Egypt. J. Chem. **Vol. 66** No. 8 pp. 41 - 46 (2023)

Egyptian Journal of Chemistry

http://ejchem.journals.ekb.eg/

INFLUENCE OF VANADIUM OXIDE ON THE STRUCTURE AND PROPERTIES OF SILICATE GLASSES MODIFIED BY ZINC OXIDE

Amal Behairy[1], Riham Atef[2,*], Gomaa El Damrawi[3]

[1]Basic Science Department, the High Institute of Engineering and Technology, New Damietta, Egypt
[2,]Chemical Engineering Department, the High Institute of Engineering and Technology, New Damietta, Egypt*
[3]Physics Department, Faculty of Science, Mansoura University, Mansoura, Egypt

Abstract

Different glasses of the system xV_2O_5-(40-x) SiO_2-40 ZnO-30 P_2O_5 (x = 0, 5, 15, 25 V_2O_5 mol%) were prepared by the normal quenching technique. The amorphous character of the as-prepared glasses was verified using X-ray diffraction (XRD) spectroscopy. It implies that V_2O_5 has no influence on the nature of the well-formed amorphous species. On the other hand, the thermal heat treatment at 480℃ for 12 hours produced some crystalline phases in the host glass network. Modification with zinc and vanadium oxides is totally different from that with alkali oxides. Both ZnO and V_2O_5 would be entered as intermediate oxides, resulting in the formation of nonbridging oxygen atoms (NBO). However, small amounts of V_2O_5 and ZnO can be consumed as glass formers to form VO_4 and ZnO_4 tetrahedral units. Both the structural factors $R = V_2O_5/SiO_2$ and $K = SiO_2/ZnO$ have direct impacts on the material properties. Increasing R and decreasing K led to increasing NBO in the glass network, which decreased both the hardness number (H_v) and glass transition temperature (T_g). The NBO has a high potential to crystallize some particular vanadium silicate aggregated species when the samples are thermally treated at 480^{O}C for 12 hours. Nano crystalline cluster species were identified using transmission electron microscopy (TEM). The replacement of SiO_2 with V_2O_5 enhanced the content and size of well-formed nano-sized clusters.

Keywords: Silicate glasses; Structure factors; Nano-clusters; Heat treatments

1. Introduction

It was previously known that adding modifier oxides to silicate, borosilicate, tellurite, vanadate, or phosphate systems would result in the creation of (NBO) in their network [1-6]. Increased NBO would be simply assisted in the formation of crystalline or polycrystalline phases that are favorable for certain applications depending on nanoscale produced species [7-12]. A crystalline structure is enhanced, in some cases, when the concentration of NBO is high enough to form orthophosphate, orthosilicate, and orthovanadate structural groups [8-13]. Thermal heat treatments can initiate phase separation, which leads to additional crystallization, resulting in a glass ceramic (GC) [7,14-16], which is believed to be the most practical kind of polycrystalline material [12,15]. GC is particularly interested in medical and materials engineering applications [7-10].

Amorphous structures of various glass types are used to construct the bulk of glass network. On the other hand, to promote bulk crystallization, nucleating agents (NAs) such as V_2O_5, TiO_2, Cr_2O_3, and CuO can be utilized [9-13]. NAs have been found to enhance the nucleation and growth rates of the select specific phases [7-11, 14-16] by decreasing the surface energy between crystal and glassy phases. The thermal treating processes provide a clear guidance for controlling the major phase's crystallization kinetics. In addition, increasing the (NBO) can greatly sped up the crystalline phase by means of deposition process.

