

Novel synthesis and spectroscopic analysis of gallium oxide doped zinc phosphate glass

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Phosphate glasses are known for their wide applications in the field of optical fiber, lasers, seals and sensors. Glass system containing $(40-x) \text{ZnO-xGa}_2\text{O}_3\text{-50P}_2\text{O}_5\text{-Na}_2\text{O}$, where $x=0$ to 10mol % were prepared. The effect of gallium oxide on the properties of these glasses were studied. To observe the structure of prepared phosphate glasses FTIR was used under the wavelength range of $400\text{-}4000 \text{ cm}^{-1}$. The prominent peaks appeared in region 400 cm^{-1} to 2500 cm^{-1} . The glasses were transparent up to 1500 cm^{-1} which make them suitable in the field of lasers. The FTIR also confirmed that Q2 structure dominates these glasses.

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1. Introduction

Phosphate glasses are commercially useful glasses that have wide applications in optical fibers, laser glass hosts, glass polymer composites, seals, sensors, solid state batteries and in semiconductors. They are also used in disposal of nuclear wastes, biomaterial engineering and in the biomedical field due to their properties of low melting points, short glass transition temperature, less softening along with more thermal expansion coefficient, etc. [1-7]. But low chemical and moisture resistance of phosphate glasses restricts their applications. However, this point could be easily handled by researchers by the addition of some metal oxides [8-16]. Among all metal oxides zinc oxide possess excellent features for improving the performance of phosphate glass hence, Zinc phosphate glass system is reported as lead free glass system that requires low temperature for melting. Zinc oxide improves the mechanical strength and chemical durability of phosphate glasses and decreases the transition temperature. It has good optical, magnetic and electrical properties [17-27]. It gives a wider glass forming region. It can act as a glass modifier or glass former. When zinc oxide behaves as a glass modifier, it is present at interstitial positions of phosphate glass system with 6 coordination number whereas in the metaphosphate glass system, zinc acts as a glass former with coordination number 4 as ZnPO_4 units [28-30]. Zinc phosphate glasses are used in lasers, LED light sources, optical waveguides, in seals and welds, glass polymer composites, Bioactive zinc glasses have antimicrobial effect against staphylococcus aureus [31].

Gallium oxide is also added in phosphate glasses as it increases the chemical durability. The Ga^{3+} ions when incorporated into the phosphate glass system make cation- phosphate interactions that are highly covalent, thus increasing the chemical resistance. Among widely reported metal oxides the ionic radius of gallium oxide is far better and greater for efficiently improving the refractive index of prepared phosphate glasses [31, 32]. Additionally, gallium oxide also improves the solubility of rare earths that is necessary for the mineralization of optical components. Gallium oxide phosphate glasses have wide applications in the medical field as they possess high antibacterial effects. Controlled delivery of gallium oxide ions helps in combating the localized infections [33-35].

Gallium trioxide acts as glass modifier or glass former in the presence of other metallic oxides. Through X-ray diffraction and Raman spectroscopy, it is found that the presence of GaO_4 and GaO_6 depends upon the concentration of gallium [36, 37]. It is also evident from structural

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studies of gallium zinc phosphates glasses that the coordination number of gallium ions is six, four or possibly five [38-40].

Gallium oxide glasses are interesting optical materials that have good transmittance in IR region up to 6.5 μ m. These glasses are widely used in fiber lasers and amplifiers in (near and mid IR ranges). High transparency in the spectral range of 0.5-10 μ m is seen in gallium oxide glasses. Gallium oxide is used as a dopant in bioactive glasses. Gallium oxide acts as a diagnostic, therapeutic agent in bone, cancer and infectious diseases. Gallium phosphate glasses are used in nonlinear optics, glass seals, low glass solders and electrolytes in solid state electrochemical cells. Gallium phosphate glasses are also used in infrared windows, ultrafast optical insulators and photonic devices of communications and advanced computer applications [38, 41-47].

