

MAGNETIC BEHAVIOUR OF $(\text{Fe}_2\text{O}_3)_x (\text{TeO}_2)_{1-x}$ GLASS SYSTEM DUE TO IRON OXIDE

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Homogeneous $(\text{Fe}_2\text{O}_3)_x (\text{TeO}_2)_{1-x}$ were synthesis using melt- quenching technique for $x=0.1-0.3$ in the interval of 0.05. The binary glasses were dark brown in colour. The amorphous structure of glasses was confirmed by the X-ray diffraction spectrum. The physical properties such as density and molar volume have been determined in room temperature and were found decrease with Fe_2O_3 contents increase. From the vibrating-sample magnetometer (VSM) measurement it was observed that that magnetization of glass increase almost linearly with applied fields and shows paramagnetic materials behavior.

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1. Introduction

Telluride based glass have physical properties that important for both fundamental and practical applications which is low melting temperature, high dielectric constant, high refractive index, good infrared transmittance and high chemical durability [1]. Telluride glasses are important for practical applications due to nonlinear optical properties for example optical modulators and memories [2] while oxide glass with iron oxide important due to their magnetic, optical and electrical properties [3]. Glass with transition metal ions is vital in electronic properties; this is because of the presence of multivalence states. It was reported that glasses containing transition metal ions are used as elements in memory switching devices and cathode material in batteries [4].

IR spectroscopy is used to investigate the structural of the glass studies. In telluride glass Te ions form in a structure of trigonal bipyramidals (tbp) with TeO_4 structure units. In this structure there are two oxygen ions are located in the axial vertices while in the equatorial positions there are two oxygen ions and lone electron pair of tellurium, where axial Te-O bonds are longer than equatorials bonds [5]. Effect of Fe_2O_3 in the glass studied has been reported before [6] that Fe_2O_3 influences IR absorptions spectra of $x\text{Fe}_2\text{O}_3 (1-x) [3\text{B}_2\text{O}_3.\text{MO}]$ where (MO=CaO or CaF₂) glasses indirectly.

In the previous study was found that magnetic properties are related with the iron oxide content in the glass series [7,8]. An earlier report [9] on $\text{CaO-SiO}_2\text{-P}_2\text{O}_5\text{-Na}_2\text{O-Fe}_2\text{O}_3$ glass ceramics stated that samples with composition of iron oxide $x \geq 2$ mol% exhibit magnetic behaviors similar to soft material which has low coercivity and narrow hysteresis loop.

The main objective of this work is to study magnetic properties and structural properties of $(\text{Fe}_2\text{O}_3)_x (\text{TeO}_2)_{1-x}$ glass system with different composition of Fe_2O_3

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2. Experimental

Sample of binary glass system $(\text{Fe}_2\text{O}_3)_x (\text{TeO}_2)_{1-x}$ were prepared using Fe_2O_3 (99.5% purity) and TeO_2 (99+%, purity) with different composition of iron ($x = 0.1$ to 0.3 with interval of 0.05). The chemicals were weight accurately using an electronic balance and manually mixed and ground in agate mortar and pestle to fine powder. The chemical were placed in platinum crucible and preheat in electrical furnace at temperature of 350°C for 30 minutes to evaporate water from the batch which may be absorbed during weighing and mixing process. After that, the crucible was transferred to second furnace and melted at temperature of 950°C . After 2 hours, the melt in the crucible was cast into preheat stainless steel mold. The mold was preheated first at temperature 350°C to reduce thermal stress during casting process. After it solidified, the glass sample was put into first furnace at temperature 350°C for annealing process. After 3 hours, the furnace was switched off and the glass was allowed to cool to room temperature. The samples were then cut and polished to desired dimension. Some of the samples were crushed into fine powder using agate mortar and pestle for DTA, XRD and FTIR measurement.

The densities of these glasses were determined using Archimedes's method with acetone as the immersion liquid. The density of the sample was then calculated using the relationship

$$\rho_{\text{glass}} = \rho_{\text{acetone}} \times \frac{\text{weight of glass in air}}{\text{weight of glass in acetone}}$$

The amorphous nature of the glass was determined by X-ray Diffractometer (PANalytical (Philips) X'Pert Pro PW 3040/60).

Infrared (IR) spectra were recorded using Fourier Transform Infrared Spectroscopy (FTIR) in the frequency range $280\text{--}4000\text{ cm}^{-1}$ at room temperature.

The magnetic properties of samples were measured at room temperature by a vibrating-sample magnetometer (VSM) in a field of 15 kOe .