To our knowledge, the relationship between NBO production and clustering processes in vanadium silicate glasses has never been investigated. As a result, the goal of this study is to shed some insight on

*Corresponding author e-mail: rihamatef99@gmail.com
Receive Date: 14 March 2022; Revise Date: 22 July 2022; Accept Date: 30 November 2022
DOI: 10.21608/EJCHEM.2022.126603.5657

the influence of V_2O_5 substitution for SiO_2 on glass structure and properties in terms of developing glass compositions and thermal heat treatment processes. The latter is useful to generate nano-crystalline species such as apatite and wollastonite crystals which have beneficial applications as biomaterials [14-16]. Limited studies on biomaterials containing V_2O_5 were carried out. Therefore, this study is devoted to shed light on the role played by V_2O_5 and thermal heat treatment for producing glass ceramic materials suitable for bio applications. In future, the durability and *invitro* properties of the studied vanadium silicate glasses and glass ionomer cements will be investigated further in order to shed light on their bio-applications.

2. Experimental

2.1 Preparation

Glass samples were prepared from chemically pure V_2O_5, $ZnCO_3$, SiO_2 and di-ammonium hydrogen phosphate ($NH_4H_2PO_4$) with the nominal composition xV_2O_5-(40-x) SiO_2-40ZnO-30 P_2O_5. (x=0,5,15,25 mol%). Glasses with different V_2O_5 mole% are prepared by rapid-quenching method. The analytical-grade materials of purity more than 99.6% of SiO_2, $ZnCO_3$ and $NH_4H_2PO_4$ provided by E-Merck, Germany were used. The batches were precisely weighed before being melted in silica crucibles in an electric furnace at temperature ranged from 1150 ℃ to 1350 ℃. The melts were shacked several times to achieve homogeneity.

2.2 Experimental Techniques

The amorphous aspect of the samples was investigated using X-ray diffraction (XRD). A Burker D8 Advance powder XRD instrument was used to obtain the diffraction patterns. A Vantech super speed position sensitive detector and a Cu Ka X-ray tube with a Gobel mirror are included. Measurements were taken on a multiple scale from 4 to 70 degree.

The morphological properties of glass samples were investigated using a transmission electron microscope (TEM) model JEOL-JEM-2100, Japan, outfitted with an electron diffraction pattern unit (EDP). TEM experiments were carried out at a voltage of 200 Kv for electron acceleration.

The distribution of various building units is determined using ^{29}Si NMR spectra of selected glasses. The experiments were carried out with the help of a JEOL RESONANCE GSX-500 High Resolution Solid State MAS NMR spectrometer. The spectra were recorded in a high external magnetic field (11.747T), at a frequency of 96.2 MHz, and at a spinning rate of 7 KHz.

2.2 Infrared Spectra (IR)

The spectra are measured in the 400-4000 cm^{-1} region with a spectral resolution of 2 cm^{-1} using a Mattson 5000 FTIR spectrometer. The obtained spectra were standardized to that of a blank KBr pellet, and a two-point baseline was used to adjust for background and dark currents. To minimize the concentration impact of the powder sample in the KBr disc, normalization is required.

2.3 DSC Measurements

Thermal analysis was performed using a Universal V2.6D TA Instrument in the temperature range of 30–1000 ℃ and a heating rate of 10℃/min

2.4 Hardness

Hardness was obtained from a HV-1000B Vickers micro- hardness tester with a load of 300g applied for 5sec on a mirror finish surface (Physics Department-Mansoura University)

3.Results and Discussion

3.1 XRD spectra

To distinguish between crystalline and amorphous phases upon increasing V_2O_5 in the xV_2O_5-(40-x) SiO_2-40ZnO-30P_2O_5 (x=0,5,15, 25 mol%) system, the obtained structural configuration should be examined frequently using XRD diffraction. The data obtained confirmed that the amorphous structure is a feature shared by all of the composition of the glasses studied, see figure 1. This suggests that V_2O_5 has no effect on the short-range order structure of any of the as obtained compositions.