The basic structure of phosphate glasses were described on the basis of four different phosphate structural units that are derived from PO₄ tetrahedral represented as on, where n can be 0,1,2 and 3, depending upon the bridging oxygen (BOs) per phosphate tetrahedron. When n= 0 , Q₀ are isolated orthophosphates, similarly pyrophosphates, metaphosphates and ultraphosphates are formed when n is 1,2 and 3 (Q₁, Q₂ and Q₃) respectively [48].

Phosphate glasses possess wide commercial applications in the field of lasers, optical fibers, seals, solid state batteries as well in the field of biomedical and biomaterial engineering. The low chemical and water durability, restricts application of phosphate glasses. To solve this problem, metal oxides are added to the phosphate glasses to enhance the durability. In this paper glass system gallium oxide is added to the phosphate glass system in the presence of zinc oxide and soda.

2. Experimental

2.1. Preparation of gallium doped Zinc phosphate glasses

Glass system containing xGa₂O₃ (50P₂O₅-10Na₂O-40ZnO- x) where the amount of gallium oxide varied from 1-10 mol% at expense of zinc oxide while the concentration of other constituents phosphorus penta-oxide and sodium oxide remained constant at 50 mol% and 10 mol% respectively (Table 1). The glasses were prepared by careful weighing using an electric furnace. The weighted constituents were homogeneously mixed in agate mortar and transferred into Aluminium crucible. The muffle furnace was preheated at 250 °C to avoid excessive effervescence. After this the temperature of the muffle furnace was raised to 980 °C. The crucible was then transferred to annealing furnace at transition temperature of the glass for two hours. The glass melt prepared were then transferred to the mold and transparent glass discs were obtained. The obtained glasses were odorless and transparent. The participation of other raw materials, sodium oxide and zinc, have made it possible for this glass system to be prepared at a low temperature in a muffle furnace. The zinc phosphate melt containing soda has made gallium oxide to melt at a much lower temperature (980°C) although its melting temperature is very high about 1900° C.

Table 1. Showed varied composition ZnO and Ga₂O in glass sample with constant composition of 10% Na₂O and 50% P₂O₅ in each sample.

Glass	ZnO	Ga ₂ O
FO	40	00
F1	39	01
F2	38	02
F3	37	03
F4	36	04
F5	35	05
F6	34	06
F7	33	07
F8	32	08
F9	31	09
F10	30	10

2.2. Density measurements

Annealed glass was cut into a rectangular shape slab using a diamond edge wheel cutter. The dimensions of the glass samples were 3 mm x 3 mm x 12.5 mm. The surfaces were made flat and were measured by a micrometer. Archimedes method was utilized to measure the density of these phosphate glasses. To measure the density a beaker was placed over the weighing pan over which a beaker was placed. The samples for weight measurements in water were measured by hanging glass samples one by one with the hook of balance beam. The obtained results were compared with general method of density measurement (Table 2). The table 2 showed that with the increase in the concentration of gallium oxide in the samples the density of phosphate glass gradually increases.

Table 2. Showed the density and weight measurement in air and water respectively.

Glass sample	Weight in air (g)	Weight in water (g)	Density (g/cm ³)
FO	4.65	2.93	2.70
F1	2.44	1.58	2.83
F2	3.48	2.30	2.95
F3	3.49	2.35	2.97
F4	3.67	2.45	3.00
F5	3.69	2.49	3.07
F6	3.07	2.60	3.36
F7	3.73	2.65	3.45
F8	3.77	2.70	3.52
F9	3.80	2.73	3.55
F10	3.83	2.76	3.57

2.3. Characterization

Dilatometer instrument named Orton 1600 D was employed for the thermal investigation or expansion of prepared glass. The Dilatometer instrument contained the sample of about one inch with flat ends at the temperature range of 25°C-500°C at heating rate of about 10°C/min, respectively. From this technique the thermal expansion coefficient, glass transition temperature and softening temperature can be easily computed. After the samples were prepared, they were taken for IR test using Bruker instrument (model). As this instrument does not need a KBr disc, finely powdered (-200 BSS mesh) samples were used to get IR spectra. 4000-600cm⁻¹ range was used for observation. Transmission mode was used in the instrument.

