STRUCTURAL AND OPTICAL PROPERTIES OF UNDOPED AND MANGANESE DOPED CALCIUM ZINC BOROPHOSPHATE GLASSES

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Dedicated to my beloved parents and siblings,

for their endless love, supports and encouragements.

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ABSTRACT

Five series of glasses with the chemical compositions xB_2O_3–(50–x)P_2O_5–20CaO–30ZnO, ($0 \le x \le 50$ mol%), xZnO–(50–x)CaO–$20B_2O_3$–$30P_2O_5$, ($0 \le x \le 50$ mol%), $20B_2O_3$–$30P_2O_5$–20CaO–30ZnO–$xMnO_2$, ($0 \le x \le 10$ mol%), xB_2O_3–(50–x)P_2O_5–19CaO–30ZnO–$1MnO_2$, ($0 \le x \le 50$ mol%) and xZnO–(30–x)CaO–$35B_2O_3$–$34P_2O_5$–$1MnO_2$, ($0 \le x \le 30$ mol%) were prepared using conventional melt quenching technique following by annealing process. The structure of the glasses were characterized using X–ray diffraction (XRD), Fourier transform infrared (FT–IR) and Raman spectroscopy. XRD analysis confirmed amorphous phase of the glass samples. The IR spectra reveal the coexistence of BO_3, BO_4, PO_3 and PO_4 structural units in the glass samples. While the Raman spectra reveals the presence of P–O–B network in the glass samples. The optical properties of the glass samples were characterized using ultraviolet visible near infrared (UV–Vis–NIR) spectroscopy and photoluminescence spectroscopy. The UV–Vis–NIR spectra reveal the presence of both Mn^{2+} and Mn^{3+} ions when manganese was doped in borophosphate glasses. Meanwhile, the emission spectra of borophosphate glasses exhibited a green light emission due to tetrahedral symmetry and a red light emission due to octahedral symmetry. The decay curves of $^4T_{1g}$ energy level of Mn ions were examined for all concentrations and the measured lifetimes were dependent on concentration of Mn ions and composition of the glass. The paramagnetic properties were studied using electron spin resonance (ESR) spectroscopy. The ESR spectra reveal that the resonance peak occurring at $g_{eff} \approx 2.0$, 3.3 and 4.3. The resonance peak at $g_{eff} \approx 2.0$ with six lines hyperfine structure due to Mn^{2+} ions in an environment close to octahedral symmetry whereas the resonance peak at $g_{eff} \approx 3.3$ and $g_{eff} \approx 4.3$ is attributed to the rhombic surroundings of the Mn^{2+} ions.

ABSTRAK

Lima siri kaca dengan komposisi kimia xB$_2$O$_3$–(50–x)P$_2$O$_5$–20CaO–30ZnO, ($0 \leq x \leq 50$ mol%), xZnO–(50–x)CaO–20B$_2$O$_3$–30P$_2$O$_5$, ($0 \leq x \leq 50$ mol%), 20B$_2$O$_3$–30P$_2$O$_5$–20CaO–30ZnO–xMnO$_2$, ($0 \leq x \leq 10$ mol%), xB$_2$O$_3$–(50–x)P$_2$O$_5$–19CaO–30ZnO–1MnO$_2$, ($0 \leq x \leq 50$ mol%) dan xZnO–(30–x)CaO–35B$_2$O$_3$–34P$_2$O$_5$–1MnO$_2$, ($0 \leq x \leq 30$ mol%) telah disediakan menggunakan kaedah pelindapan lebur diikuti dengan proses sepuh lindap. Struktur sampel kaca telah dianalisis dengan menggunakan teknik pembelauan sinar–X (XRD), spektroskopi inframerah transformasi Fourier (FT–IR) dan spektroskopi Raman. Analisis pembelauan sinar–X menunjukkan fasa amorfus dari sampel kaca. Spektrum inframerah menunjukkan struktur unit BO_3, BO_4, PO_3 dan PO_4 dalam sampel kaca. Manakala spektrum Raman menunjukkan kewujudan rangkaian P–O–B dalam sampel kaca. Sifat optik sampel kaca telah dikaji dengan menggunakan spektroskopi UV–Vis–NIR dan spektroskopi fotoluminesen. Spektrum UV–Vis–NIR menunjukkan kewujudan ion Mn^{2+} dan Mn^{3+} apabila mangan didopkan dalam sampel kaca. Sementara, garis spektra pancaran dari sampel kaca mempamerkan pancaran cahaya hijau disebabkan oleh simetri tetrahedral dan satu pancaran cahaya merah disebabkan oleh simetri oktahedral. Lengkuk pereputan aras tenaga $^4T_{1g}$ dari ion Mn telah menunjukkan ia bergantung kepada kepekatan Mn^{2+} dan komposisi sampel kaca. Ciri paramagnet telah dikaji dengan menggunakan spektroskopi resonans putaran elektron (ESR). Spektra ESR menunjukkan puncak resonans pada $g_{eff} \approx 2.0$, 3.3 dan 4.3. Puncak resonans pada $g_{eff} \approx 2.0$ menunjukkan terdapat enam garis struktur halus dari persekitaran ion Mn^{2+} yang hampir kepada simetri oktahedral manakala puncak resonans pada $g_{eff} \approx 3.3$ dan $g_{eff} \approx 4.3$ disebabkan oleh persekitaran rombus pada ion Mn^{2+}.

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LIST OF SYMBOLS

c	-	Speed of Light
C	-	Celsius
d	-	Length
k	-	Force Constant
T_f	-	Freezing Temperature
T_g	-	Transformation Range Temperature
τ	-	Tau
^{o}	-	Degree
μ	-	Reduced Mass
v	-	Frequency
λ	-	Lambda
θ	-	Angle
T_m	-	The Melting Temperature
Δ	-	Optical Path Difference
δ	-	Delta
e	-	Electric charge
P_o	-	Radiant Power
T	-	Transmittance
E	-	Urbach Energy
$\Lambda_{\boldsymbol{th}}$	-	Optical Basicity
γ_i	-	Basicity Moderating Parameter
x_i	-	Pauli Electronegativity
h	-	Plank’s Constant
B_o	-	Applied Magnetic Field

μ_o	-	Permeability of Vacuum
g_{eff}	-	g Effective Value
ΔB	-	Peak–to–peak Linewidth
J	-	Line Intensity

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CHAPTER 1

INTRODUCTION

1.1 Research Background

Glass has been used by mankind since 4000 years ago during ancient Egypt. Normally, the characteristic of glasses is hard and transparent. The applications of the glasses are so wide and we may be using it every day in our daily life. For example, glasses are mainly used in packaging, housing and buildings, appliances and electronics, automotive and transport, optical glass, fibre optic cables and renewable energy. Meanwhile, for scientific research purpose, it is particularly interesting due to the unique properties of glass such as its corrosion resistance and inertness, thermal shock resistance and electrical insulation. Due to the wide applications and unique properties of glass, further studies are needed. These studies include the structural studies and the type of bonding in the glass network and the effect of additive in the glass network. The positive research outcome is quite important in the glass industry and can be contributed to the future of glass products.

Oxides like SiO_2, Ge_2O_3, P_2O_5 and B_2O_3 are known as glass formers which are able to produce glass by themselves or by incorporating with other network formers. Such situation can occur due to these oxides will provide a strong covalent bond by forming a 3D network with oxygen. However, some oxides cannot form a glass by themselves. These oxides are called conditional glass former oxides. Yet, these conditional glass former oxides (TeO_2, Al_2O_3 and Va_2O_3) can mix with other oxides with suitable quantity in order to increase the glass forming ability and to decrease the crystallization effect. In order to produce a glass, melt quenching, vapor deposition and sol–gel processing solutions are the three common methods that are usually used in industrial process and in research. However, melt quenching technique is the most conventional way to produce glass in which the glass will not crystalline. Besides, this technique is simple and low cost compared to other methods.