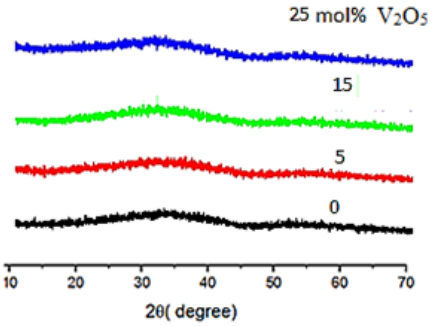
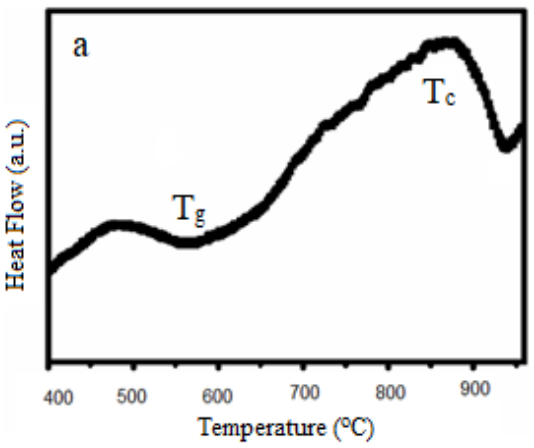


Fig. 1. XRD patterns of glasses containing 0,5,15 and 25 mol% V_2O_5

As can be seen from figure 1 that, there no any x-ray diffraction lines related to crystalline form. This behavior was recently conformed [8,11], since the amorphous structure is the dominant even the concentration of V_2O_5 reaches its highest limit in CdO-V_2O_5 -P_2O_5 and CuO-V_2O_5 -P_2O_5 glasses [8,11]. There is another effective factor (thermal treatment) that has an impact on changing the range order structure of the

amorphous glasses. Therefore applying thermal heat treatment processes is useful to change the amorphous structure of the short-range order (SRO) to glass ceramics containing some specific crystalline phases of intermediate range order (IRO). The latter phases having useful applications such as bioactive glass ceramic (GC) [9,14,16].
To transform the amorphous glass to GC material, it should apply the advantages of differential scanning calorimetry to determine the temperature around which the glasses can be thermally treated. The advantage of the present glasses is that it can easily be crystallized by effect of thermal treatments on glasses containing V_2O_5, since the high crystallinity is obtained at lowering temperature when compared with glasses free from V_2O_5 [7-12].

Figure 2 is a DSC curve for two glass containing 0 and 25 mol% V_2O_5 presented as examples. It can be seen from the curves that the glass transition temperature Tg is around 560^{O}C and 440^{o}C respectively for sample free from V_2O_5 (curve a) and one contains 25 mol% (curve b). The applied exposure time of thermal treatment is chosen to be 12 hours**.** As a result of THT, the glasses become relatively opaque due to formation or precipitation of some nano-crystalline species [7,8,16]. Presence of sharp and intense diffraction line spectra of all investigating compositions figure 3 can be correlated to formation of the more ordered crystalline phases in the matrix of the investigated treated samples. Then the thermally treated glasses contain nano sized crystalline species which can be separated from amorphous glasses through even preliminary heat treatment processes just around T_g [8,9,14]. The nano-crystalline species are usually indicated by presence of some sharp XRD peaks at 2θ between 10 and 20 and between 20 -45^{O}.



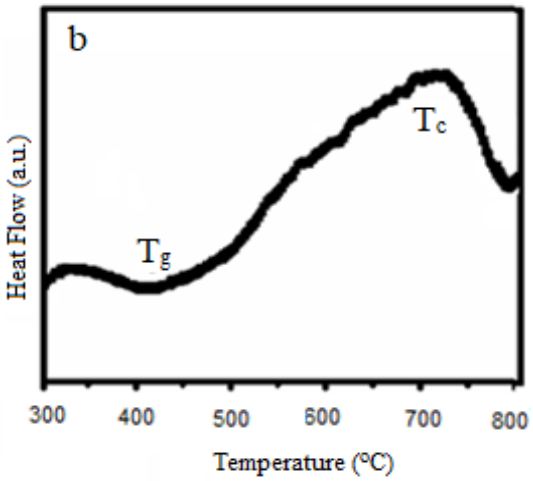


Fig. 2. Differential scanning calorimetric of 0 mol% V_2O_5 (curve a) and 25 mol% V_2O_5 (curve b)

