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Structural and spectroscopic investigations of multi-component $PbO–Al_2O_3–TeO_2–GeO_2–SiO_2$ glass ceramics doped with NiO

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ABSTRACT

Multi-component glass ceramics with composition $PbO–Al_2O_3–TeO_2–GeO_2–SiO_2$ doped with NiO ranging from 0 to 1.6 mol % were synthesized through melt quenching technique subsequent by heat treatment. XRD and SEM techniques were employed for confirmation of ceramic nature of the prepared samples. Besides this some other analytical techniques *viz*., optical absorption and FTIR studies were also employed on these glass ceramics. XRD patterns of the prepared samples have exhibited different crystalline phases. Optical absorption spectra of these samples have exhibited three octahedral bands around 1405, 805 and 435nm and one tetrahedral band at about 648 nm. Optical band gap energies were computed from the Tauc's plots and these are found to increase slowly from 0.2 to 1.0 mol% of nucleating agent NiO beyond this concentration the decreasing trend in it is noticed. FTIR spectrum of the titled glass ceramics have exhibited various vibrational bands *viz*., Si-O-Si; Si-O-Ge; O-Si-O; and different asymmetrical structural units, such as PbO_6; GeO_6; TeO_3; AlO_6 and symmetrical structural units *viz*., SiO_4; GeO_4; PbO_4 and TeO_4 etc., in the glass ceramic network. Therefore, the analysis of these spectroscopic investigations suggests that the glass ceramics doped with 1.6 mol% of NiO exhibit semiconducting nature.

1. Introduction

Among various oxide glasses, silicate glasses have combined the worth of low thermal expansion coefficient, stable physical and chemical properties and high thermal shock resistance. It is well known that the structure of GeO_2 glass is described in terms of the continuous random network of GeO_4 tetrahedral structural units and the formation of GeO_6 depends on the availability of oxygen ions provided by the modifier oxides. The incorporation of Ge ions in the silicate glass has also allowed the fabrication of Bragg's gratings, which, by exploiting the photosensitivity of the so obtained glass, are the basic components of routers; add drop multiplexers and filters, used in telecom and sensor applications [1]. The addition of heavy metal oxide PbO to the glass matrix exhibits high density, high refractive index, strong infrared (IR) cut-off frequencies, good thermal stability and infrared optical transmission. Tellurium oxide (TeO_2) based glasses have been the subject of much interest for optical applications such as fast optical switches, broad band amplifiers and optical fibers for fiber-optic communications due to their wide infrared transparency, good chemical resistance, high linear and non-linear refractive indices [2]. Aluminum ions may also participate in the glass network with AlO_5 and AlO_6 structural units in addition to AlO_4 structural units depending up on the composition of the glass, and these ions influence the physical properties of the glasses to larger extent [3]. Among various transition metal ions, the divalent nickel ion is an interesting paramagnetic ion to probe in the glass systems. Nickel ions mostly exist in the divalent state with $3d^8$ electronic configuration are extremely stable even at room temperature and there is no need for special care in experimentation in retaining nickel ions in the divalent state. Ni^{2+} ions occupy both tetrahedral and octahedral positions in the glass or glass ceramic matrices. It has been also reported that Ni^{2+} doped glasses and glass ceramics exhibit broad infrared emission property, lasing action and used in telecommunications [4]. Keeping in view these potential applications of NiO doped glasses, the present work is aimed to synthesize the multi-component $PbO-Al_2O_3-TeO_2-GeO_2-SiO_2$ glass ceramics doped with different concentration of NiO ranging from 0 to 1.6 mol% as nucleating agent so as to assess the influence of the nickel ions on the characterization, structural and spectroscopic features of these glass ceramics by performing XRD, SEM and conventional spectroscopic studies *viz*., optical absorption and FTIR.