Among oxides, borates are one of the most important glass forming oxides and has been integrated into several forms of the glass system in parliamentary procedure to make the desired physical and chemical attributes (Wan *et al*., 2014). Borates glasses have been of exceptional scientific interest for many years (Agarwal *et al*., 2010, El–Falaky and Guirguis, 2012, Singh and Kaur *et al*., 2014) owing to the special properties of this glass such as melting point (<1000 ^{o}C), transparency, high solubility of transition metal ions, etc (Lin *et al*., 2005). Moreover, borate glass is normally used in thermo luminescence applications due to its high sensitivity, inexpensive and simple preparation (Li *et al*., 2009). In order to to form the trigonal planar BO_3 or tetrahedral BO_4 structural units in the structure of the borates, it has to joined together via shared oxygen atoms in its structure (Wiberg and Holleman, 2001). Meanwhile, according to Saddeek (2009), when the content of PbO is in the range of 30–60 mol%, the BO_3 units convert to the BO_4 units which enhances the connection between the BO_3 and BO_4 units by building up the boron oxygen rings.

Since phosphate glass can hold large concentrations of active ions without losing the useful attributes of framework, it becomes an exceptionally attractive host compared to the borate glasses (Brow *et al*., 1998). Besides that, phosphate glass are easy to be prepared due to the low melting point of phosphate glasses (<1000 ^{o}C). Phosphate glasses also offer an important range of compositional possibilities (ultra, meta, pyro, and orthophosphate), in which its physical and chemical property can vary and contributes in particular to technological applications. Due to the unique properties such as low melting point (<1000 ^{o}C) and good electrical conductivity, this phosphate glasses reveals a better characteristic than silica glasses in industrial application when it is doping with rare earth ions (Day *et al*., 2001).

Owing to the flexibility of borate and phosphate base glasses, the study of their structure and properties is important. As a result, continuing studies are still going. Unfortunately borate glasses alone are not a stable compound even though it is well known as the glass former, while the pure phosphate network is hygroscopic, which often limit their practical uses (Wan *et al*., 2014).

Today, the mixture of the two glass formers, B_2O_3 and P_2O_5 (glasses) are among the multicomponent glasses studied for some interesting applications. Unlike borate or phosphate, borophosphate glasses become more attractive and widely used in the industrial area owing to it as a more stable compound with high transparency (Layne *et al*., 1976, Ehrt and Seeber, 1991). In addition, additional oxides to the mixture of B_2O_3 and P_2O_5 in the same glass matrix will result in property enhancements. Among the oxides, CaO and ZnO are chosen to be added in borophosphate glasses. According to Takebe *et al*. (2006), ZnO with large ionic radius and with 18 electrons in the outermost shell was widely used to enhance the chemical stability of the phosphate glass network (Boiko *et al*., 1998). Besides that, Zn^{2+} can either form ZnO_4 (Fujino *et al*., 2003) or P–O–Zn bridges (Brow and Tallant., 1997) via phosphate chains linkages in the glass network.

A study by Koudelka *et al*. (2009) shows that the chemical durability of the glass can be enhanced by the addition of trivalent oxides together with the replacement of alkali oxides by divalent oxides. Besides that, phosphate glasses can also be stabilized by the addition of B_2O_3 along with either zinc oxide or lead oxide. Furthermore, the material such as lead oxide and zinc oxide are normally combined with lithium oxide, sodium oxide and potassium oxide in the borophosphate glass system (Koudelka *et al*., 2006, Mosner *et al*., 2007). Such materials offer better chemical durability than borate, phosphate or borophosphate glasses. Besides, the degree of polymerization will be increased by addition of modifier oxides in the borate network. This will lead to the boron coordination changes from three to four which alter the metaphopshate chain into three–dimensional network (Brow and Tallant., 1997).

Nowadays, addition of a small amount of transition metal ions in the glass network system becomes more favorable due to their memory and photoconductivity properties. Owing to the outer *d*–electron orbital functions have a broad radial distribution, variety of the glass structures are probed by the transition metal ions (Rao *et al*., 2011). A study by Buddhudu and Thulasiramudu (2006) reveals that when transition metal ions doped to the glass system, this glass exhibits the luminescence properties owing to these ions normally exists in the divalent states. Based on the study by other researchers, they found that manganese ions (Mn^{2+}) are attractive as a dopant in borophosphate glasses owing to Mn^{2+} ions can be in varoius valence states (Bratu *et al*., 1999, Magon *et al*., 2006). Normally, five *d* electrons of Mn^{2+} ions are distributed in the t_{2g} and e_g orbitals, with three in the former whereas other two in the latter orbitals. So, its ground state configuration is $(t_{2g})^3(e_g)^2$. Besides that, the energy levels that form from this configuration are ^6A_g, $^4A_{1g}$, ^4E_g, $^4T_{1g}$, $^4T_{2g}$ and $^6A_{1g}$ (spherically non–degenerated, octahedral symmetry) lies lowest (ground state) according to Hund's rule. Through the photoluminescence property of the glass system, the differences in valence state can be observed.

According to the Gao *et al*. (2011), they found that the optical absorption spectra of Mn^{2+} ions exhibit only spin forbidden transition owing to the excited states of the Mn^{2+} ions are in quartets or doublets. Normally, the spin–forbidden $^4T_{1g}\rightarrow{}^6A_{1g}$ (S) transitions cause the appearance of bands in the UV–Vis spectral region and photoluminescence spectra. Due to its *d*–shell is not strongly shielded from its environment, the *d–d* transitions are affected by the field strength of the surrounding ligands (Wondraczek and lakshminarayana, 2011). Generally the luminescence emission of Mn^{2+} ($^3d_5$) reveals the emission color from green to dark red which is usually determined by its field strength between the manganese ions with the host ligand. Normally the Mn^{2+} ions are in the tetrahedral coordination (CN=4) (IV Mn^{2+}, weak crystal field) when it emits green light, and in octahedral coordination (CN=6) (VI Mn^{2+}, stronger crystal field) when it emits red light (Gao *et al*., 2011).

In the view of the non–stable borate compound and hygroscopic properties of the pure phosphate network, borophosphate glasses are important for now and future owing to borophosphate glasses have a lot of applications such as the used in batteries that reported by Agarwal *et al*. (2010) and electronic equipment (Ali *et al*., 1999). Moreover, based on the study by Thulasiramudu and Buddhudu, (2006) they found that good moisture resistant optical systems can be obtained by adding PbO and ZnO to the borate glasses. Furthermore, the obtained result shows that it is suitable as novel luminescent optical materials. Over decades, it is believed that rare earth ions can be replaced by transition metal ions (Mn^{2+}) as a dopant in the glass system become popular and has a great potential in photoluminescence applications. In order to obtain more information on the structural features and optical properties of glasses doped with manganese ions, further studies are required.

1.2 Problem Statement

Various new phosphor materials based on different combinations of host material are being studied in recent years. In the earlier years, borate and phosphate based glasses have gained a lot of interest. However, due to their weak chemical durability and hygroscopic properties, “mixed glass former” based glass is introduced. In this present studies, borophosphate based glass have been chosen to dope with different concentration of manganese ions. Borophosphate glasses doped with rare earth ions had been studied widely by many researchers. On the other hand, works on borophosphate glass system doped with manganese ions are still very less being reported. Furthermore, the doping of transition metal ions especially manganese ions into the borophosphate network can enhance the phosphorescent lifetime. Manganese ions are of interest due to its valence states are depending on the concentration of these ions in the glass network. Rao *et al*. (2009, 2011) have published works on borophosphate glasses system doped with Mn^{2+} ions. However, there are still limited studies on the structural features and optical properties of borophosphate glasses doped with high concentration (> 5 mol %) of manganese ions. Besides that, calcium zinc borophosphate glasses doped with manganese ions have not been studied by other researchers. Thus, calcium zinc borophosphate glass system is chosen to study.