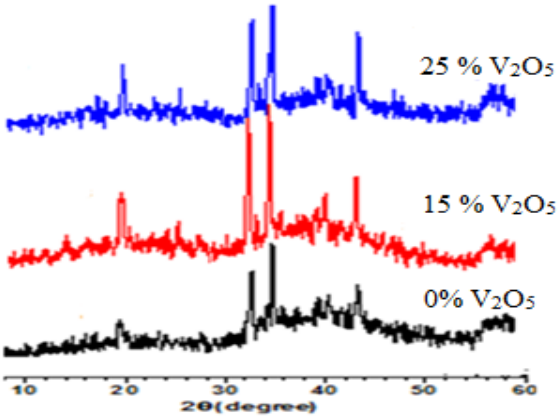


Fig.3. XRD spectra for glasses containing 0, 15 and 25 mol% V_2O_5 treated thermally at 480 ℃ for 12 hours.

3.2 TEM-EDP

Micrographs based on TEM and its electron diffraction patterns, EDP (figure 4) confirm the features based on XRD spectra. Upon the heat treatment, the accumulated crystalline species increases with increasing V_2O_5 contents (Figure 4 b and c). Formation of an ordered structure is related to interaction of V_2O_5 with the thermally treated glass network [8-11], since V_2O_5 adds new ordered bonds at expense of distorted nonbridging Si-O bonds. Formation of phosphate, vanadate and silicate units containing non bridging bonds (NBO) are considered the main formed species particularly in the as obtained glasses.

3.3 FTIR and NMR spectra

Figure 5 showed two FTIR spectra for glass free from V_2O_5 and of glass containing 25 mol% V_2O_5 presented as examples. It can be shown that there are three absorbance band characterized silicate structural units. The band between 600-800 cm^{-1} characterizes the mixed vibration of Si-O and P-O bonds in both

orthosilicate and orthophosphate groups [9,14]. The peaks at 950 cm^{-1} are assigned to Q^1 species (SiO_2 units continuing one bridging oxygen atom). The peak at about 1150cm^{-1} is related to Si-O vibration in Q^2 species (silicate units containing 2BO). It can be noticed that the relative intensity of the band at 950cm^{-1} of glass containing 25 mol% V_2O_5 is higher than that of vanadium free glass. That means that the concentration of NBO increases with increasing V_2O_5 content. Then vanadium ions can be simply participated in the depolymerization of the glass network, creating more bonding defects and non-bridging oxygens (NBOs).

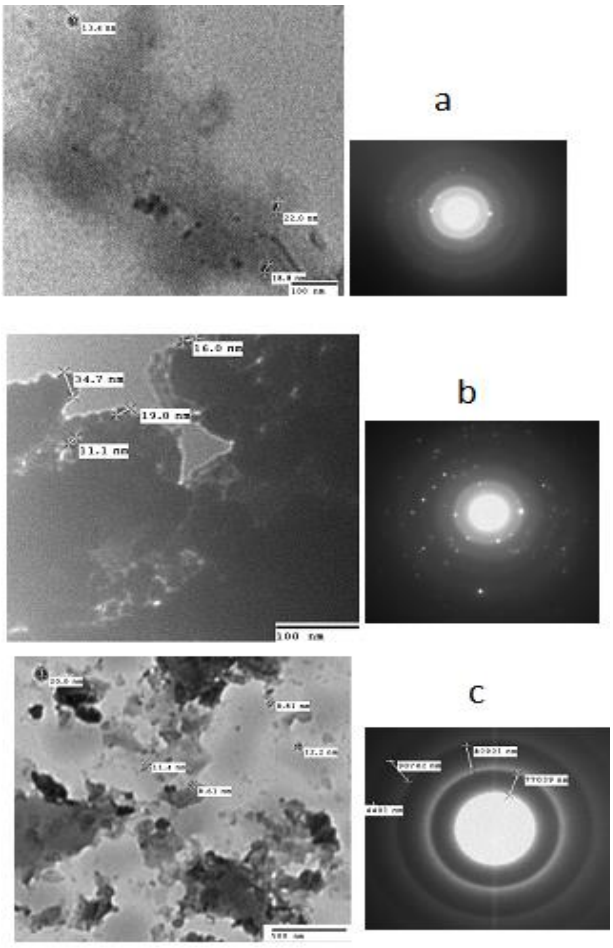


Fig. 4. TEM micrographs for sample of vanadium (micrograph a) and of samples containing 15 and 25 V_2O_5 treated at 560^{O}C for 12 hours.