3. Results and discussion

Figure 1 (a,b) showed the presence of straight line with the increase in temperature in prepared glass sample. The appearance of straight line specifically in the temperature range of 150 °C - 350 °C indicate the high thermal expansion of synthesized glass. The graphs showed the highest value of thermal expansion of about 13.11/ °C in the absence of gallium oxide. However, on increasing the concentration of gallium oxide the value of thermal expansion coefficient gradually decreases with lowest value at 10 mol % concentration as shown in figure 1. Among thermal properties, the glass transition temperature also known as T_g was studied in this work. The results showed that slope abruptly changed due to thermal expansion. Basically, the abrupt change in slope is due to the phase changes from solid to liquid, respectively. This change is also known as T_g or glass transition temperature. Table 3 and figure 2 also indicate the T_g of all prepared glass samples and results displayed that on increasing the concentration of gallium oxide the T_g value in glass system gradually increases. However, the glass network showed lowest T_g values in the absence of gallium oxide. Additionally, greater value of T_g show high stability of glass due to the lowering of Zinc component (that play key role in decreasing the temperature) and increasing

value of gallium oxide that possess high melting point as shown in figure 2. The T_s value was studied at the peak of thermal expansion trace and after that T_s value the expansion graph decrease due to penetration of the silica probe rod in the glass sample that soft. The T_s steadily increase with increase in gallium oxide as shown in Figure 3. The addition of gallium oxide not only led to the stability of glass system occur but also great softening temperature. The T_g value increases gradually upon increasing concentration of gallium oxide that also increase the strength of glass network. Additionally, the addition of zinc oxide act as system modifier in phosphate glass providing P-O-Zn ionic bonding. However, the addition of gallium oxide in zinc phosphate glass replace mono zinc ion with divalent gallium ions along with substitution of one oxygen with other three oxygen atoms that make glass structure highly compact. The increase in concentration of gallium oxide the zinc ions removes gradually led to the formation of stronger and stable P-O-Ga covalent bond.

Additionally, the co-ordination number also vary on increasing the concentration of gallium ions such as at 5mol% the 5 co-ordination number was obtained while 4 co-ordination number at 10 mol %, respectively. However, on further increasing the concentration of gallium ions the glass changed its stage form metaphosphate to pyrophosphate and then to orthophosphate which finally changed into crystalline phase or glass forming ability of glass network.

Table 3. Displayed the T_g and T_s of prepared glass samples.

Sample	T_g (°C)	T_s (°C)
F0	356	385
F2	361	387
F4	387	419
F6	400	427
F8	410	432
F10	420	437

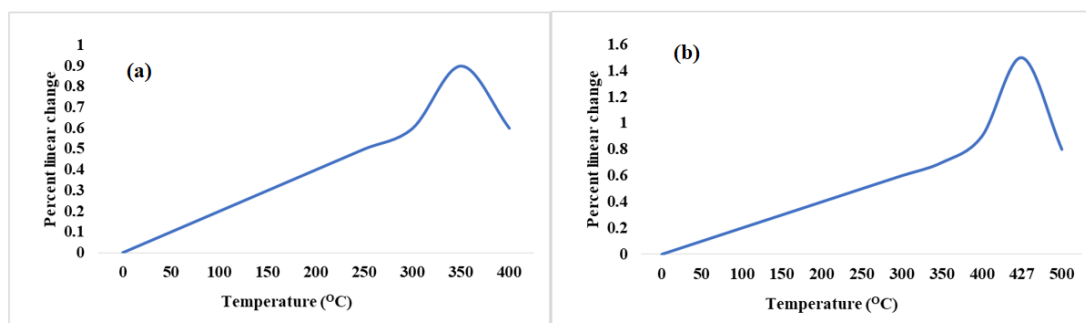


Fig. 1. Showed thermal expansion curve of glass sample a) F_1 b) F_{10} .