1.3 Research Objectives

i. To prepare the undoped calcium zinc borophosphate glasses and calcium zinc borophosphate glasses doped with manganese.
ii. To determine the structural features of the undoped and doped glass samples.
iii. To determine the optical and luminescence properties of calcium zinc borophosphate glasses doped with manganese.
iv. To determine paramagnetic properties of calcium zinc borophosphate glasses doped with manganese.

1.4 Scope of Study

In attempt to reach the goal, five series of glasses were prepared using conventional melt quenching technique. Firstly, phosphate was gradually replaced by borate in order to determine the optimum content of borate and phosphate content in the glass system. Then a series of gradually change in calcium and zinc oxide was also being prepared. After that, these two series of glass samples were doped with 1 mol% of manganese ions. Finally, the selected compositions of calcium zinc borophosphate glasses doped with different concentration of manganese ions (0.5–10 mol%) were also prepared. The phases of the prepared samples were determined by the X–Ray diffraction measurement. The structural features for all undoped and doped glasses were determined using Fourier transform infrared (FT–IR) and Raman spectroscopy. Meanwhile, the optical properties for all doped glass samples were determined by Ultra–violet visible near infrared spectroscopy. The luminescence properties and the decay curve for all the doped glass samples were determined by luminescence spectroscopy. Finally, the paramagnetic properties of all the doped samples were also determined by electron spin resonance spectroscopy.

1.5 Significance of Study

This present study has been done in order to have a further understanding on the structural features, optical, luminescence and paramagnetic properties of the glass due to the limited study based on calcium zinc borophosphate glass. By doping manganese to the borophosphate glass, new materials can be developed so called "luminescence materials". These materials are possible to emit light at visible range. Besides that, it can be used as long afterglow material. Furthermore, the relationship between the host and modifier with the luminescence properties can also be understood. This information is useful in glass technology and hopefully can develop a new long afterglow material such as used in glow in the dark materials in order to reduce the electrical energy consumption in our country. Furthermore, undoped and calcium zinc borophosphate glasses doped with manganese of highly transparent and chemically stable were prepared through melt quenching technique. This melt quenching technique is simple and cost effective which is suitable for mass production and have greater potential in producing luminescent glass of higher efficiency for technological application.

1.6 Outline of Study

This thesis can be divided into five chapters in which Chapter 1 is introduction for present studies, including the basic background knowledge and the purpose of this research. Chapter 2 and Chapter 3 focus on the literature reviews and methodology respectively. Meanwhile Chapter 4 including the results and discussion where this is the most important chapter and is the core of this thesis. Finally Chapter 5 is the conclusion and recommendation for future work.

also be extensively studied using density functional theory (DFT) in order to gain more information and postulate a structural model.

Finally, the photoluminescence measurement can be carried out in difference temperature. The excitation, emission and decay rate of the doped glass samples could be influenced by various temperatures, thereby given effect to the luminescence properties of the investigated samples. So, difference temperature should be proceeded to photoluminescence measurement in the investigated glass samples in the future.

REFERENCES

Abdelghany, A.M., ElBatal, F.H., Azooz, M.A., Ouis, M.A. and ElBatal, H.A. (2012). Optical and infrared absorption spectra of 3*d* transition metal ions-doped sodium borophosphate glasses and effect of gamma irradiation. *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*. 98, 148-155.

Abragam, A. and Bleaney, B. (1970). Electron Paramagnetic Resonance of Transition Ions, Oxford, Clarendon.

Agarwal, A., Sanghi, S., Rani, S. and Bhatnagar, V. (2010). Influence of Nb_2O_5 on the structure, optical and electrical properties of alkaline borate glasses. *Materials Chemistry and Physics*. 120 (2-3), 381-386.

Akagi, R., Ohtori, N. and Umesaki, N. (2001). Raman spectra of K_2O-B_2O_3 glasses and melts. *Journal of Non-Crystalline Solids*. 293-295, 471-476.

Ali, A.F., Mustarelli, P., Quartarone, E., Tomasi, C., Baldini, P. and Magistris, A. (1999). Sol-gel lithium borophosphates. *Journal of Materials Research*. 14(4), 1510-1515.

Almeida, R.M., Kharlamov, A.A. and Heo, J. (1996). Vibrational spectra and structure of heavy metal oxide glasses. *Journal of Non-Crystalline Solids.* 202(3), 233-240.

Ardelean I. and Filip S. (2003). Structural and Magnetic Investigations of Transition Metal Ions in TeO_2 Based Glasses. *Journal of Optoelectronics and Advanced Materials*. 5, 157-169.

Ardelean, I., Cora, S., Lucacel, R.C. and Hulpus, O. (2005). EPR and FT-IR spectroscopic studies of B_2O_3-Bi_2O_3-MnO glasses. *Solid State Sciences*. 7(11), 1438-1442.

Ardelean, I., Ilonca, Gh. and Peteanu, M. (1984). The valence states of manganese ion in potassium-borate oxide glasses. *Solid State Communications*. 52(2), 147-149.

Ardelean, I., Lungu, R. And Pascuta, P. (2007). Structural changes induced by Fe_2O_3 addition in strontium-borate glass matrix. *Journal of Materials Science: Materials in Electronics.* 18, 837-841.

Ardelean, I., Peteanu, M., Filip, S., Simon, V. and Todor, I. (1998). EPR and magnetic susceptibility studies of manganese ions in Bi_2O_3-GeO_2 glasses. *Solid State Communications*. 105(5), 339-344.

Ardelean, I., Rusu, D., Andronache, C. and Ciobota, V. (2007). Raman study of xMeO ·(100-x)[P_2O_5 ·Li_2O] (MeO ⇒ Fe_2O_3 or V_2O_5) glass systems. *Materials Letters*. 61(14-15), 3301-3304.

Bae, B.S., Koo, J. and Na, H.K. (1997). Raman spectroscopy of copper phosphate glasses. *Journal of Non-Crystalline Solids*. 212(2-3), 173-179.

Bale, S., Rao, N.S. and Rahman, S. (2008). Spectroscopic studies of Bi_2O_3-Li_2O-ZnO-B_2O_3 glasses. *Solid State Sciences*. 10(3), 326-331.

Boiko, G.G., Andreev, N,S. and Parkachev, A.V. (1998). Structure of pyrophosphate 2ZnO-P_2O_5-2Na_2O-P_2O_5glasses according to molecular dynamics simulation. *Journal of Non-Crystalline Solids*. 238(3), 175-185.

Borsa, F., Torgeson, D.R., Martin, S.W. and Patel, H.K. (1992). Relaxation and fluctuations in glassy fast-ion conductors: Wide-frequency-range NMR and conductivity measurements. *Physical Review B: condensed matter and materials physics.* 46, 795-800.

Bratu, I., Ardelean, I., Barbu, A., Mih, V., Maniu, D. and Botezan. G. (1999). Spectroscopic investigation of some lead phosphate oxide glasses containing manganese ions. *Journal of Molecular Structure*. 482-483, 689-692.

Brow, R.K. (2000). Review: the structure of simple phosphate glasses. *Journal of Non-Crystalline Solids*. 263-264, 1-28.

Brow, R.K. and Tallant, D.R. (1997). Structural design of sealing glasses. *Journal of Non-Crystalline Solids*. 222, 396-406.

Brow, R.K., Hudgens, J.J., Tallant, D.R. and Martin, S.W. (1998). Raman spectroscopy study of the structure of lithium and sodium ultraphosphate glasses. *Journal of Non-Crystalline Solids*. 223(1-2), 21-31.

Brow, R.k., Tallant, D.R., Myers, S.T. and Phifer, C.C. (1995). The short-range structure of zinc polyphosphate glass. *Journal of Non-Crystalline Solids.* 191(1-2), 45-55.

Buddhudu, S. and Thulasiramudu, A. (2006). Optical characterization of Mn^{2+}, Ni^{2+} and Co^{2+} ions doped zinc lead borate glasses. *Journal of Quantitative Spectroscopy & Radiative Transfer*. 102(2), 212-227.