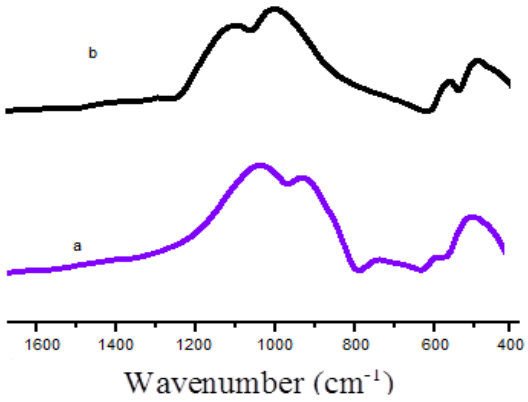


Fig. 5. FTIR spectra of V_2O_5 free glass(a) and of glass containing 25 mol% V_2O_5 (b)

Figures 6 showed NMR spectra of ^{29}Si nuclei for the same compositions which are examined by FTIR spectroscopy, one is free from V_2O_5 and the other contains 25 mol% V_2O_5. The spectral features (resonance position, band width, and order of symmetry) of the two glass compositions are clearly different, as shown in the figure 6. The NMR spectra of the vanadium free sample have a sharper resonance line, which is a distinguishing feature. The effect of increasing V_2O_5 content changes this feature, since both chemical shift and full width at half maximum (FWHM) are noticed to increase with increasing V_2O_5 content. The differences in FWHM and chemical shift values are correlated with changes in the local structure surrounding the Si atoms. In such situation, most of ZnO can be completely consumed in the first situation to modify the silicate and phosphate sub networks, resulting in producing non-bridging bonds (NBO). In the sample of containing 25 mol% V_2O_5, the resonance spectra of higher chemical shift and FWHM is obtained due to more formation of NBO atoms.

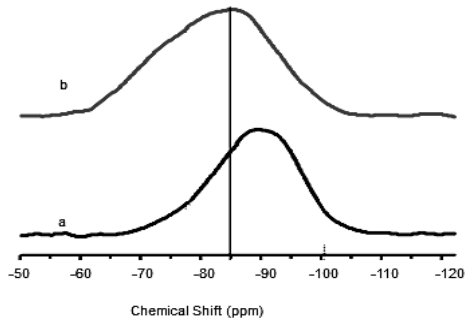


Fig. 6. ^{29}Si NMR spectra of V_2O_5 free glass (a) and of glass containing 25 mol% V_2O_5 (b)

Increasing both values of FWHM and chemical shifts leads to formation of Vanadyl (VO^{2+}) groups that can play a role of additional glass modifiers. Increasing NBO and VO^{2+} in the relevant silicate and vanadate units decreases the shielding of silicate nuclei and correspondingly increasing their measured value of chemical shift. This leads to the conclusion that the formation of effective weaker bonds (NBO) is the main reason for the formation of clustered species from semi metallic vanadate molecules, which is compensated by Zn cations, resulting in some effects on the investigated material's properties. In such situation the hardness (H_v), molar volume (V_m) and glass transition temperature (T_g) of the glasses are the main properties to be affected when the clusters species are formed.

Hardness is a measure of the resistance to localized deformation induced by the mechanical indentation [11,17]. The change of (H_v) with the V_2O_5 content is shown in Figure 7. It can be seen that the there is a large decrease in hardness value of the investigated system from about 4 to 2.3 GP as vanadium oxide content increases from 0 to 25 mol%. It is known that the decrease in the hardness number is related to the decrease of the rigidity of glass [11,17]. These results are consistent with the result based on figure 8, since upon V_2O_5 addition, V_m increases and T_g is inversely proportional to the V_2O_5 concentration. The structural changes predicted from FTIR and NMR spectroscopy lent support the changes based on Tg, Hv and Vm, since increasing NBO in the glass network with increasing V_2O_5 is considered the main cause.