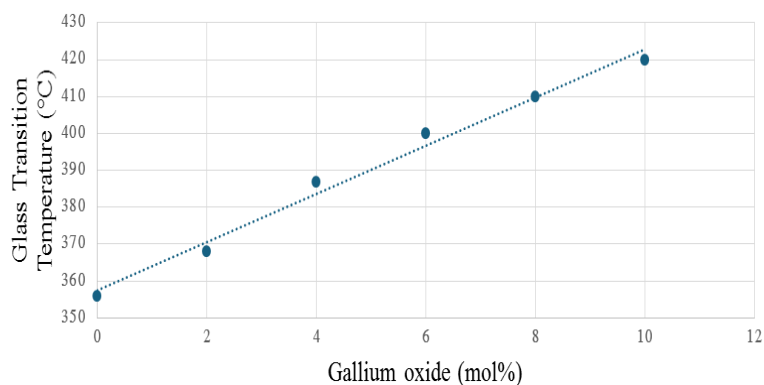


Fig. 2. Displayed changes in T_g of prepared glass samples with the addition of Gallium oxide (mol%).

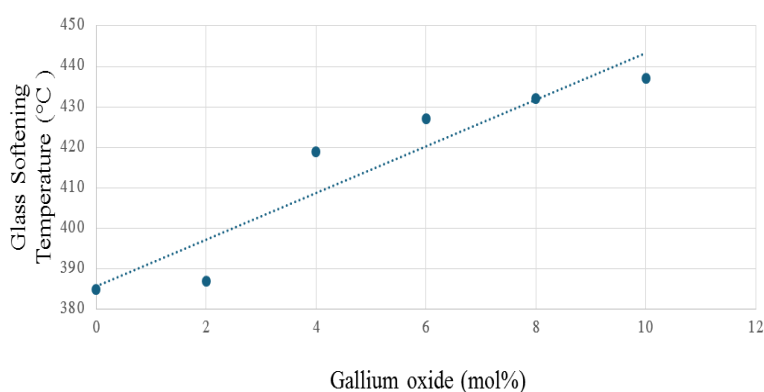


Fig. 3. Displayed changes in T_s of prepared glass samples with the addition of Gallium oxide (mol%).

Table 4 display the thermal expansion and co-efficient of glass samples and also found that synthesized glasses have efficient high thermal expansion and co-efficient which decrease with increasing gallium oxide concentration. Table 5 shows the thermal expansion coefficients of some metals and alloys respectively.

Table 4. Thermal expansion and thermal expansion coefficients of glass samples.

Sample	Thermal expansion at 150 °C	Thermal expansion at 300 °C	Sample length l (inches)	Change in length Δl (inches)	Thermal expansion coefficient $\Delta l / l (\alpha)$
FO	0.3085	0.4844	1.208	0.1759	0.00001311
F1	0.2701	0.4776	1.108	0.2028	0.00001248
F2	0.2658	0.4686	1.074	0.2028	0.00001258
F4	0.2774	0.4427	1.027	0.1653	0.0000107
F6	0.2684	0.4014	1.109	0.133	0.00001199
F8	0.2817	0.4382	1.183	0.1565	0.00000881
F10	0.3085	0.4844	1.208	0.1759	0.000091

Table 5. Thermal Expansion coefficients of some metals and alloys.

Substance	Thermal Expansion Coefficient (α) $\times 10^{-6}/^{\circ}\text{C}$
Pt	8.9
Fe	10.2
10 % Ni	13
30 % Ni	12
Steel	10.5 - 11.6
Au	13.9
Abbreviations: Nickel (Ni), Gold (Au), Platinum (Pt), Iron (Fe)	

The phosphate glasses are highly efficient in metal glass sealing application and thermal expansion of phosphate glasses are 36 times more than silicate glasses (figure 4). Phosphate glasses possess many properties such as effective structural flexibility, less melting point and improved better matrices for nuclear waste storage than borosilicate glasses.