Byun, J.O., Kim, B.H., Hong, K.S., Jung, H.J., Lee, S.W. and Izyneev, A.A. (1995). Properties and structure of RO-Na_2O-Al_2O_3-P_2O_5 (R = Mg, Ca, Sr, Ba) glasses. *Journal of Non-Crystalline Solids*. 190(3), 288-295.

Chakradhar, R.P.S., Murali, A., Rao, J.L. (2000). A study of electron paramagnetic resonance and optical absorption in calcium manganese phosphate glasses containing praseodymium. *Journal of Material Science*.35(2), 353-359.

Chaminade, J.P., Gacem, L., Artemenko, A., Ouadjaout, D., Garcia, A., Pollet, M. and Viraphong, O. (2009). ESR and fluorescence studies of Mn-doped $Na_2ZnP_2O_7$ single crystal and glasses. *Solid State Sciences*. 11(11), 1854-1860.

Chandrasekhar, A.V., Ravikumar R.V.S.S.N., Reddy, B.J., Reddy, Y.P. and Rao, P.S. (2002). EPR and optical absorption spectra of Mn (II) ions in sodium phosphate glasses. *Physics and Chemistry of Glasses-European Journal of Glass Science and Technology Part B.* 43(4), 173-175.

Corbridge, D.E.C. and Lowe, E.J. (1954). The infra-red spectra of some inorganic phosphorus compounds. *Journal of the Chemical Society.* 493-502.

Cotton, F.A. and Willkinson, G. Advanced Inorgorganic Chemistry, Wiley. Eastern, New Delhi, 1976.

Crabtree, D. F. (1974). Luminescence, optical absorption, and ESR of ZnS-Se:Mn. *Physica status solidi (a)*. 22(2), 543-552.

Da, N., Gao, G.J., Reibstein, S. and Wondraczek, L. (2010). Enhanced photoluminescence from mixed-valence Eu-doped nanocrystalline silicate glass ceramics. *Optics Express*. 18(4), A575-A583.

Da, N., Peng, M.Y., Krolikowski, S. and Wondraczek, L. (2010). Intense red photoluminescence from Mn^{2+} doped (Na^{+}, Zn^{2+}) sulfophosphate glasses and glass ceramics as LED converters. *Optics Express*. 18(3), 2549-2557.

Damian , G., Cozar, O., Magdas, D.A., Nasdala, L. and Ardelean, I. (2006). Raman spectroscopic study of some lead phosphate glasses with tungsten ions. *Journal of Non-Crystalline Solids.* 28-29, 3121-3125.

Davis, E.A. and Matt, N.F. (1979). Electronic Processes in Non-crystalline Materials, second edition , Clarendon Press, Oxford.

Day, D.E., Karabulut, M., Melnik. E., Stefan. R., Marasinghe. G.K., Ray, C.S. and Kurkjian. C.R. (2001). Mechanical and structural properties of phosphate glasses. *Journal of Non-Crystalline Solids*. 288(1-3), 8-17.

Ducel, J.F. and Videau, J.J. (1992). Physical and chemical characterizations of sodium borophosphate glasses. *Material Letters*. 13(4-5), 27l-274.

Duffy, J.A. (2002). The electronic polarisability of oxygen in glass and the effect of composition. *Journal of Non-Crystalline Solids*. 297(2-3), 275-284.

Duffy, J.A. and Ingram, M.D. (1975). Optical basicity-IV: Influence of electronegativity on the Lewis basicity and solvent properties of molten oxyanion salts and glasses. *Journal of Inorganic and Nuclear Chemistry*. 37(5), 1203-1206.

Durny. R. (1980). EPR study of Mn^{2+} in chalcogen-rich Ge-Se glasses. *Journal of Non-Crystalline Solids*. 41(2), 273-278.

Dwivedi, B.P., Rahman, M.H., Kumar, Y. and Khanna, B.N. (1993). Raman scattering study of lithium borate glasses. *Journal of Physics and Chemistry of Solids*. 54(5), 621-628.

Edwards, J.O., Morrison, G.C., Ross, V.F. and Schultz, J.W. (1954). The structure of the aqueous borate ion. *Journal of the American Chemical Society*. 77, 266-268.

Ehrt, D and Seeber, W. (1991). Glass for high performance optics and laser technology. *Journal of Non-Crystalline Solids*. 129(1-3), 19-30.

Ehrt, D. (2004). Photoluminescence in the UV-VIS region of polyvalent ions in glasses. *Journal of Non-Crystalline Solids*. 348, 22-29.

ElBatal, F.H.A, Morsi, R.M., Ouis, M.A. and Marzouk, S.Y. (2010). UV-visible, Raman and E.S.R. studies of gamma-irradiated NiO-doped sodium metaphosphate glasses. *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*. 77(4), 717-726.

El-Falaky, G.E. and Guirguis, O.W. (2012). Effect of zinc on the physical properties of borate glasses. *Journal of Non-Crystalline Solids*, 358(15), 1746-1752.

Elliot, S.R. (1990). Physics of Amorphous materials 2nd Edition. Longman.

Faber, A. J., Die, A.V., Blasse, G. and van der Weg, F. (1987). Luminescence of manganese of different valencies in oxide glasses. *Physics* and *Chemistry* of *Glasses-European Journal of Glass Science and Technology Part B*. 28, 150-155.

Fargin, E., Cardinal, T., Nazabal, V., Le Flem, G., Le Boiteux, S. and Ducasse, L. (1998). Glass local structure and optical nonlinearities of oxide glasses. J*ournal of Non-Crystalline Solids*. 239(1-3), 131-138.

Fragoso, W.D., Donega, C. de M. and Longo, R.L. (2005). A structural model of La_2O_3-Nb_2O_5-B_2O_3 glasses based upon infrared and luminescence spectroscopy and quantum chemical calculations. *Journal of Non-Crystalline Solids.* 351(37-39), 3121-3126.

France, P. W., Carter, S. F. and Parker, J. M. (1986). Oxidation States of 3*d* Transition Metals in ZrF_4 Glasses. *Physics and Chemistry of Glasses*. 27, 32-41.

Fujino, S., Toyoda, S. and Morinaga, K. (2003). Density, viscosity and surface tension of 50RO-50P_2O_5 (R: Mg, Ca, Sr, Ba, and Zn) glass melts. *Journal of Non-Crystalline Solids*. 321(3), 169-174.

Gaafar, M.S., Abd El-Aal, N.S., Gerges, O.W. and El-Amir, G. (2009). Elastic properties and structural studies on some zinc-borate glasses derived from ultrasonic, FT-IR and X-ray techniques. *Journal of Alloys and Compounds*. 475(1-2), 535-542.

Gaafar, M.S., Afifi, H.A. and Mekawy, M.M. (2009). Structural studies of some phospho-borate glasses using ultrasonic pulse-echo technique, DSC and IR spectroscopy. *Physica B: Condensed Matter*. 404(12-13), 1668-1673.

Gao, G., Reibstein, S., Peng, M. And Wondrazek, L. (2011). Dual-mode photoluminescence from Mn^{2+} doped Li, Zn aluminosilicate glass ceramics. *Physics and Chemistry of Glasses: European Journal of Glass Science and Technology part B*. 52(2), 59-63.

Garcia, U.C., Serrano, J.R., Madrigal, E. and Ramos, F. (1997). Optical spectroscopy of Mn^{2+} ions in $CdCl_2$ single crystals. *Journal of Luminescence*. 71(2), 169-175.

Ghoneim, N.A., Moustaffa, F.A. and EzzElDin, F.M. (1985). *Physics Chemistry Glasses*. 26(3), 55-58.

Goubeau F.L. and Keller H. (1953). Raman-Spectren und Structur von Boroxol-Verbindungen. *Zeitschrift fuer Anorganische und Allgemeine Chemie.* 272(5-6), 303-312.