2. Materials and Methods

Glass ceramics with composition $29PbO–5Al_2O_3–1TeO_2–10GeO_2–(55–x) SiO_2$: x NiO ($0 \leq x \leq 1.6$ mol %, in steps of 0.2 designated as Ni0, Ni2, Ni4,….Ni16) were prepared by conventional melt quenching technique and subsequently with heat treatment. The batches of 15g weight from the proportionate amounts of raw materials *viz*., Al_2O_3, TeO_2, GeO_2, SiO_2 (Sigma Aldrich, 99.99% pure), PbO and NiO (LOBA, 99.99% pure) were mixed homogeneously then taken in a silica crucible (Infusil make) and melted at 1400°C for 10 min in a high temperature programmable furnace. Then the molten material was quenched to room temperature by pouring on to a brass plate. Then subsequently these were annealed around 400°C to remove the internal stress of the samples. All samples were heat treated in another furnace at their crystalline temperature 800ºC for 36hrs and subsequently they were allowed to cool to room temperature slowly.

The densities and molar volumes of these ceramic samples were measured to an accuracy ±0.001 g/cm^3 by the standard Archimedes principle using O-xylene (99.99% pure) as a buoyant liquid with a programmable VIBRA HT density measurement kit. The experimental details of various techniques *viz*., X-ray diffraction (XRD), scanning electron microscopy (SEM), optical absorption and Fourier transform infrared (FTIR) employed for the titled glass ceramics are same as that reported in our previous paper [5].

3. Results and discussion

3.1. Physical parameters

The density, p values of PbO–Al $_2$O$_3$–TeO$_2$–GeO$_2$–SiO$_2$: NiO glass ceramic samples are found to increase trivially with the increasing content of nucleating agent NiO. The observed increase in the density of the prepared glass ceramics is explained in terms of its molecular mass of NiO (74.692 g/mole) is high compared to that of SiO$_2$ (60.08 g/mole) and structural modification such as the formation of octahedron germanium and lead in the glass network results in better packing and leads to increase in the density of the sample [6]. Other physical parameters such as molar volume V_m, nickel ion concentration N_i, mean inter-ionic separation R_i, and polaron radius R_p were evaluated, with the help of the measured values of the density, p and average molecular weight, M of the samples, using conventional formulae [7] and all these are presented in Table-1.

Table-1 Physical parameters of PbO–Al$_2$O$_3$–TeO$_2$–GeO$_2$–SiO$_2$: NiO glass ceramics.

Sample	Density ρ (g/cm^3) (±0.001)	Molar Volume V_m (cm^3/mole) (±0.001)	Nickel ion conc. N_i (x10^{21} /cm^3) (±0.001)	Inter ionic separation R_i (Å) (±0.001)	Polaron radius R_p (Å) (±0.001)
Ni0	4.513	25.467	–	–	–
Ni2	4.526	25.400	4.743	5.952	2.399
Ni4	4.547	25.289	4.763	5.943	2.395
Ni6	4.559	25.229	4.775	5.939	2.394
Ni8	4.583	25.103	4.799	5.929	2.390
Ni10	4.596	25.035	4.812	5.923	2.387
Ni12	4.604	24.999	4.819	5.921	2.386
Ni14	4.618	24.928	4.832	5.915	2.384
Ni16	4.632	24.864	4.845	5.910	2.382

3.2 XRD

XRD patterns of the titled glass ceramics are shown in Fig.1. From these patterns it can be seen that nickel oxide free sample has exhibited three crystalline phases *viz*., PbTeO$_3$ (JCPDS No. 035–1045), PbAl$_2$Si$_2$O$_8$ (JCPDS No. 087–1003), PbGe(O(Ge$_2$O$_6$)) (JCPDS No. 083–1403). Besides these another five phases such as NiPb$_3$Ge$_5$O$_{14}$ (JCPDS No. 039–1263), Ni$_3$Al$_2$SiO$_8$ (JCPDS No. 074–0730), NiTe$_2$O$_5$ (JCPDS No. 074– 0856), Pb$_8$Ni(Si$_2$O$_7$)$_3$ (JCPDS No. 032–0527) and Ni$_2$SiO$_4$ (JCPDS No. 076– 1502) were also observed in NiO doped samples. All the above mentioned eight crystal phases were identified using the JCPD data [8] and are kinetically as well thermodynamically feasible. Distinct variation in the intensity of diffraction peaks was observed with increasing the nucleating agent NiO. The prepared glass ceramic samples retain the transparency even after crystallization.

