iJRASET
International Journal For Research in Applied Science and Engineering Technology

INTERNATIONAL JOURNAL FOR RESEARCH

IN APPLIED SCIENCE & ENGINEERING TECHNOLOGY

Volume: 6 **Issue:** I **Month of publication:** January 2018

DOI: http://doi.org/10.22214/ijraset.2018.1325

www.ijraset.com

Call: 08813907089 | E-mail ID: ijraset@gmail.com

International Journal for Research in Applied Science & Engineering Technology (IJRASET)
ISSN: 2321-9653; IC Value: 45.98; SJ Impact Factor :6.887
Volume 6 Issue I, January 2018- Available at www.ijraset.com

Spectroscopic Studies of Magnesium Manganese Borate Glasses

P. Vasantharani[1], S. Neelayathashi alias Vichitra[2]
Department of Physics, Annamalai University, Annamalai Nagar, Chidambaram 608 002, Tamilnadu, India

Abstract: ***Glass samples belonging to the general formula 60B2O3- (40-x) MnO2- xMgO with x=2,4,6,8,10 mol% were prepared by the conventional melt quenching technique was studied. Characterisation of the system was carried out using XRD, FTIR, DTA analyses. XRD confirms the amorphous nature of the samples. Thermal and spectroscopic behavior of the glass system was studied by DTA and FTIR analyses. FTIR reveals the presence of various functional groups present as well as the conversion of BO3 to BO4 units on the subsequent addition of modifier MgO. DTA gives an insight into the glass transition temperature, crystallization temperature, melting temperature and hence the stability of the glasses.***

Keywords: ***Melt quenching technique, XRD, FTIR and DTA***

I. INTRODUCTION

Over the past few years, there has been a considerable interest in the study of borate based glasses due to their interesting structural, optical and physical properties. The structure of the borate glasses is not a random distribution of BO_3 triangle and BO_4 tetrahedra. But a gathering of these units form well defined and stable borate groups such as diborate, triborate, and tetraborate that constitute the three-dimensional random network (1). On the other hand, borate glasses show high transparency, low melting point, high thermal stability and good glass forming nature (2). Because of these reasons, borate glasses are the best choice for doping transition metal ions compared to several other conventional glassy systems. Borate glasses incorporated with heavy metal oxides lead intense fluorescence in the visible region which are used as electro-optic modulators, electro-optic switches, solid state laser materials and non-linear parametric converters (3). Glasses containing transition metals like Cr^{3+}, Mn^{2+} posses better semiconducting properties and hence they are used for several applications such as memory switching, electrical threshold (4, 5). It is known that glass containing transition metal ions have many colors depending on the chemical composition of the glass system, the type or the characteristics of the transition metal ions in the structure. Among all transition metal ions, manganese (Mn) ion is particularly interesting because it exists in different valence states in different glass matrices (6). Manganese ions have been frequently used as paramagnetic probes to explore structure and properties of vitreous systems, as manganese ions have a strong influence on optical and magnetic properties of glass. A large number of studies are available on the environment of manganese ion in various inorganic glass systems (7).

Many studies have focused on metal oxide addition such as Sr^{2+} Mg^{2+} and Cd^{2+} which are usually incorporated as oxides and considered as network modifiers. Among the various metal oxides, MgO is of interest in the biological viewpoint because Mg^{2+} is known to play a physiological role in positively influencing bone strength when it is substituted into apatites (8). The advantages of Magnesium based glasses are i) Mg is less hygroscopic compared to lithium, potassium and sodium ii) it is eco-friendly and MgO acts as a network modifier at low concentrations and glass network former at higher concentrations of the glass system.