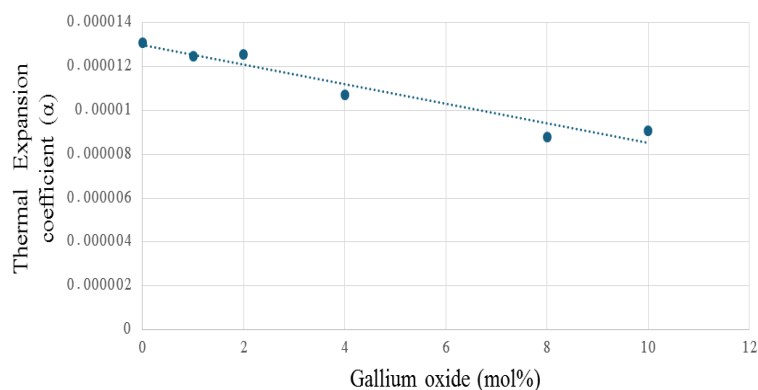


Fig. 4. Displayed changes in thermal expansion coefficient (α) of prepared glass samples with the addition of Gallium oxide (mol%).

3.1. Thermogravimetry

Figure 5 indicate the Thermogravimetric analysis which predict that on increasing temperature the weight loss occur which led to the volatilization of phosphate.

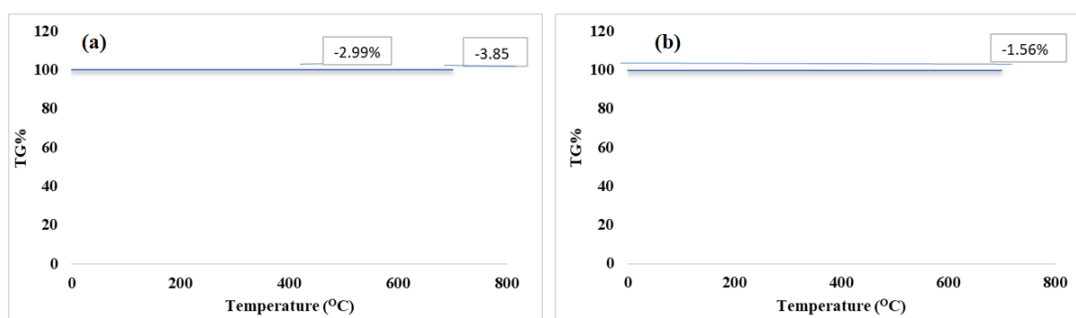


Fig. 5. Thermogravimetric plot of a) F1b) F10.

3.2. Durability studies

In the durability studies different glass samples named as F0, F2, F4, F6, F8 and F10 were used. In this each sample was added in 200 ml water to prevent the saturation of leached ions. Additionally, a comparatively 60 °C temperature was adjusted to leached the appreciable or greater amount of ions in leaching experiment. The leaching of ions are very effective and necessary because it will not only reduce experimental or human errors but also aid in the determination of sodium oxide, zinc oxide and phosphorous pentoxide, respectively. Additionally, the each samples was weighed before adding in water and these samples were added in separate jars for about 5 hrs along with temperature fluctuations $\pm 2^\circ\text{C}$. The temperature was also evaluated by adding the mercury thermometer in water bath.

3.3. Weight loss measurements

Table 6 displayed that weight loss occurred during at 60 °C/5hr in F0 and F2 were comparatively higher than other glasses. Additionally, on increasing the gallium oxide concentration the glass resistance to the water attack improved and weight loss decreased from 0.1758 to 0.0021 figure 6.

Table 6. Weight loss measurements of gallium oxide containing glasses after 5, 10 and 15 hr soaking at temperature of about 60 °C.