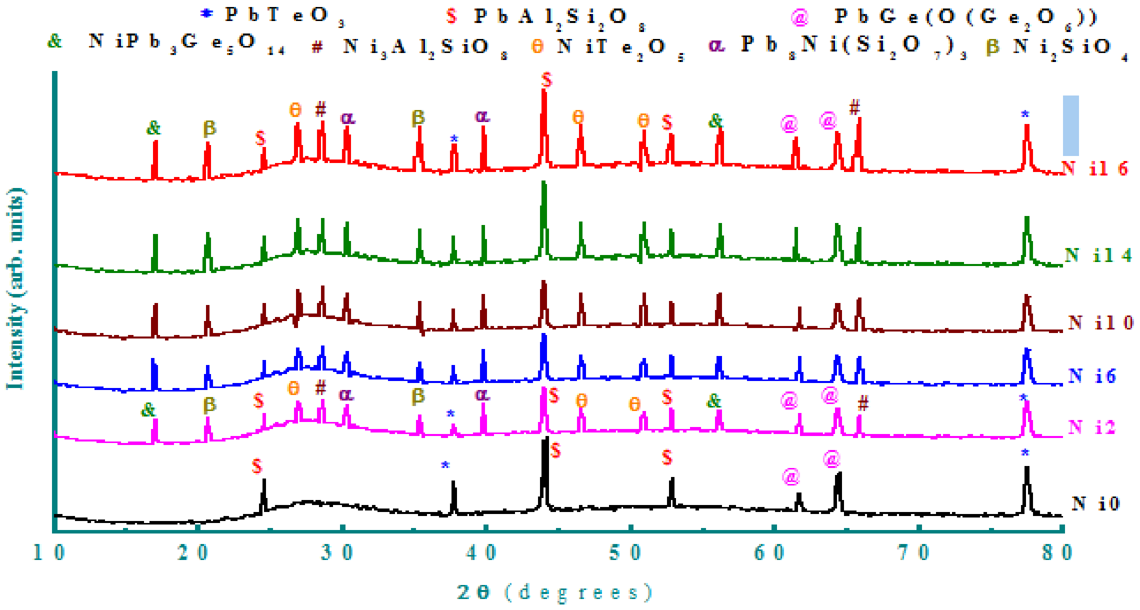

Fig.1 XRD patterns of some of the PbO–Al$_2$O$_3$–TeO$_2$–GeO$_2$–SiO$_2$: NiO glass ceramics.

3.3 SEM

Fig. 2 shows the SEM images of some of PbO–Al_2O_3–TeO_2–GeO_2–SiO_2: NiO glass ceramic samples. These images of crystallized samples exhibited well-defined and randomly distributed crystals of different sizes entrenched in the glassy matrix. The reactivity of nickel with the other oxides precipitates as a high density of fine nickel rich tiny crystals which act as heterogeneous nuclei for the crystallization of the remaining glass. SEM images confirmed that the titled glass ceramics consist of small crystals of irregular and distorted form aggregated into spherulites, with the residual glass phase which makes the samples free of voids and cracks by interconnecting the crystallized portions.