Griscom, D. L. and Griscom, R. E. (1967). Paramagnetic Resonance of Mn^{2+} in Glasses and Compounds of the Lithium Borate System. *Journal of Chemical Physics*. 47(8), 2711-2722.

Griscom, D.L. (1980). Electron spin resonance in glasses. *Journal of Non-Crystalline Solids*. 40(1-3), 211-272.

Hassan, M. A. and Hogarth, C. A. (1988). A study of the structural, electrical and optical properties of copper tellurium oxide glasses. *Journal of Materials Science.* 23(7), 2500-2504.

Hayes, G.R. and Deveaud, B. (2002). " Is luminescence from quantum wells to Ex citons?". *Physica Status Solidi (a)*. 190(3), 637-640.

Henderson, B. and Bartram, R.H. (2000). Crystal-Field Engineering of Solid-State Laser Ions in Crystals, Nauka, Moscow, in Russian.

Hussin, R., Xian, J.L., Hamdan, S., Deraman, K., Ismail, B., Bakar, N.H.A., Ahmad, N.E., Shamsuri, W.H.W., Yusof, M. and Hamzah, K. (2010). Identification of crystalline phase in xMgO-(40-x)SrO-60TeO_2 doped with Eu^{2+} and Dy^{3+} ions by infrared and Raman spectroscopy. *Regional Annual Fundamental Science Symposium*. 436-445.

Ivascu, C., Gabor, A.T., Cozar, O., Daraban, L. and Ardelean, I. (2011). FT-IR, Raman and thermoluminescence investigation of P_2O_5-BaO-Li_2O glass system. *Journal of Molecular Structure*. 993(1-3), 249-253.

Ivascu, C., Timar Gabor, A., Cozar, O., Daraban, L. and Ardelean, I. (2011). FT-IR, Raman and thermoluminescence investigation of P_2O_5-BaO-Li_2O glass system. *Journal of Molecular Structure*. 993(1-3), 249-253.

Johnson, I.D. and Davidson, M.W. (2012). Jablonski Energy Diagram. *Olympus America Inc.* Retrieved July 23, 2013, from http://www.olympusmicro.com.

Kabi, S., and Ghosh, A (2011). Correlation of structure and electrical conductivity of CdI_2 doped silver borophosphate glass and nanocomposite._*The Journal of Physical Chemistry C.* 115 (19), 9760-9766.

Kamitos E. L., A.P. Patsis and G.D. Chryssikos (1993). Infrared reflectance investigation of alkali diborate glasses. *Journal of Non-Crystalline Solids*. 152(2-3), 246-257.

Kamitsos, E.L., Karakassides, M.A. and Cryssikos, G. D. (1987). Vibrational spectra of magnesium-sodium-borate glasses. 2. Raman and mid-infrared investigation of the network structure. *The Journal of Physical Chemistry*. 91(5), 1073-1079.

Karakassides, M.A. , Saranti, A. and Koutselas, I. (2004). Preparation and structural study of binary phosphate glasses with high calcium and/or magnesium content. *Journal of Non-Crystalline Solids*. 347(1-3), 69-79.

Karmakar, B., Singh, S.P., Chakradhar, R.P.S. and Rao, J.L. (2010). EPR, optical absorption and photoluminescence properties of MnO_2 doped $23B_2O_3$-5ZnO-$72Bi_2O_3$ glasses. *Physica B: Condensed Matter*. 405(9), 2157-2161.

Kasuga, T. and Abe, Y. (1999). Calcium phosphate invert glasses with soda and titania. *Journal of Non-Crystalline Solids*. 243(1), 70-74.

Kerkouri, N., Haddad, M., Et-tabirou, M., Chahine, A. and Laanab, L. (2011). FTIR, Raman, EPR and optical absorption spectral studies on V_2O_5-doped cadmium phosphate glasses. *Physica B: Condensed Matter*. 406(17), 3142-3148.

Khafagy, A. H., Ewaida, M. A., Higazy, A. A., Ghoneim, M. M. S., Hager, I. Z. and El-Bahnasawy, R. (1992). Infrared spectra and composition dependence investigations of the vitreous V_2O_5/P_2O_5 system. *Journal of Materials Science*. 27(6), 1435-1439.

Kistaiah, P. and Subhadra, M. (2012). Infrared and Raman spectroscopic studies of alkali bismuth borate glasses: Evidence of mixed alkali effect. *Vibrational Spectroscopy*. 62, 23-27.

Kityk, I.V., Kumar, A.V.R., Rao, Ch.S., Rao, N.N., Kumar, V.R. and Veeraiah, N. (2012). Influence of valence and coordination of manganese ions on spectral and dielectric features of Na_2SO_4-B_2O_3-P_2O_5 glasses. *Journal of Non-Crystalline Solids*. 358(10), 1278-1286.

Komatsu, T. and Dimitrov, V. (1999). Electronic polarizability, optical basicity and non-linear optical properties of oxide glasses. *Journal of Non-Crystalline Solids*. 249(2-3), 160-179.

Koudelka, L. and Mosner, P. (2000). Borophosphate glasses of the ZnO-B_2O_3-P_2O_5 system. Materials Letters. 42(3), 194-199.

Koudelka, L. and Mosner, P. (2001). Study of the structure and properties of Pb-Zn borophosphate glasses. *Journal of Non-Crystalline Solids*. 293-295, 635-641.

Koudelka, L., Jirak, J., Mosner, P., Montagne, L. and Palavit, G. (2006). Study of lithium-zinc borophosphate glasses. *Journal of Materials Science*. 41(4), 4636-4642.

Koudelka, L., Mosner, P. and Subcik, J. (2009). Study of Structure and Properties of Modified Borophosphate Glasses. *IOP Conf. Series: Materials Science and Engineering*. 2, 12-15.

Koudelka, L., Mosner, P., Zeyer, M. and Jager, C. (2005). Structure and properties of mixed sodium-lead borophosphate glasses. *Journal of Non-Crystalline Solids*. 351(12-13), 1039-1045.

Koudelka, L., Vosejpkova, K., Cernosek, Z., Mosner, P., Montagne, L., Revel, B. (2012). Structural studies of boron and tellurium coordination in zinc borophosphate glasses by ^{11}B MAS NMR and Raman spectroscopy. *Journal of Physics and Chemistry of Solids*. 73(2), 324-329.

Krogh-Moe (1965). Interpretation of the infrared spectra of boron oxide and alkali borate glasses. *Journal of Physics and Chemistry of Glasses.* 6, 46-54.

Layne, C.B., Saroyan, R.A. and Milam, D. (1976). Low-index fluoride glasses for high-power Nd lasers. *Optics Communications*. 18(1), 171-172.

Lee, J.D. (1996). Concise Inorganic Chemistry, Blackwell Scientific, Oxford.

Li, C.Y., Jiang, L.H., Zhang, Y.L., Hao, J.Q. and Su,Q. (2009). Synthesis, photoluminescence, thermoluminescence and dosimetry properties of novel phosphor $KSr_4(BO_3)_3$:Ce. *Journal of Alloys and Compounds*, 482(1-2), 313-316.

Li, X.Y., Lu, A.X. and Yang, H.M. (2014). Structure of $ZnO–Fe_2O_3–P_2O_5$ glasses probed by Raman and IR spectroscopy. *Journal of Non-Crystalline Solids*. 389, 21-27.

Li, X.Y., Yang, H.M., Song, X.L. and Wu, Y. (2013). Glass forming region, structure and properties of zinc iron phosphate glasses. *Journal of Non-Crystalline Solids*. 379, 208-213.

Liang, X.F., Lai, Y.M., Yang, S.Y., Wang, J.X. and Zhang, B.T. (2012). Raman spectra study of iron phosphate glasses with sodium sulfate. *Journal of Molecular Structure*. 1013, 134-137.

Lin, H., Yang, D.L., Liu, G.S., Ma, T.C., Zhai, B., An, Q.D.,Yu, J.Y., Wang, X.J., Liu, X.R. and Pun. E.Y.B. (2005). Optical absorption and photoluminescence in Sm^{3+} and Eu^{3+} doped rare-earth borate glasses. *Journal of Luminescence*, 113(1-2), 121-128.