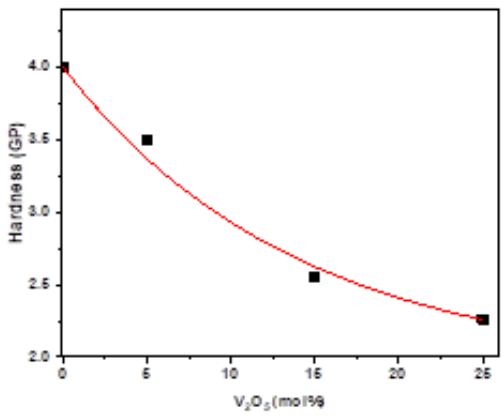


Fig.7. The change of hardness number with V_2O_5 concentration

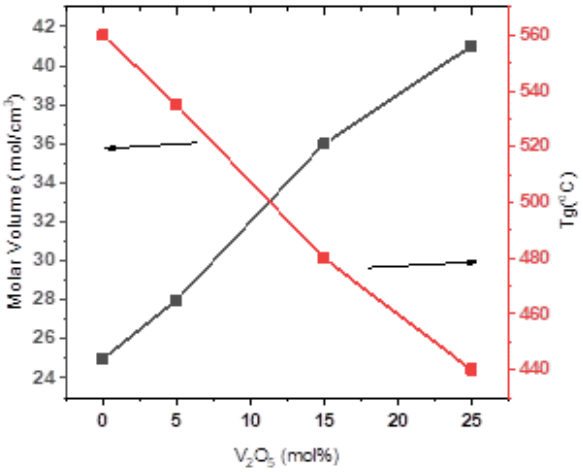


Fig. 8. Change of Molar volume and glass transition temperature with V_2O_5 concentration

In contrast with the previous studies [18-21], based on silicate, phosphate or phosphor-silicate glasses, The ZnO as in the present study is different from that of modification with alkali or silver oxides. ZnO plays a dual role as a modifier and as a former. However, the alkali oxide or silver oxide play one specific role as a strong glass modifier. The latter is consumed to form non bridging oxygen atoms (NBO) in the glass network. However, ZnO can create NBO and can also form ZnO_4 former units.

4. Conclusion

Several spectroscopic and morphological methods are used to monitor the modification of the silicate host glass network modified with V_2O_5. ^{29}Si NMR spectroscopy is used to determine the local structure around Si nuclei. The obtained results show that when SiO_2 is replaced with V_2O_5, the fraction of NBO atoms increases. With increasing the modifier contents, the fraction of tetrahedral VO_4 units is likewise enhanced at the expense of VO_5 groups. XRD measurements were taken on a variety of components from both the as prepared and thermally treated glasses. In the treated glasses, the NBO improved the crystallization potential. The significant amount of NBO produced by the addition of V_2O_5 is important in the creation of crystalline clusters made up of NBO and VO^{2+} ions. Clusters of species were indicated using TEM microscopy. The use of V_2O_5 instead of SiO_2 enhances the size of the well-formed clusters.

5. Conflicts of Interest

Authors declare that we have no conflict of interest. We are agreed upon all the Ethical Rules applicable for this journal.

6. Formatting of funding sources

The authors declare that no funds, grants, or other support were received during the preparation of this manuscript.

7. References

[1] Nayak, M.T. and Desa J.E.(2018) Roles of iron and lithium in silicate glasses by Raman spectroscopy. Journal of Raman Spectroscopy **49**(9): 1507-1513.