II. EXPERIMENTAL TECHNIQUES

The glass samples of composition 60 B_2O_3 – (40-x) MnO_2 - x MgO (where x = 2, 4, 6, 8, 10) were prepared by conventional melt quenching method using the required chemicals of reagent purity grade. The batches were mixed and ground into fine powder using a porcelain mortar and then melted by keeping in a porcelain crucible in a thermal cyclic furnace at 1100^{o}c for 1 hr. The melt was removed from the furnace several times and shaked well to ensure homogeneity. Then the molten samples were quenched at room temperature by pouring into cooler mould having dimensions of 10 mm diameter and 6 mm thickness and subsequently annealed for two hours to avoid any mechanical strain developed. The samples prepared were chemically stable and non- hygroscopic. Then they were polished and surfaces were made perfectly plane and smoothened by diamond disc and diamond powder. The nominal compositions BMM glass samples are given in Table 1.

The XRD patterns of powdered glass samples are recorded by X ray diffraction technique using the G.E. Inspection Technology 300377 model made in Germany of copper target of operating voltage 40 Kv, 300 mA. The FTIR transmission spectra of the glasses

were recorded in the 400-4000 cm^{-1} spectral range with a resolution of 4 cm^{-1} by FTIR spectrophotometer using the KBr pellet technique

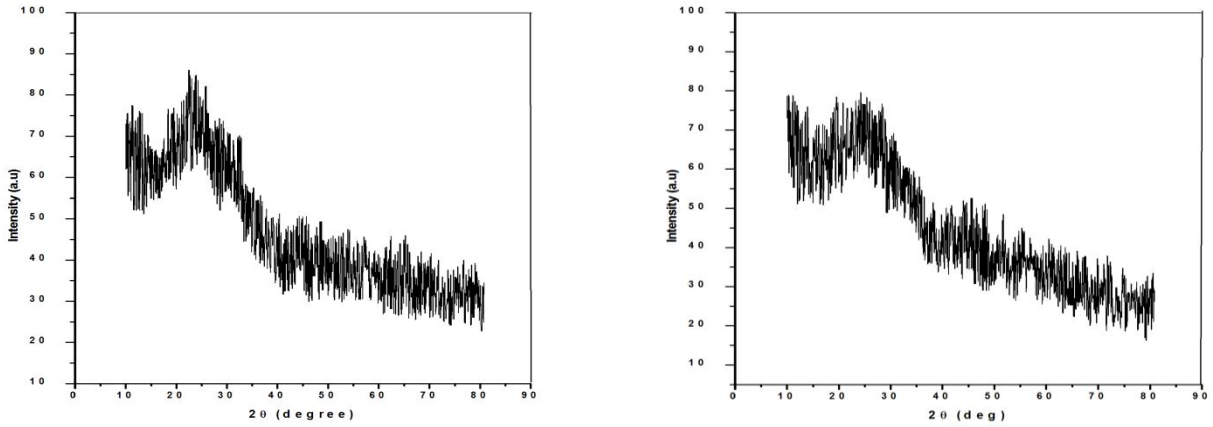
Table 1 Nominal composition of BMM glass samples

Specimen	Nominal composition (mol %)		
	B_2O_3	MnO_2	MgO
BMM1	60	38	02
BMM2	60	36	04
BMM3	60	34	06
BMM4	60	32	08
BMM5	60	30	10

III. RESULTS AND DISCUSSION

A. XRD analysis

The X-ray diffraction patterns of the BMM1 and BMM5 glasses are shown in Fig.1. The XRD spectrograms of the prepared samples show no sharp Bragg's peaks but only a broad hump around low angle region which shows the absence of long range atomic arrangement, indicating the amorphous nature of the studied glasses.



BMM1 BMM5

Fig 1 XRD patterns of BMM Glasses

B. FTIR Spectra Analysis

FTIR spectroscopy is a basic technique widely employed to understand the behavior of glass structure well (9 H.Darwish et. al., 2013). Study of FTIR spectra gives significant information about molecular vibrations as well as rotations associated with covalent bonding. The FTIR spectra occurs due to change in the dipole moment of the molecules. The spectra involves twisting, bending, rotation and vibrational motions in molecules. This method is used for the characterization of the local order and type of building structural units and provides information about the interaction between added metal ions and borate glass network

Fig.2 shows the FTIR spectra of the BMM glasse samples. The FTIR spectra of MgO doped manganese borate glasses exhibited three characteristic groups of bands representing vibrations of the molecules

1) 1200 – 1400 cm^{-1} region of band which occur due to the asymmetric stretching vibrations of B-O bond of trigonal BO_3 units

2) Band in the range of 800- 1200 cm^{-1} is due to B-O bond stretching vibrations of tetragonal BO_4 units

3) The band around 700 cm^{-1} represents bending of B – O – B linkages in the borate networks.