Liu, H.L., Yang, R.J., Wang, Y.H., Jiang, W.L., Hao, X.P., Zhan, J. And Liu, S.Q. (2012). Structure and properties of ZnO-containing lithium-iron-phosphate glasses. *Journal of Alloys and Compounds*. 513, 97-100.

Liu, S.Q., Yang, R.J., Liu, H.L., Wang, Y.H., Jiang, W.L., Hao, X.P. and Zhan, J. (2012). Structure and properties of ZnO-containing lithium-iron-phosphate glasses. *Journal of Alloys and Compounds*. 513, 97-100.

Lucacel, R.C. and Ardelean, I. (2007). FT-IR and Raman study of silver lead borate-based glasses. *Journal of Non-Crystalline Solids*. 353(18-21), 2020-2024.

Lucacel, R.C. and Ponta, O. (2012). Viorica Simon Short-range structure and in vitro behavior of ZnO-CaO-P_2O_5 bioglasses. *Journal of Non-Crystalline Solids*. 358(20), 2803-2809.

Lucacel, R.C., Maier, M. and Simon, V. (2010). Structural and *in vitro* characterization of TiO_2-CaO-P_2O_5 bioglasses. *Journal of Non-Crystalline Solids*. 356(50-51), 2869-2874.

Lucacel, R.C., Marcus, C., Timar, V. And Ardelean, I. (2007). FT-IR and Raman spectroscopic studies on B_2O_3-PbO-Ag_2O glasses doped with manganese ions. *Solid State Sciences*. 9(9), 850-854.

Magdas, D.A., Cozar, O. And Ardelean, I. (2008). EPR study of molybdenum-lead-phosphate glasses. *Journal of Non-Crystalline Solids*. 354(10-11), 1032-1035.

Magon, C.J., Franco, R.W.A.,Lima, J.F., Donoso, J.P.and Messaddeq, Y. (2006). Magnetic resonance study of the crystallization behavior of InF_3-based glasses doped with Cu^{2+}, Mn^{2+} and Gd^{3+}. *Journal of Non-Crystalline Solids*. 352(32-35), 3414-3422.

Maniu, D., Iliescu, T., Ardelean, I., Cinta-Pinzaru, S., Tarcea, N. and Kiefer, W. (2003). Raman study on B_2O_3-CaO glasses. *Journal of Molecular Structure*. 651-653, 485-488.

Marzouk, S.Y., Elalaily, N.A., Ezz-Eldin, F.M. and Abd-Allah, W.M. (2006). Optical absorption of gamma-irradiated lithium-borate glasses doped with different transition metal oxides. *Physica B: Condensed Matter*. 382(1-2), 340-351.

Marzouk, S.Y., Elbatal, F.H., Salem, A.M. and Abo-Naf, S.M. (2007). Absorption spectra of gamma-irradiation TM-doped cabal glasses. *Optical Materials*. 29(11), 1456-1466.

Mascaros, S.M. and Ramos, J.V.G. (2008). The Use of Lasers in Conservation and Conservation Science. COST Office Brussels, Belgium. Materials, Cambridge Press, Cambridge.

Meera, B.N. and Ramakrishna, J. (1993). Raman spectral studies of borate glasses. *Journal of Non-Crystalline Solids*. 159(1-2), 1-21.

Meyer, K. (1997). Characterization of the structure of binary zinc ultraphosphate glasses by infrared and Raman spectroscopy. *Journal of Non-Crystalline Solids*. 209(3), 227-239.

Mogus-Milankovic, A., Gajovic, A., Santic, A. and Day, D.E. (2001). Structure of sodium phosphate glasses containing Al_2O_3 and/or Fe_2O_3. Part I. *Journal of Non-Crystalline Solids*. 289(1-3), 204-213.

Mohan, N.K., Reddy, M.R., Jayasankar, C.K. and Veeraiah, N. (2008). Spectroscopic and dielectric studies on MnO doped $PbO-Nb_2O_5-P_2O_5$ glass system. *Journal of Alloys and Compounds*. 458(1-2), 66-76.

Mohapatra, M., Dhobale, A.R., Natarajan, V. and Godbole, S.V. (2012). Synthesis and photoluminescence investigations of the white light emitting phosphor, vanadate garnet, $Ca_2NaMg_2V_3O_{12}$ co-doped with Dy and Sm. *Journal of Luminescence*. 132(2), 293-298.

Montagne, L., Grussaute, H., Palavit, G. and Bernard, J.L. (2000). Phosphate speciation in $Na_2O-CaO-P_2O_5-SiO_2$ and $Na_2O-TiO_2-P_2O_5-SiO_2$ glasses. *Journal of Non-Crystalline Solids*. 263–264, 312-317.

Montagne, L., Palavit, G. and Maitresse, G. (1996). P-31 MAS NMR and FT-IR analysis of $(50\text{-}x/2)Na_2O.xBI_2O_3.(50\text{-}x/2)P_2O_5$ Glasses. *Physics and Chemistry of Glasses-European Journal of Glass Science and Technology Part B*. 37(5), 26-211.

Morgan, S.H., Pan, Z.D. and Long, B.H. (1995). Raman scattering cross-section and non-linear optical response of lead borate glasses. *Journal of Non-Crystalline Solids*. 185(1-2), 127-134.

Mosner, P., Koudelka, L., Zeyer-Dusterer, M. and Jager, C. (2007). Study of potassium-zinc borophosphate glasses. *Journal of Physics and Chemistry of Solids*. 68(4), 638-644.

Mozzi, R. L. and Warren, B.E. (1970). The structure of vitreous boron oxide. *Journal of Applied Crystallography*. 3, 251-257.

Natura, U. and Ehrt, D. (2001). Generation and healing behavior of radiation-induced optical absorption in fluoride phosphate glasses: The dependence on UV radiation sources and temperature. *Nuclear Instruments and Methods in Physics Research B.* 174, 143-150.

Orgel, L. E. (1955). Spectra of Transition-Metal Complexes. *Journal* of *Chemical Physics*. 23(6), 1004-1014.

Pascuta, P., Borodi, G. and Culea, E. (2008). Influence of europium ions on structure and crystallization properties of bismuth borate glasses and glass ceramics. *Journal of Non-Crystalline Solids*. 354(52-54), 5475-5479.

Pascuta, P., Borodi, G., Popa, A., Dan, V. and Culea, E. (2010). Influence of iron ions on the structural and magnetic properties of some zinc-phosphate glasses. *Materials Chemistry and Physics*. 123(2-3), 767-771.

Pascuta, P., Bosca, M., Borodi, G. and Culea, E. (2011). Thermal, structural and magnetic properties of some zinc phosphate glasses doped with manganese ions. *Journal of Alloys and Compounds*. 509(11), 4314-4319.

Pascuta, P., Stefan, R., Popa, A., Raita, O., Indrea, E. and Culea, E. (2012). XRD and EPR structural investigation of some zinc borate glasses doped with iron ions. *Journal of Physics and Chemistry of Solids*. 73(2), 221-226.

Pauling, L. (1960). The nature of Chemical Bond, 3rd edition, Cornell University, New York, 1960. P. 93.

Pavani, P.G., Sadhana, K. And Mouli, V.C. (2011). Optical, physical and structural studies of boro-zinc tellurite glasses. *Physica B: Condensed Matter*. 406(6-7), 1242-1247.

Peteanu, M., Ardelean, I., Cozar, O., Simon, V., Mih, V. And Botezan, G. (1999). Structural and Magnetic Properties of MnO-P_2O_5-PbO Glasses. Journal of Materials Science & Technology. 15(5), 453-456.

Peteanu, M., Ardelean, I., Filip, S. and Alexandru, D. (1996). EPR of Mn^{2+} ions in $70TeO_2$-$25B_2O_3$-5PbO glasses. *Romanian Journal of Physics*. 41(7-8), 593-601.