[2] El-Damrawi G, Muller-Warmuth W, Doweidar H, Gohar I A(1993) ^{11}B, ^{29}Si and ^{27}Al nuclear magnetic resonance studies of Na_2O-Al_2O_3-B_2O_3-SiO_2 glasses, Physics and Chemistry of Glasses 34: 104-110

[3] Krins N, Rulmont A, Grandjean J, Gilbert B, Lepot L, Cloots R , Vertruyen B(2006) Structural and electrical properties of tellurovanadate glasses containing Li_2O. Solid state ionics 177(35-36):3147-50.

[4] Salehizadeh S.A, Melo B.M, Freire F.N, Valente M.A, Graça M.P(2016) Structural and electrical properties of TeO_2–V_2O_5–K_2O glassy systems. Journal of Non-Crystalline Solids. Jul 1(443):65-74.

[5] Sakurai Y, Okada S , Yamaki J, Okada T.(1987) Electrochemical behavior of amorphous V_2O_5 - P_2O_5 cathodes for lithium secondary batteries. Journal of Power Sources. 1;20(3-4):173-7.

[6] Souri D (2008) Seebeck coefficient of tellurite–vanadate glasses containing molybdenum. Journal of Physics D: Applied Physics. 8;41(10):105102.

[7] El-Damrawi G, Müller-Warmuth W , Doweidar H (1992), Structure and heat treatment effects of sodium borosilicate glasses as studied by ^{29}Si and ^{11}B NMR Journal of non-crystalline solids, 146: 137-144.

[8] El Damrawi G, Abdelghany M, Mnaaa E (2019), Nuclear magnetic resonance studies on vanadium phosphate glasses, Magn. Reson. Solids 21, 19504 do 10.26907/mrsej-19504

[9] El Damrawi G., Hassan A. K., Kamal H., Aboelez M., Labeeb S (2016). Structural Investigations on Na2O-CaO-V_2O_5-SiO_2 Bioglass, British Journal of Applied Science & Technology 16:1-9

[10] El-Damrawi G, Hassan A K, Shahboub A (2018) 31P and 27Al nuclear magnetic resonance studies on silver phosphate glasses Magn. Reson. Solids 20 (2), 18202

[11] Abed H, EL Danrawi G, M sherbiny M, Farouk M, (2021) A new focus on the structure and mechanics of CuO-modified P_2O_5-V_2O_5 glasses Journal of Non-Crystalline Solid 568 120959

[12] A Agarwal, S Khasa , V P Seth, M Arora .(2013) J. Alloys Compd568, 112

[13] A Yadav, S Khasa, A Hooda, M Dahiya, A Agarwal, P Chand (2016), EPR and impedance spectroscopic investigations on lithium bismuth borate glasses containing nickel and vanadium ions Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy 157 :129–137

[14] G El Damrawi, R Ramadan, M El Baiomy (2021), New Journal of Glass and Ceramics 11 45-56

[15] El-Damrawi G, Abd-El-Nour K, Ramadan RM (2019), Silicon 11:495-500

[16] El-Damrawi G, Doweidar H, Kamal H, Hassan KA ((2018)), Silicon, 10:395-402

[17] Morten M.; John C. Mauro; Yuanzheng Yue (2010). Prediction of Glass Hardness Using Temperature-Dependent Constraint Theory". Phys. Rev. Lett. **105** (11): 2010

[18] Mansour E, El Damrawi G. (2010) Electrical properties and FTIR spectra of ZnO–PbO–P_2O_5 glasses. Physica B Condensed Matter. 405(8):2137-2143.

[19] Wang Ping X, Xu, H. (2017) Role of Surface Adsorption in Tuning the Properties of Black Phosphorus. Physical Chemistry Chemical Physics 20(1): 223-240.

[20] Balamurugan A, Balossier S Kannan G, Michel J, Rebelo H S, Ferreira M F. (2007) Development and in vitro characterization of sol-gel derived CaO-P_2O_5-SiO_2-ZnO bioglass, Acta Biomaterial. 3(2) :255-62.

[21] Liu X, Morra M, Carpi A, Li B. Liu X. (2008) Bioactive calcium silicate ceramics and coatings. Biomed. 62(8):526-9