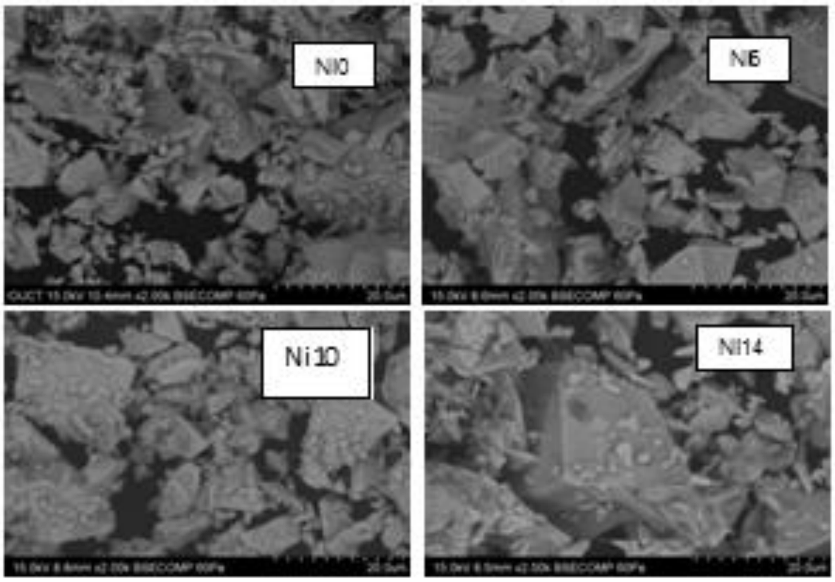

Fig.2 SEM images of some of PbO–Al_2O_3–TeO_2–GeO_2–SiO_2: NiO glass ceramics.

3.4 Optical absorption spectra

The optical absorption spectra of PbO–Al_2O_3–TeO_2–GeO_2–SiO_2: NiO glass ceramics recorded at room temperature in the wavelength range of 250–1600 nm are shown in Fig. 3. Data on optical absorption spectra of titled samples are presented in Table- 2. The absorption edge observed at 407 nm for sample Ni0 is blue shifted with the introduction of nucleating agent up to 1.0 mol% and beyond this concentration it has taken red shift. Besides this the spectrum exhibited clearly four intense absorption bands in NIR and visible regions at about 1405 nm (O_{h1}), 805 nm (O_{h2}), 648 nm (T_d), and 435 nm (O_{h3}). As the concentration of nucleating agent NiO is increased from 0.2 mol% to 1.0 mol% the intensity of three octahedral bands is observed to decrease with blue shift in the band positions where as the intensity of the tetrahedral band is red shifted in the band position and opposite trend is noticed beyond this concentration of nucleating agent NiO.