4) The region around 500 cm^{-1} represents spectra vibrations of metal cations.

Pure B_2O_3 contains only boroxol rings and three co–ordinated boron units. In general, addition of alkaline earth oxides to borate glasses changes the co ordination of boron atoms from three to four. In addition , complicated structures containing BO_3 and BO_4 units like di, tri, meta, penta borates are formed without changing B-O distance in short range order (10). When Mg^{2+} ions are

added, they are capable of breaking these rings, forming BO_4 groups and hence now the network consists of only BO_3 and BO_4 units (11). The well known characteristic bond at 806 cm^{-1} is the characteristic of symmetric stretching vibrations of boroxol rings (12) and the absence of which indicates that MgO acts as a modifier and changes the glass network structure.

Generally in borate rich glasses, BO_3 and BO_4 structural unit cover two broad bands stretching from 800 to 1500 cm^{-1}. The broad band around 1395 cm^{-1} represents the stretching vibration of BO_3 units while the band around 1046 cm^{-1} represents stretching vibration of BO_4 units. The band around 472 cm^{-1} is due to the vibration of metal atoms in bivalent state (13). The bands comprising of vibrations in the range 3200-3600 cm^{-1} are attributed to the hydroxyl or water groups originating from molecular water and hence the peak around 3521 is due to the vibrations of hydroxyl molicules. The bands at 2700 cm^{-1} , 2924, and 2850 cm^{-1} ascertain the presence of hydrogen bonding (14).

The relative area of I group of bands is relatively larger than that of II group. It is seen that the doping of MgO causes the I band to decrease gradually which indicates the convertion into BO_4 units (15). The absorption bands in the range of 695 cm^{-1} indicates the bending vibrations of B-O- B linkages as described earlier.

The addition of MgO to manganese borate glass network contributes an oxygen to the network while Mg^{2+} occupies the interstitial space, and this oxygen supply helps the triangular boron to convert into tetrahedral boron. Hence the gradual addition of MgO results in the decrease in the area of BO_3 units which implies that MgO acts as a glass network modifier bringing about the structural changes in the glass. Similar conclusion was also obtained by Ezhilpavai et al 2015.The observed third band around 692 cm-1 is due to the bending vibration of B – O – B linkages in the manganese borate network (16). Thus the addition of MgO to the manganese borate glass network decreases trigonal BO_3 units which means BO_4 units increase and hence resulting in the a more compact, strong glass network.

Table 2 Band positions and their corresponding assignment of IR spectra of CMB glass compositions

Wavenumber (cm^{-1})	Assignment
~ 472	Specific vibration of Mg-O
~ 697	Bending vibration of B-O-B
~ 1046	Stretching vibration of BO_4 tetrahedral
~ 1395	B-O stretching vibration of trigonal BO_3
~ 2900	O-H stretching vibration of water molecules