Sample	Weight before test	At 60 °C weight (mg) after			Weight loss mg/cm ² /200ml water		
		a) 5 hrs	b) 10 hrs	c) 15 hrs	a) 5 hrs	b) 10 hrs	c) 15 hrs
F ₀	3.93	a) 3.75	b) 3.58	c) 3.93	a) 0.175	b) 0.34	c) 0.547
F ₂	3.24	a) 3.07	b) 2.91	c) -	a) 0.172	b) 0.332	c) -
F ₄	2.95	a) 2.94	b) 2.93	c) 2.92	a) 0.0095	b) 0.021	c) 0.0335
F ₅	1.71	a) 1.64	b) 1.64	c) -	a) 0.06	b) 0.068	c) -
F ₆	2.31	a) 2.29	b) 2.27	c) -	a) 0.013	b) 0.033	c) -
F ₈	2.74	a) 2.73	b) 2.73	c) 2.74	a) 0.0044	b) 0.011	c) 0.0169
F ₁₀	2.89	a) 2.83	b) 2.832	c) 2.839	a) 0.0021	b) 0.0064	c) 0.0106

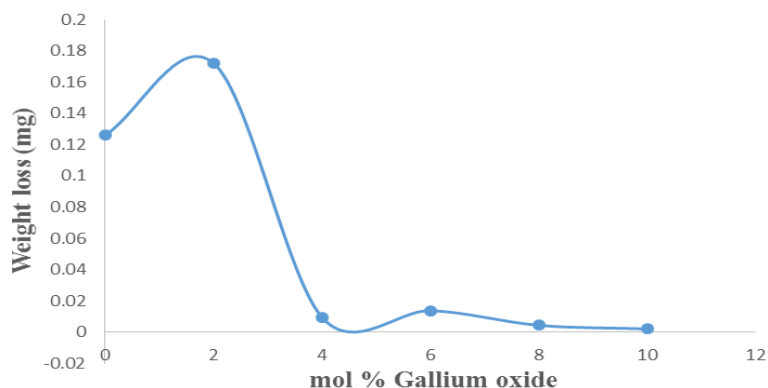


Fig. 6. Changes in weight loss in mg with addition of gallium oxide concentration (mol%) at 5hr/60 °C.

Figure 6 showed that the graph plotted between weight loss and mole % gallium oxide indicate a sharp drop in weight loss in range between 2 mole % - 4 mole % of gallium oxide. After 4 mol% about a slight change in weight loss was also observed. In that leaching experiment the sample was soaked for 5hr at 60 °C and weight loss was measured as given in Table 6. Similarly, F0 and F1 displayed more leaching while the all samples after F4 showed glasses resisted water attack and the weight losses in F0 are 0.3473 g while 0.3324 g in F2 (figure 7). Additionally, among all samples F4 possess ten times less weight loss. However, the addition of gallium oxide in the zinc phosphate glass network possess huge impact on durability and effectiveness of prepared glasses.

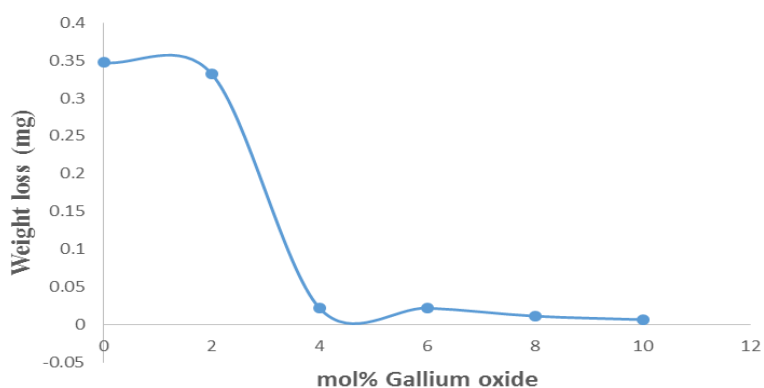


Fig. 7. Changes in weight loss in mg with addition of gallium oxide concentration (mol%) at 10hr/60 °C.

The same experiment was performed for another 5 hr and F0, F4, F8 and F10 samples were selected and weight loss was found to be 0.5478 g, 0.0335 g, 0.0169 g and 0.0106 g, respectively Table 6. These results indicate that gallium oxide played a key role in prohibiting the aqueous attack as shown in Figure 8. A sharp fall in weight loss with addition of gallium oxide is a common feature of these experiments.