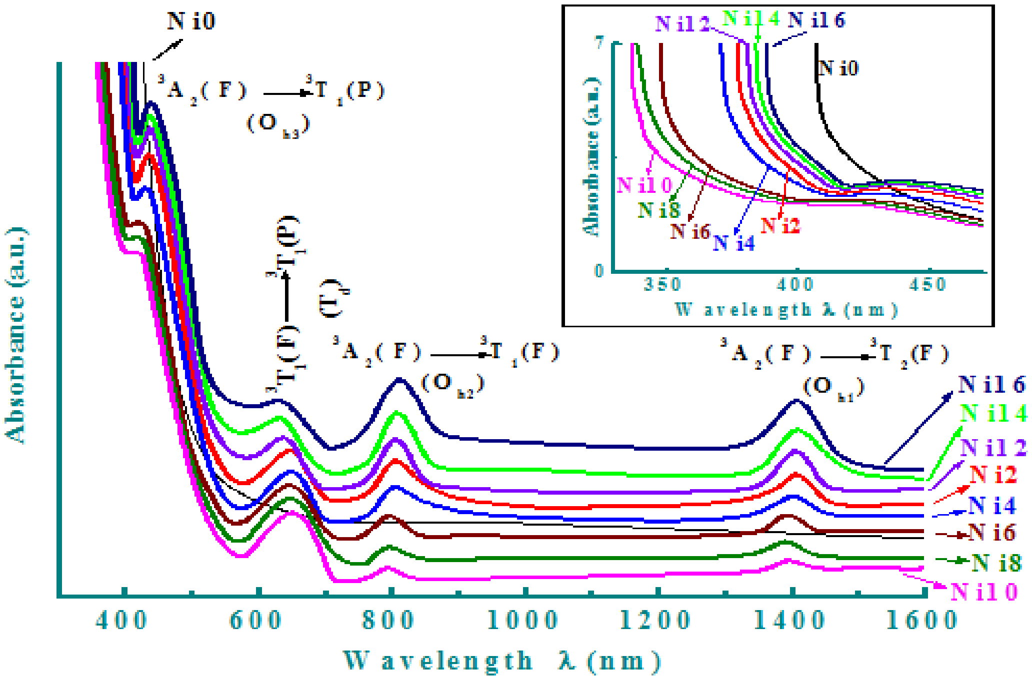

Fig.3 Optical absorption spectra of PbO–Al_2O_3–TeO_2–GeO_2–SiO_2: NiO glass ceramics. Inset shows the cut-off wavelength of PbO–Al_2O_3–TeO_2–GeO_2–SiO_2: NiO glass ceramics.

Table-2 Data on optical absorption spectra of PbO–Al_2O_3–TeO_2–GeO_2–SiO_2: NiO glass ceramics.

Assignment	Ni0	Ni2	Ni4	Ni6	Ni8	Ni10	Ni12	Ni14	Ni16
Absorption edge λ_c (nm)	407	377	371	348	339	337	381	384	388
Optical band gap E_o (eV) (± 0.01)	2.99	3.23	3.27	3.49	3.51	3.60	3.18	3.16	3.13
Urbach energy ΔE (eV) (±0.001)	0.279	0.252	0.243	0.221	0.208	0.205	0.256	0.259	0.262
Band positions of O_h transitions of Ni^{2+} ions (nm) (± 1)									
$^3A_2$ (F)→$^3T_2$(F) (O_{h1})	–	1405	1402	1396	1393	1392	1407	1409	1412
$^3A_2$ (F)→$^3T_1$(F) (O_{h2})	–	805	803	797	795	794	807	809	811
$^3A_2$ (F)→$^3T_1$(P) (O_{h3})	–	435	433	429	427	426	438	439	441
Band positions of T_d transitions of Ni^{2+} ions (nm)									
$^3T_1$ (F)→ $^3T_1$(P) (T_d)	–	648	651	655	658	662	644	641	639

Additionally, the observed trend in the intensity of the absorption bands of the glass ceramics with an increase in the content of nucleating agent NiO up to1.0 mol% suggests that majority of the Ni^{2+} ions prefer to occupy the tetrahedral positions where as beyond this concentration these ions occupy octahedral sites in the glass ceramic work. Therefore, Ni^{2+} ions seem to exist in both four- and six-fold coordination in the glass ceramic structure and also the d-d transitions are electric dipole allowed for the tetrahedral complexes and electric dipole forbidden for octahedral complexes which are mainly due to the static or dynamic distortions from the regular octahedral geometry of the glass network. In general, octahedrally positioned Ni^{2+} ions participate in the glass ceramic network with NiO_6 structural units and stimulate the formation of NBOs which results in the formation of cross linkages *viz*., Si-O-Pb , Si-O- Ge, Si-O- Te, Si-O-Al, Si-O-Ni, Ge-O-Pb, Ge-O-Ni etc., Such type of cross linkages enhances the depolymerization in the glass network which in turn pick up the conductivity of the glass ceramic material. Whereas the tetrahedrally positioned Ni^{2+} ions may participate in the glass ceramic network with NiO_4 structural units to strengthen the ceramic structure and significantly enhances the insulating strength of the material [9].

Therefore, from the analysis of the optical absorption it is clear that in the present glass ceramic samples the ratio $Ni^{2+}(O_h)/Ni^{2+}(T_d)$ decreases with increasing concentration of NiO up to 1.0 mol%. Thus in the glass ceramic matrix up to 1.0 mol% of NiO, the concentration of NBOs is found to be minimal and it leads to the decrease in the degree of localization of electrons thereby decreasing the donor centers in the glass matrix. The presence of such smaller concentration of these donor centers increases the optical band gap due to changing of the absorption edge towards lower wavelength which in turn enhances the rigidity or insulating strength of the sample doped with 1.0 mol% of NiO to the maximum extent