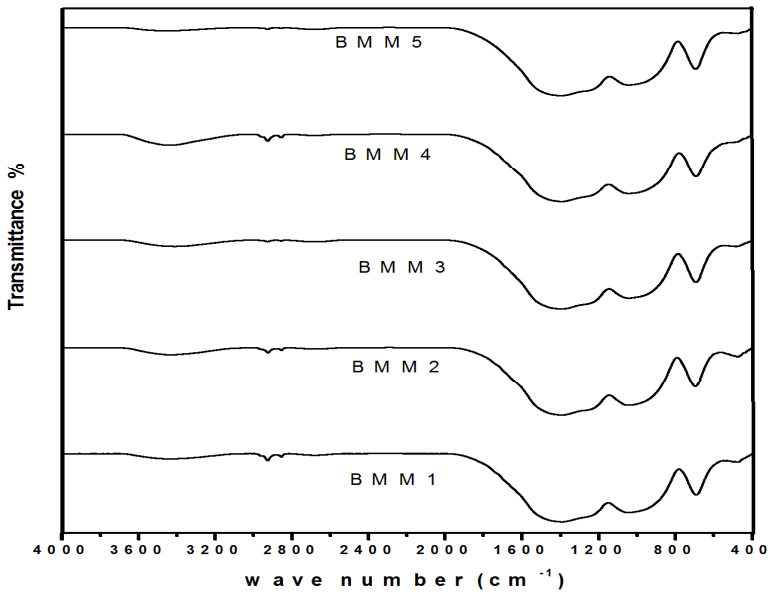


Fig 2 FTIR spectra of BMM glasses

C. DTA Analysis

Study of thermal behavior of glasses can be done by TG – DTA investigations. DTA is a dynamic technique used for quantitative or qualitative analysis of thermal properties of materials. These techniques are used to determine the characteristic temperatures and thermal stability of glass. Thermal studies of the glasses reflect the change in the coordination number of the network forming atoms or the formation of bridging as well as non bridging oxygens indicated by the glass transition temperature T_g. The DTA profiles of three BMM glass system are shown in Fig. 3 which consists of a small endothermic peak corresponding to glass transition temperature T_g , an exothermic peak corresponding to T_c followed by another endothermic T_m.

In DTA, endothermic peak represents heat absorbing transitions such as crystallization or decomposition of materials. Generally the glass transition temperature (T_g) can be used to indicate the glass network rigidity and is related to the cross link density and the connectivity.

The network modifiers directly influence the Tg because glass transition involves modification of chemical bonds between the glass former and glass modifiers (17). The point of slope change of endothermic peak in DTA curve indicates the glass transition temperature T_g as marked in the DTA profile. Generally, the glass transition Tg is known to depend on several independent parameters as the band gap, bond energy, effective molecular weight, the type and fraction of various structural units formed and the average coordination number (18). Exothermic peak is identified as the crystallization temperature T_c and the glass stability factor has been measured from the T_g and T_c values of DTA curve by using the relation $S= T_c - T_g$. The glass transition (T_g) shows a monotonic increase for the composition of MgO added. Table 3 gives the values of transition temperature, T_g melting temperature (T_m) and crystalline temperature T_c. All the values increases as MgO content increases. In the investigated glass samples, as manganese is gradually replaced by the magnesium oxide, Mg^{2+} occupies the interstitial positions and the bridging oxygens created cause BO_3 units to be transformed into more denser BO_4 units and hence the concentration of available non bridging oxgens are lowered. and hence the network polymerization of the glass network structure increases which is reflected in the increase of Tg values.

As for the Mg^{2+}, it has the largest electrical field strength, which could lead to a more compact glass network so that this effect will improve the durability of the glasses. For glass to be thermally stable, ΔT value should be greater than 100°C. In this case, the value of ΔT for all the glasses BMM1 ,BMM3 and BMM5 are found to be greater than 100, which indicates high thermal stability of all the glass samples. The higher the value of ΔT, the lower is the tendency towards crystallization (19). It is always preferable to get maximum ΔT as it is essential to achieve a large working range of temperature in sample fiber drawing. T_g is related to the density of covalent cross linking, the number and strength of the coordinate links formed between oxygen atoms and the cation and the oxygen density of the network (20).

Thermal stability is also calculated by Hruby's parameter (H) using the relation $H = (T_c - T_g) / (T_m - T_c)$ which gives the information against devitrification. Larger the stability factor, better is the thermal stability. The increase in both stability factor (33) and Hrubys parameter confirm the increase in the packing density and rigidity leading to formation of stronger structural building blocks in the glass network. Therefore, it is well understood that the incorporation of MgO into the manganese borate glasses causes the glass network to become stronger and closely packed glass.