Prado, L., Machado, I.E.C., Gomes, L., Prison, J.M. and Martinelli, J.R. (2004). Optical properties of manganese in barium phosphate glasses. *Journal of Non-Crystalline Solids*. 348, 113-117.

Rada, M., Rada, S., Pascuta, P. and Culea, E. (2010). Structural properties of molybdenum-lead-borate glasses. *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*. 77(4), 832-837.

Raju, C.L., Sumalatha, B., Omkaram, I. and Rao, T.R. (2013). The structural, optical and magnetic parameter of manganese doped strontium zinc borate glasses. *Physica B: Condensed Matter*. 411, 99-105.

Ramakrishna, J., Chakradhar, R.P.S., Ramesh, K.P. and Rao, J.L. (2003). Mixed alkali effect in borate glasses-EPR and optical absorption studies in $x$$Na_2O$-(30-$x$)$K_2O-70B_2O_3$ glasses doped with Mn^{2+}. *Journal of Physics and Chemistry of Solids*. 64(4), 641-650.

Rao, J.L., Chakradhar, R.P.S., Yasoda, B. and Gopal, N.O. (2007). EPR and optical studies of Mn^{2+} ions in Li_2O-Na_2O-B_2O_3 glasses-An evidence of mixed alkali effect. *Journal of Non-Crystalline Solids*. 353(24-25), 2355-2362.

Rao, J.L., Chakradhar, R.P.S., Sivaramaiah, G. and Gopal, N.O. (2005). EPR and optical investigations of manganese ions in alkali lead tetraborate glasses. *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*. 62(4-5), 761-768.

Rao, J.L., Kesavulu, C.R., Muralidhara, R.S., Anavekar, R.V. and Chakradhar, R.P.S. (2009). EPR and photoluminescence studies on lithium-potassium borophosphate glasses doped with Mn^{2+} ions. *Journal of Alloys and Compounds*. 486(1-2), 46-50.

Rao, J.L., Kiran, N., Kesavulu, C.R. and Kumar, A.S. (2011). Spectral studies on Mn^{2+} ions doped in sodium-lead borophosphate glasses. *Physica B: Condensed Matter*. 406(20), 3816-3820.

Rao, J.L., Murali, A. and Chakradhar, R.P.S. (2005). Allowed and forbidden hyperfine structure of Mn^{2+} ions in sodium tetraborate glasses-an EPR and optical study. *Physica B. Condensed Matter*. 358(1-4), 19-26.

Rao, J.L., Rao, A.S., Sreedhar, B. and Lakshman, S.V.J. (1992). Electron paramagnetic resonance and optical absorption spectra of Mn^{2+} ions in alkali zinc borosulphate glasses. *Journal of Non-Crystalline Solids*. 144, 169-174.

Rao, K.J. and Ganguli, M. (1999). Structural Role of PbO in Li_2O-PbO-B_2O_3 Glasses. *Journal of Solid State Chemistry*. 145(1), 65-76.

Rao, K.V., Sudhakar, B.K., Chand, N.R.K., Prasanna, H.N.L., Rao, G.S. and Dhand, V. (2010). Vibrational spectral analysis of structural modifications of Cr_2O_3 containing oxyfluoroborate glasses. *Journal of Non-Crystalline Solids*. 356(43), 2211-2217.

Rao, L., Murali, A. and Chakradhar, R.P.S. (2005). Allowed and forbidden hyperfine structure of Mn^{2+} ions in sodium tetraborate glasses-an EPR and optical study. *Physica B: Condensed Matter*. 358(1-4), 19-26.

Rao, P.R.V., Joseph, K., Premila, M., Amarendra, G., Kutty, K.V.G. andSundar, C.S. Structure of cesium loaded iron phosphate glasses: An infrared and Raman spectroscopy study. (2012). *Journal of Nuclear Materials*. 420(1-3), 49-53.

Rao, R.B. and Gerhardt, R.A. (2008). Effect of alkaline earth modifier ion on the optical, magnetic and electrical properties of lithium nickel borate glasses. *Materials Chemistry and Physics*. 112(1), 186-197.

Rao, T. R., Raju, C.L., Sumalatha, B. and Omkaram, I. (2013). The structural, optical and magnetic parameter of manganese doped strontium zinc borate glasses. *Physica B: Condensed Matter*. 411, 99-105.

Ravikumar, R.V.S.S.N., Komatsu, R., Ikeda, K., Chandrasekhar, A.V., Reddy, B.J., Reddy, Y.P. and Rao, P.S. (2003). EPR and optical studies on transition metal doped $LiRbB_4O_7$ glasses. *Journal of Physics and Chemistry of Solids*. 64(2), 261-264.

Reddy, M.R., Kumar, A.R., Rao, T.G.V.M. and Veeraiah, N. (2013). Fluorescence spectroscopic studies of Mn^{2+} ions in $SrO-Al_2O_3-B_2O_3-SiO_2$ glass system. *Optical Materials*. 35(3), 402-406.

Roiland, C., Fayon, F., Simon, P. and Massiot, D. (2011). Characterization of the disordered phosphate network in $CaO-P_2O_5$ glasses by ^{31}P solid-state NMR and Raman spectroscopies. *Journal of Non-Crystalline Solids*. 357(7), 1636-1646.

Ronda, C.R. and Amrein, T. (1996). Evidence for exchange-induced luminescence in Zn_2SiO_4: Mn. *Journal of Luminescence*. 69(5-6), 245-248.

Rulmont, A., Cahay, R., Liegois-Duyckaencs, M. and Tarte, P. (1991). *European Journal* of *Solid State* and *Inorganic Chemistry*. 28, 207.

Ryu, B.K., Im, S.H., Na, Y.N., Kim, N.J., Kim, D.H. and Hwang, C.W. (2010). Structure and properties of zinc bismuth phosphate glass. *Thin Solid Films.* 518(24), e46-e49.

Ryu, B.K., Kim, N.J., Im, S.H., Kim, D.H. and Yoon, D.K. (2010). Structure and properties of borophosphate glasses. *Electronic Materials Letters*. 6(3), 103-106.

Saddeek, Y. (2009). Structural and acoustical studies of lead sodium borate glasses. *Journal of Alloys and Compounds*. 467(1-2), 14-21.

Saddeek, Y.B. and Doweidar, H. (2009). FTIR and ultrasonic investigations on modified bismuth borate glasses. *Journal of Non-Crystalline Solids.* 355(6), 348-354.

Sahar, M.R. (1998). Sains Kaca. Penerbit Universiti Teknologi Malaysia.

Sastry, S.S. and Rao, B.R.V. (2014). Spectroscopic studies of copper doped alkaline earth lead zinc phosphate glasses. *Physica B.* 434, 159-164.

Satyanarayana, T., Valente, M.A., Nagarjuna, G. and Veeraiah, N. (2013). Spectroscopic features of manganese doped tellurite borate glass ceramics. *Journal of Physics and Chemistry of Solids*. 74(2), 229-235.

Scagliotti, M., Villa, M. and Chiodelli, G. (1987). Short range order in the network of the borophosphate glasses: A ^{31}P NMR-MAS (Magic Angle Spinning) study. *Journal of Non-Crystalline Solids*. 94(1), 101-121.

Sdiri, N., Elhouichet, H. Dhaou, H. and Mokhtar, F. (2014). Effects of the substitution of P_2O_5 by B_2O_3 on the structure and dielectric properties in (90-x) P_2O_5-$x$$B_2O_3-10Fe_2O_3$ glasses. *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*. 117, 309-314.

Sekiya, T., Mochida, N., Ohtsuka, A. and Soejima, A. (1992). Raman spectra of $BO_{3/2}$-TeO_2 glasses. *Journal of non-crystalline solids*. 151(2), 222-228.

Shelby, J.E. (2005). Introduction to glass science and technology 2nd edition. New York State College of Ceramics at Alfred University School of Engineering, Alfred, NY, USA.