3.5 FTIR spectra

Fig. 4 shows the FTIR spectra of PbO–Al_2O_3–TeO_2–GeO_2–SiO_2:NiO glass ceramic samples. These spectra have exhibited the conventional vibrational bands at about 1170, 1045, 899, 767, 708, 645, 475 and 440 cm^{-1}. It is worth mentioning that nickel ions participate in the glass network with NiO_4 and NiO_6 structural units even though the IR vibrational bands of Ni-O are not resolved in the FTIR spectrum of the titled glass ceramics [10]. The assignment of various vibrational bands observed in FTIR spectra of the titled glass ceramics along with the references concerned is furnished in Table 3. As the concentration of nucleating agent NiO changes in the host glass ceramics from 0.2 to 1.0 mol%, the intensity of various asymmetrical vibrational bands *viz*., Si-O-Si, Si-O-Ge, O-Si-O and PbO_6, GeO_6,TeO_3 is found to decrease gradually where as that of the symmetrical bands in FTIR spectra is observed to increase. Such a decreasing trend in the intensity up to 1.0 mol% of the nucleating agent suggests that the higher fraction of Ni^{2+} ions favored to occupy tetrahedral positions in the glass ceramic network as a result the rigidity of the glass ceramic structure increases due to the less depolymerization. Beyond 1.0 mol% of NiO, largely these Ni^{2+} ions go to the octahedral sites and they act as network modifiers. Such octahedrally positioned Ni^{2+} ions are responsible to enhance the degree of depolymerization in the glass ceramic network by creating more dangling bonds which in turn induce the number of NBOs .This type of behavior also favors the formation of cross linking bonds *viz*., Si-O-Pb, Si-O-Ge, Pb-O-Ge, Te-O-Pb etc., in the glass ceramic structure particularly at higher concentration i.e., 1.6 mol% of nucleating agent NiO.

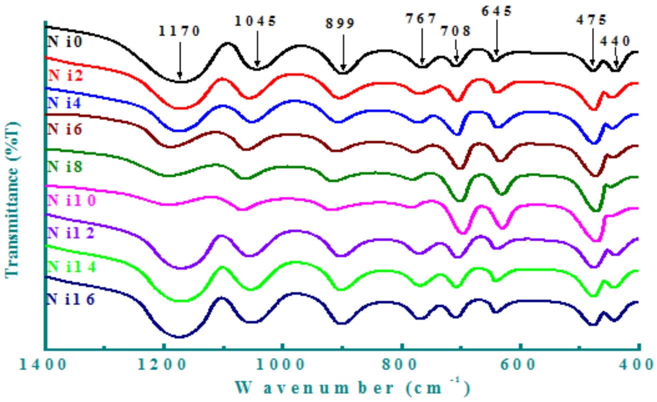

Fig.4 FTIR spectra of PbO–Al_2O_3–TeO_2–GeO_2–SiO_2:NiO glass ceramics.

However, when the percentage of PbO is >20 mol% [11] Pb is subjected to enter into the network as tetrahedral PbO_4 units and this would increase the three dimensional association of the lead-germanate network [12, 13]. As PbO presents more than 20 mol% in the present glass ceramic system hence, PbO enters into the network forming position, the additional oxygens required for tetrahedral coordination will be provided by the O^{2-} ions available from the modifier oxides in the glass ceramic composition. Therefore, in the glass ceramics samples doped with from 0.2 to 1.0 mol% of nickel oxide, PbO_4 structural units are found to increase which in turn improves the rigidity of the glass ceramic network. But beyond 1.0 mol% of nucleating agent NiO, modifier Ni^{2+} ions may enter the glass network by breaking up bonds *viz*., Si-O-Pb, Si-O-Ge, Pb-O-Ge, Te-O-Pb and TeO_4 structural units and may introduce both stable and unstable $Te\text{-}O^-$ bonds which will later on be transformed to $Te\text{-}O^-$ or TeO_{3+1} due to the contraction of one $Te\text{-}O^-$ and the elongation of another $Te\text{-}O^-$ bond. Therefore up to 1.6 mol% of NiO, cleavage of continuous network increases the fraction of TeO_{3+1}polyhedra. Further such elongation of $Te\text{-}O^-$ bond of TeO_{3+1} and its cleavage ultimately leads to the formation of trigonal prismatic TeO_3 units in addition to AlO_6 structural units. Such phenomenon increases the depolymerization of the glass ceramic network due to increase of NBOs. Finally, the analysis of these spectroscopic investigations carried out on the titled glass ceramics indicates that samples doped with 1.6 mol% of NiO are useful for semiconducting devices.