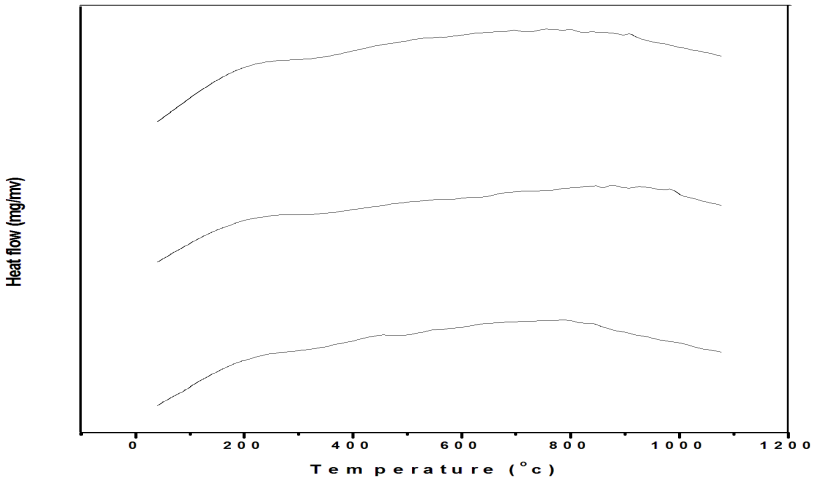


Fig 3 DTA Thermograms of BMM glasses

Generally, increase of T_g with the increase of network modifier indicate the increase in strength and connectivity of the glass which is observed in this system and hence the thermal studies confirm the increase in rigidity of the glass structure. This may be owing to the decrease in number of non-bridging oxygens and hence the increase in connectivity of the glass network (21).

Table 3 Summary of DTA results

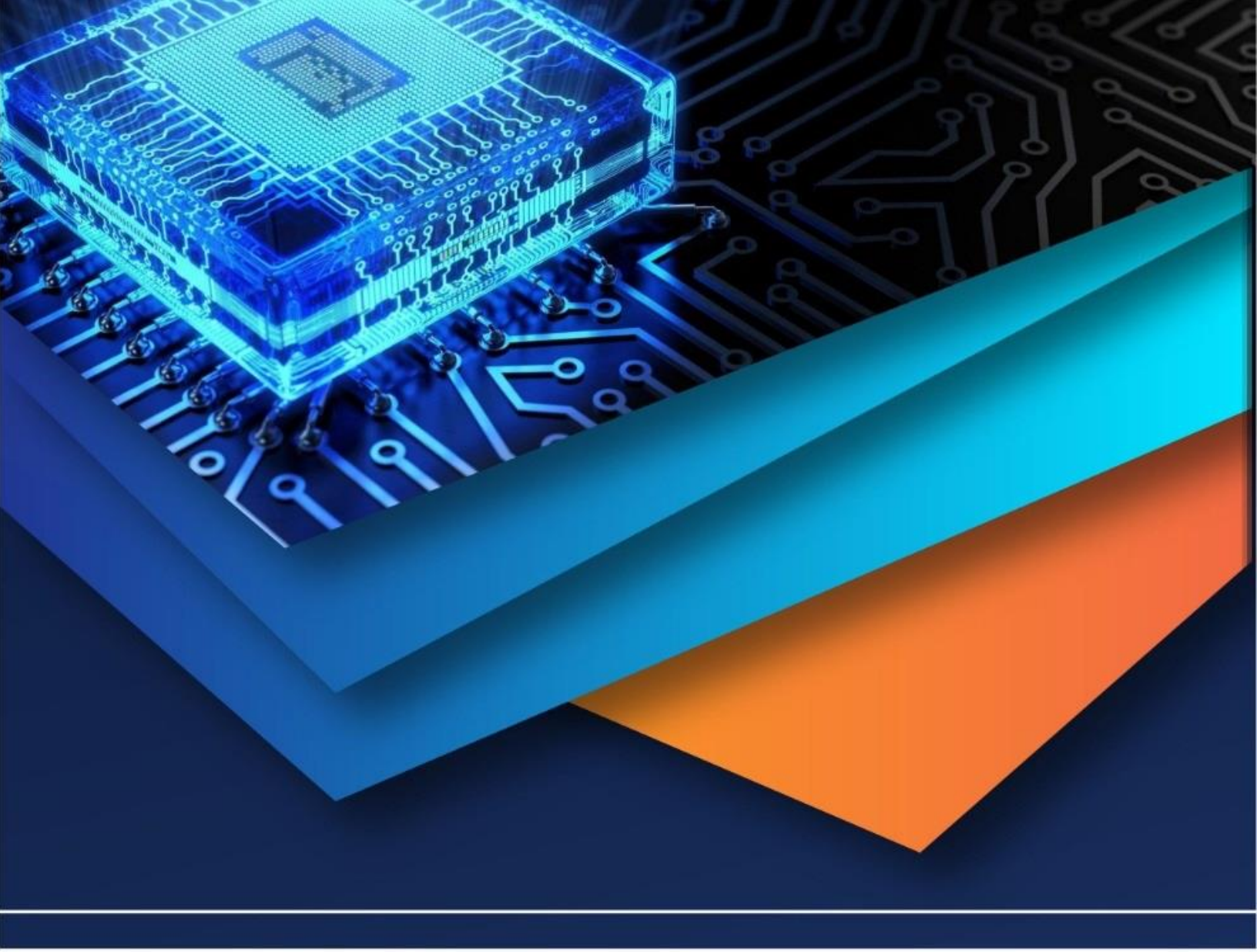
Sample	T_g (^{o} C)	T_c (^{o} C)	T_m (^{o} C)	Stability factor	Hruby's parameter
BMM 1	481	782	874	301	3.2717
BMM 3	535	842	919	307	3.9810
BMM 5	572	883	948	311	4.7846