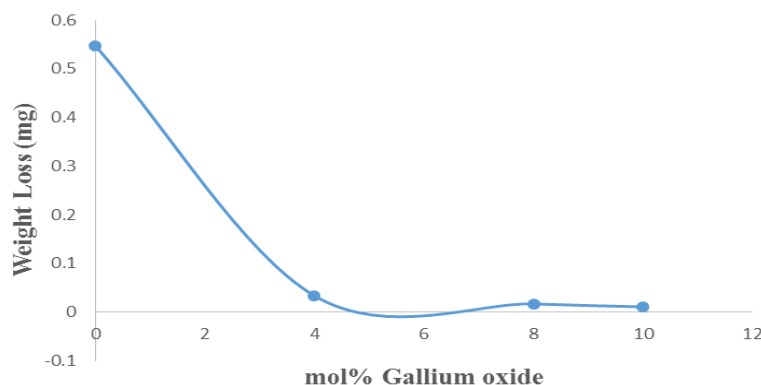


Fig. 8. Changes in weight loss in mg with addition of gallium oxide concentration (mol%) at 15hr/60 °C.

3.4. FTIR analysis

In this study, the FTIR analysis have been used to investigate the structural components preset in the Gallium doped Zinc oxide samples as shown in figures 9 and 10. The figures 9 showed the presence of metaphosphate prevailing in the glass system. Additionally, the band obtained in the range of $755-778\text{ cm}^{-1}$ indicate the presence of symmetrical stretching of P-O-P rings in the glass system. However, the band appeared in the range of $907-930\text{ cm}^{-1}$ also indicate the stretching vibrations of bridging oxygen between the bonds of phosphate zinc (P-O-Zn) or phosphate gallium (P-O-Ga), respectively [49, 50]. Additionally, the FTIR spectra's in figures also indicate the prevailing of Q_2 metaphosphate over metaphosphate Q_1 in Gallium doped zinc phosphate glass system. Gallium on low concentration $x < 5$, incorporates in the glass network with higher coordination number (6) [32, 51]. The impact of concentration of gallium oxide material on the preparation of phosphate glass system was investigated in this study. The addition of high concentration of gallium oxide successfully led to the substitution of divalent zinc with significant morphological changes in the prepared glass system. The addition of Gallium oxide (upto 10 mol%) not only caused the substitution of divalent zinc but also lead to the shortening of metaphosphate chains. Similarly, it was observed that if the concentration of gallium oxide increased above 10 mol% mol the phosphate glass structure modified gradually to metaphosphate Q_2 then pyrophosphate Q_1 and finally to orthophosphate units that will induce crystallization and finally the successful formation of glass network. The FTIR results also confirmed that the addition of gallium oxide concentration in range 0 to 10 mol% the P-O-Zn was replaced by P-O-Ga due to oxidation of phosphate bonds at $900-914\text{ cm}^{-1}$ [50]. Additionally, the band appeared at 1093 cm^{-1} showed the ionic stretching of P-O bonds that was absent in F_{10} sample while present in other glass samples (figure 9 g). However, with the increase the concentration of gallium oxide the P-O bond appeared due to the high binding of gallium cations with P=O [52-59]. Another band appeared at 1249 cm^{-1} successfully indicate the vibration of the P=O band however, this band slightly shifted toward 1235 cm^{-1} on increasing the content of gallium oxide in glass network [60].