Table-3 Data on FTIR spectra of $PbO–Al_2O_3–TeO_2–GeO_2–SiO_2$: NiO glass ceramics. (band positions are in cm^{-1})

Ni0	Ni2	Ni4	Ni6	Ni8	Ni10	Ni12	Ni14	Ni16	Assignment	Ref.
440	446	448	449	451	452	445	444	443	Rocking vibrations of Si–O–Si structural units and Al–O bonds in AlO_6 structural units.	[3]
475	472	471	468	466	465	473	473	474	Pb–O bond vibrations in PbO_4 structural units.	[3]
645	643	641	634	632	629	643	644	644	Stretching vibrations of equatorial and axial Te–O bonds in the $[TeO_4]$ tbp structural units.	[14]
708	704	703	700	698	696	705	706	707	Symmetric stretching vibrations of Si–O–Si linkages between SiO_4 structural units.	[15]
767	771	773	779	781	782	770	769	768	vibrations of TeO_3 structural units and $Ge\text{-}O^-$ vibrations in GeO_6.	[14, 16]
899	906	907	911	915	918	904	903	901	PbO_6 structural units	[17]
1045	1054	1057	1066	1069	1071	1053	1051	1049	Asymmetric stretching vibrations of Si–O–Si and Si-O-Ge linkages.	[15, 18]
1170	1174	1175	1187	1192	1193	1173	1172	1171	Asymmetric stretching vibrations of O–Si–O of SiO_4 units.	[19]

4. Conclusion

Glass ceramics with composition $29PbO–5Al_2O_3–1TeO_2–10GeO_2 – (55\text{-}x)SiO_2$: x NiO ($0 \le x \le 1.6$ mol %) were synthesized through melt quenching technique followed by heat treatment. XRD, SEM, and spectroscopic studies *viz*., optical absorption and FTIR studies were carried out on these glass ceramics. XRD patterns of the prepared glass ceramics have exhibited different crystalline phases. From the analysis of SEM pictures of the samples we conclude that introduction of NiO accelerates the phase decomposition of the glass and slows down the crystallization of different crystal phases detected in the titled glass ceramics to 1.0 mol% of the nucleating agent beyond this concentration again it enhances the rate of crystallization which causes the increase of NBOs and enhances the depolymerization of the ceramic structure as well. The bands observed around 1405, 805 and 435nm are assigned to octahedral transitions. Besides these another band around 648 nm is also noticed due to tetrahedral transition and the observed growth of this absorption band at the expense of octahedral bands with an increase in the content of nucleating agent NiO up to1.0 mol% suggests that part of Ni^{2+} ions prefer to occupy the tetrahedral positions where as beyond this concentration these ions occupy octahedral sites in the glass ceramic work. FTIR spectra of the titled glass ceramics have exhibited various asymmetrical and symmetrical structural units in the glass ceramic network. The observed decreasing trend in the intensity of the asymmetrical vibrational modes from 0.2 to 1.0 mol% of NiO suggests that the higher fraction of Ni^{2+} ions preferred to occupy tetrahedral positions in the glass ceramic net work as a result the rigidity of the glass ceramic structure increases due to less depolymerization. Beyond 1.0 mol% of NiO, these Ni^{2+} ions largely go to the octahedral sites and they act as network modifiers. Such octahedrally positioned Ni^{2+} ions are responsible to increase the degree of disorderedness in the glass ceramic network by creating more dangling bonds which in turn induce the more number of NBOs. Therefore the analysis of these spectroscopic investigations suggests that the glass ceramics doped with higher content i.e.,1.6 mol% of NiO are suitable for semiconducting devices.

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