IV. CONCLUSION

Magnesium doped manganese borate glasses had been synthesized and investigated using XRD, FTIR and DTA studies. The XRD spectra confirm the amorphous nature of the glasses prepared. From IR spectroscopy, it is clear that the doping of magnesium oxide leads to the formation of BO_3 and BO_4 units and the increase in concentration of MgO results in the narrowing of BO_3 bands revealing the decrease in the NBOs indicating the increase in the stability of the glass network. DTA studies showed that there is increase in T_g values corresponding to the congruent increase of magnesium added which also confirms the increase in the compactness and hence the rigidity of the manganese borate glass as an impact of dopant MgO. The FTIR and DTA results revealed the same trend of results.

REFERENCES

[1] Doweidhar, H., Y.B.Saddeek. FTIR and ultrasonic investigations on modified bismuth borate glasses. J.Non. Cryst.Sols., 355 (2009) : 348-354.
[2] Kawa M. Kaky, G. Lakshminarayana, S.O. Baki, Y.H. Taufiq-Yap, I.V. Kityk, M.A.Mahdi. Structrural, thermal and optical analysis of Zinc boro-aluminosilicate glasses containing different alkali and alkaline modifier ions. J.Non. Cryst.Sols., (2016) 456, 55-63.
[3] Gaffar M.S., F.H.El Batel, M.El- Gazery and S.A.Mansour. Effect of doping by different transition metals on the acoustical properties of alkali borate glasses. Acta.Phy.Pol.A., 115 (2009): 3 , 671-678.
[4] Hirashima H., Y. Watamatea and T.Yohida. Switching of TiO2-V2O5-P2O5 glasses. J.Non. Cryst.Sols., (1987) 95/96: 825-832.
[5] Nakamma S., and N.Ichinose. Study on amorphous ferrite CaO-Bi2O3- Fe2O3 system. J.Non. Cryst.Sols., (1987) 95/96: 849-855.
[6] Durga D.K., N.Veeraiah. Role of manganese ions on the stability of ZnF2-P2O5-TeO2 glass system by the study of dielectric dispersion and some other physical properties. J.Phy.Chem .Sols.,(2003) 64: 133-146.
[7] Chakradhar, R.P.S., G.Sivaramaiah, J.L.Rao and N.O.Gopal. EPR and optical investigations of manganese ions in alkali lead tetraborate glasses. Spectrochem. Acta., (2005) 62: 761-768.
[8] Lee, I.Ho., S. Hee Shin, F. Foroutan, N.J.Lakhkar, M.S.Gong, J.C.Knowles. Effects of magnesium content on the physical, chemical and degradation properties in a MgO−CaO−Na2O−P2O5 glass system. J.Non. Cryst.Sols., (2013) 363: 57-63.