Shih, P.Y., Yung, S.W. and Chin, T.S. (1998). Thermal and corrosion behavior of P_2O_5-Na_2O-CuO glasses. *Journal of Non-Crystalline Solids*. 224(2), 143-152.

Shih, P.Y., Yung, S.W. and Chin, T.S. (1999). FTIR and XPS studies of P_2O_5-Na_2O-CuO glasses. *Journal of Non-Crystalline Solids*. 244(2-3), 211-222.

Sidek, H.A.A., Collier, I.T., Hampton, R.N., Saunders, G.A. and Bridge, B. (1989). Electrical conductivity and dielectric constant of samarium phosphate glasses. *Philosophical Magazine B*, 59(2), 221-232.

Singh, K.J. and Kaur, S. (2014). Investigation of lead borate glasses doped with aluminium oxide as gamma ray shielding materials. *Annals of Nuclear Energy*, 63, 350-354.

Singh, R.K. and Srinivasan, A. (2009). EPR and magnetic properties of MgO-CaO-SiO_2-P_2O_5-CaF_2-Fe_2O_3 glass-ceramics. *Journal of Magnetism and Magnetic Materials*. 321(18), 2749-2752.

Singh, V., Chakradhar, R.P.S., Rao, J.L. and Kim, D.K. (2008). Characterization, EPR and luminescence studies of $ZnAl_2O_4$:Mn phosphors. *Journal of Luminescence*. 128(3), 394-402.

Stefan, R., Radu, A., Borodi, G., Biris, A.R. and Baia, L. (2014). Highlighting of structural units of B_2O_3-Li_2O-P_2O_5 system under heat treatment. *Materials Chemistry and Physics*. 143(3), 1271-1277.

Stevels, J.M. (1953). Ultraviolet transmittivity of glasses. Proceedings 11th International Congress Pure and Applied Chemistry. 5, 519-521 .

Su, Q., Liang, H.B., Zeng, Q.H., Tao, Y. and Wang, S.B. (2003). VUV-UV excited luminescent properties of calcium borophosphate doped with rare earth ions. *Materials Science and Engineering part B*.98, 213-219.

Subbalakshmi and Veeraiah, N. (2002). Study of CaO-WO_3-P_2O_5 glass system by dielectric properties, IR spectra and differential thermal analysis. *Journal of Non-Crystalline Solids*. 298(1), 89-98.

Suresh, S., Pavani, P.G. and Mouli, V.C. (2012). ESR, optical absorption, IR and Raman studies of $x TeO_2 + (70 - x) B_2O_3 + 5TiO_2 + 24R_2O$:1CuO ($x$ = 10, 35 and 60 mol%; R = Li, Na and K) quaternary glass system. *Materials Research Bulletin*. 47(3), 724-731.

Sviridov, D.T., Sviridova, R.L. and Smirnov, F. (1976). Optical Spectra of Transition Metal Ions in Crystals, Nauka, Moscow, in Russian.

Takebe, H., Baba, Y. and Kuwabara, M. (2006). Dissolution behavior of ZnO-P_2O_5 glasses in water. *Journal of Non-Crystalline Solids*. 352(28-29), 3088-3094.

Takebe, H., Kawano, M., Kuwabara, M. (2009). Compositional dependence of the luminescence properties of Mn^{2+}-doped metaphosphate glasses. *Optical Materials*. 32(2), 277-280.

Takebe, H.,Baba, Y.and Kuwabara, M. (2006). Dissolution behavior of ZnO-P_2O_5 glasses in water. *Journal of Non-Crystalline Solids*. 352(28-29), 3088-3094.

Tallant, D.R. *and* Nelson, C. (1986). Raman investigation of glass structures in the Na_2O-SiO_2-P_2O_5-Al_2O_3 system. *Physics* and *Chemistry* of *Glasses-European Journal of Glass Science and Technology Part B*. 27, 75-79.

Tanabe, Y. and Sugano, S. (1954). On the spectra of complex ions. *Journal of the Physical Society of Japan*. 9(753-766), 66-79.

Taylor, P.C. and Bray, P.J. (1970). Electron spin resonance of Mn^{2+} in strontium borate compounds and glasses. *Journal of Physics and Chemistry of Solids*. 33(1), 43-58.

Toloman, D., Giurgiu, L.M. and Ardelean, I. (2009). EPR investigations of calcium phosphate glasses containing manganese ions. *Physica B:Condensed Matter*. 404(21), 4198-4201.

Vedeanu, N., Cozar, O., Ardelean, I., Lendl, B. and Magdas, D.A. (2008). Raman spectroscopic study of CuO-V_2O_5-P_2O_5-CaO glass system. *Vibrational Spectroscopy*. 48(2), 259-262.

Veeraiah, N. and Durga, D.K. (2003). Role of manganese ions on the stability of ZnF_2-P_2O_5-TeO_2 glass system by the study of dielectric dispersion and some other physical properties. *Journal of Physics and Chemistry of Solids*. 64(1), 133-146.

Veeraiah, N., Mohan, N.K., Reddy, M.R. and Jayasankar, C.K. (2008). Spectroscopic and dielectric studies on MnO doped PbO-Nb_2O_5-P_2O_5 glass system. *Journal of Alloys and Compounds*. 458(1-2), 66-76.

Wan, M.H., Wong, P.S., Hussin, R., Lintang, H.O. and Endud, S. (2014). Structural and luminescence properties of Mn^{2+} ions doped calcium zinc borophosphate glasses. *Journal of Alloys and Compounds*, 595, 39-45.

Wang, Y.H. and Hao, Y. (2007). Luminescent properties of Zn_2SiO_4:Mn^{2+} phosphor under UV, VUV and CR excitation. *Journal of Luminescence*. 122-123, 1006-1008.

Wenger, L.E., Khattak, G.D., Khawaja, E.E., Thompson, D.J., Salim, M.A., Hallak, A.B. and Daous, M.A. (1996). Composition-dependent loss of phosphorus in the formation of transition-metal phosphate glasses. *Journal of Non-Crystalline Solids*. 194(1-2), 1-12.

Wiberg, E. and Holleman, A.F. (2001). Inorganic Chemistry elsevier. ISBN 0-12-352651-5 Academic Press. 1st Edition.

Wilder Jr, J.A. (1980). Glasses and glass ceramics for sealing to aluminum alloys. *Journal of Non-Crystalline Solids*, 38&39(2), 879-884.

Wondraczek, L. And Lakshminarayana, G. (2011). Photoluminescence and energy transfer in Tb^{3+}/Mn^{2+} co-doped $ZnAl_2O_4$ glass ceramics. *Journal of Solid State Chemistry*. 184(8), 1931-1938.

Wright, A.C., Simmons, C.J. and El-Bayoumi, O.H. (1993). In Experimental Techniques of Glass Science. The American Ceramic Society, Westwille, 205.

Yahya, N.A.K., Mohamed, B., Deni, M.S.M., Mohamed, S.N., Halimah, M.K. and Sidek, H.A.A. (2010). Effects of concurrent TeO_2 reduction and ZnO addition on elastic and structural properties of $(90-x)TeO_2$-$10Nb_2O_5$-(x)ZnO glass. *Journal of Non-Crystalline Solids*. 356(33-34), 1626-1630.

Yang, S.Y., Lai, M., Liang, X.F., Wang, J.X., Cao, L.H. and Dai, B. (2011). Raman and FTIR spectra of iron phosphate glasses containing cerium. *Journal of Molecular Structure*. 992(1-3), 84-88.

Yiannopoulos Y.D., G.D. Chryssikos and E.I. Kamitsos (2001). Structure and properties of alkaline earth borate *glasses*. *Physics and Chemistry of Glasses-European Journal of Glass Science and Technology Part B*. 42(3), 164-172.

Zachariasen, W.H. (1932). The Atomic Arrangement in Glass. *Journal of American Chemical Society*. 54(10), 3841-3851.