, BO3 and BO4 structural units. And the glass structure is greatly influenced with the metal fluoride added to the MPTBCR glass system, especially in the creation of BO3 and BO4 units. Deconvoluted Raman spectra have been drawn to locate exact band positions in MPTBCR glass system. The decrease in peak intensity at 753 cm\(^{-1}\) and growth in peak intensity at 838 cm\(^{-1}\) with the replacement of TeO2 with metal fluoride may be due to the conversion of Te–O vibrations at 753 cm\(^{-1}\) to Te–F bond vibrations at 838 cm\(^{-1}\). The increase in intensity of Te–F bond bending vibrations is found to be more in PPTBCR glasses compared to CPTBCR glasses.

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