[9] Darwish ,H., S.Ibrahim, M.M.Gomaa. Electrical and physical properties of Na2O-CaO-MgO-SiO2 glasses doped with NdF3. J. Mater.Sci. Mater. Electro (2013) 24: 1028-1036
[10] Ramadevudu ,G., S.Lakhmi Srinivasa Rao, Md. Shareefuddin, M.Narasimha Chary and M.Lakshmipathy Rao. FTIR and optical absoption studies of new magnesium lead borate glasses. Global.J. Sci.Fro.Res.Phy.Spce.Sci.,(2012) 12: 4.
[11] Galeener, F. L., G. Lucovsky, and J. C. Mikkelsen, Jr. Vibrational spectra and the structure of pure vitreous B_2O_3. Phys.Rev.B., (1980) 22: 8
[12] Hareb, M.H.A.M., S.Hasim, S.K.Goshnar, Y.S.M.Alajermi, M.A.Saleh. Optical and erbium ion concentration correlation in lithium, magnesium borate glasses. Opt.Int.J.Light. Elect.Optics (2015).
[13] Khalil, E.M.A., F.H.El Batel, Y.M.Hamdy, H.M.Zidan, M.S.Aziz and A.M.Abdelghany. UV-Visible and IR spectroscopic studies of gamma irradiated transition metal doped lead silicate glasses, Springer Science + Business Media B.V,(2009).
[14] Gurindhar Pal Singh, Simranpreet Kaur, Parvinder Kaur, Sunil Kumar and D.P.Singh. Structrural and optical properties of WO3-ZnO-PbO-B2O3 glasses. Physica B (2011) 406: 1890-1893.
[15] Ezhilpavai, R., M. Indhira.Thermal stability and FTIR studies of B2O3+K2O+MgO glasses. Int.J.Current.Res., (2015)7(6): 16811-16814.
[16] Manisha Pal., Baishakhi Roy, Mrinal Pal. Structural characterisation of borate glasses containing zinc and manganese oxides. J.Modern.Phy.,(2011) 2: 1062-1066.
[17] Dutta,A., and Ghosh, A. Structural and optical properties of lithium barium bismuthate glasses. J.Non. Cryst.Sols.,(2007) 353: 387-396
[18] Mehta N., R.S.Tiwari, A.Kumar. Glass forming ability and thermal stability of some Se–Sb glassy alloys. Mater. Res.Bulletin.,(2006) 41: 1664.
[19] Lakshminarayana, G., M.G.Brik, I.V.Kityk, Photoluminescence of Eu3+-, Tb3+-,Dy3+- and Tm3+-doped transparent GeO2–TiO2–K2O glass ceramics J.Phys.Condens. Mat.,(2008): 335106.
[20] Li, H.C., Wang, D.G.Haa, J.H.C,Chen. Effect of the partial substitution of K2O, MgO,B2O3 for CaO on crystallisation , structure and properties of Na2O-CaO-SiO2-P2O5 system of glass ceramics. J.Mat. Letters.,(2013) 106: 373-376.



10.22214/IJRASET

45.98

IMPACT FACTOR: 7.129

IMPACT FACTOR: 7.429

INTERNATIONAL JOURNAL FOR RESEARCH

IN APPLIED SCIENCE & ENGINEERING TECHNOLOGY