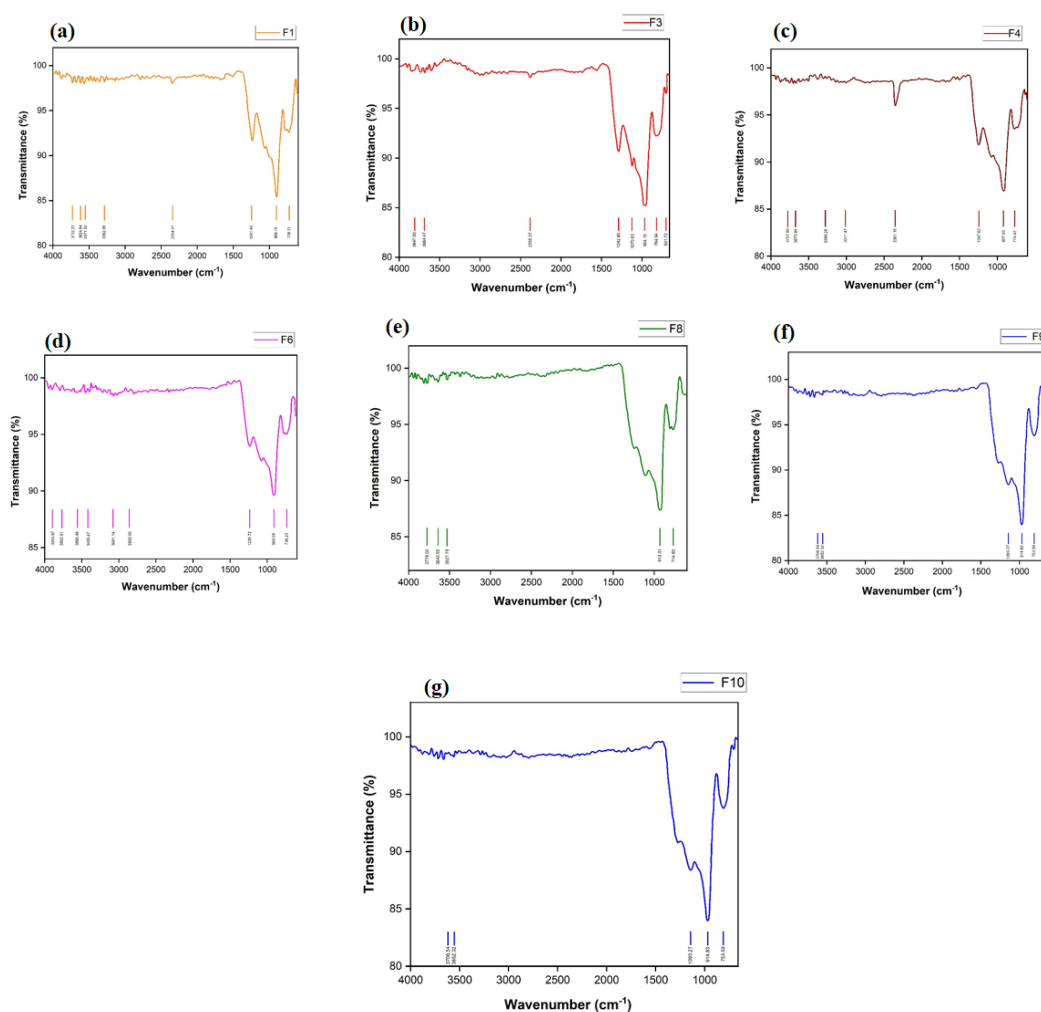


Fig. 9. IR spectrum of glass (a) F1 (b) F3 (c) F4 (d) F6 (e) F8 (f) F9 (g) F10

4. Conclusion

This study reveals the preparation of Gallium doped Zinc phosphate glasses by the incorporation of most effective Gallium oxide in the phosphate system in the presence of soda and zinc oxide in the muffle furnace at 980°C. However, the prepared The Gallium doped Zinc phosphate glasses glass system was somehow transparent up to the wavelength of 1500 cm^{-1} . The FTIR analysis has been used to investigate the presence of structural components present in the prepared glass system and it predict that between the gallium concentrations of x 0 to 10 mol% the metaphosphate (Q_2) network prevails in the prepared glass system. Additionally, the addition of gallium oxide in the sample successfully made the P-O-Ga bonds by replacing the zinc oxide. Glass having more concentration of gallium oxide were more stable and durable.

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