3. Results and discussion

The prepared glass samples were free from bubbles and dark brown in colour. The composition dependencies on the density, d and molar volume, V_m of the glass samples are shown in Fig 1. The density of $\text{Fe}_2\text{O}_3\text{-TeO}_2$ glass shows the trend of decrement when the mole fraction of Fe_2O_3 increases. The decrement of density by introducing the transition metal oxide (TMO) into telluride system is mainly due to the density of Fe_2O_3 , which is lower than the primary forming glass system. When Fe_2O_3 is introduced into the glass, the content of TeO_2 is relatively reduced as Fe_2O_3 increased. The density of Fe_2O_3 which has lower density dominates the density of glass system. The decrement of density might be related with the changes of concentration of FeO_4 and FeO_6 units and attribute to the increase in the fraction of FeO_4 tetrahedral when Fe_2O_3 increases [7] and changes from packed trigonal bipyramidal TeO_4 into TeO_3 trigonal pyramid open the glass network. The presence of non bridging oxygen also effect density of the glass system, as modifier content increase, amount of non bridging oxygen decrease as well as the density [10].

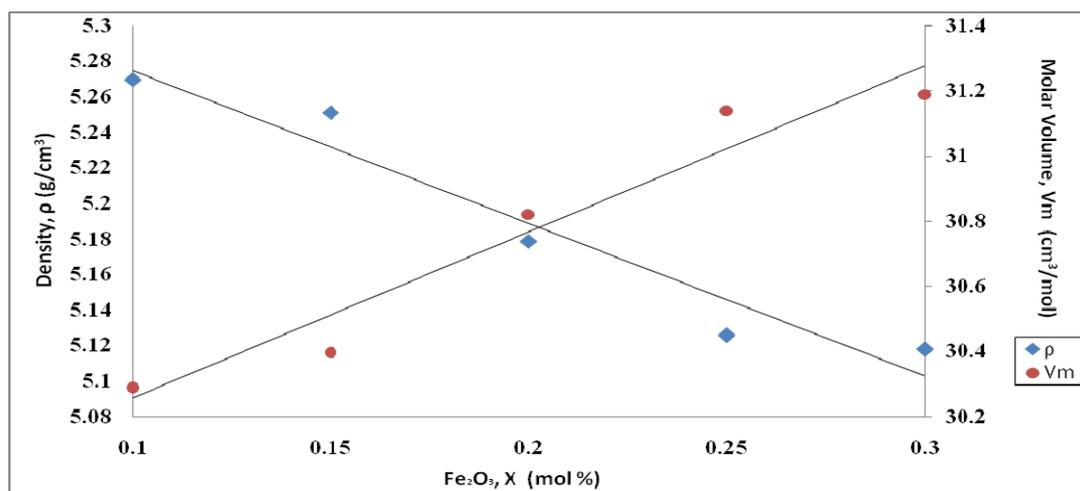


Fig.1. Composition dependence of density and Molar volume for Fe_2O_3 - TeO_2 glasses.

The result of X-ray diffraction (XRD) is shown in Fig.2. X- Ray diffraction shows that no sharp peaks observed from the spectra of Fe_2O_3 - TeO_2 with only the presence of a hunch for 2θ around 15°-35°, indicating that the prepared samples are fully amorphous.

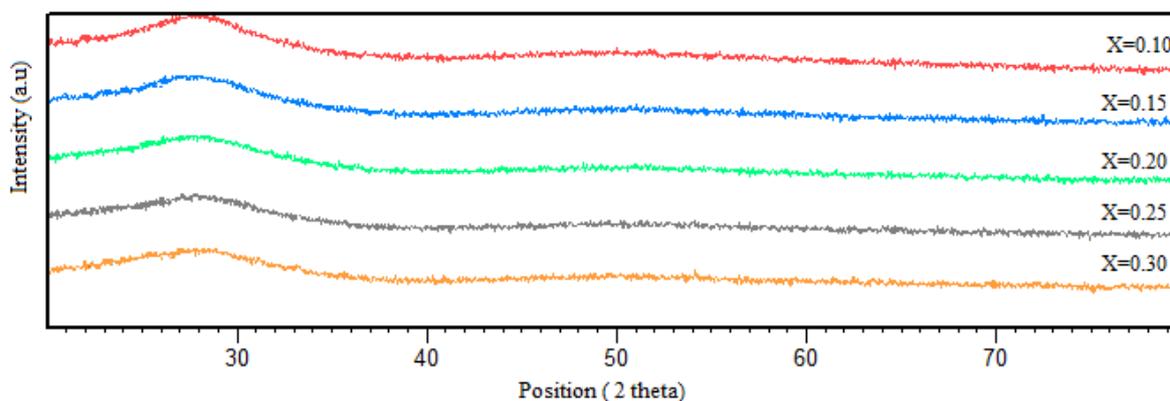


Fig. 2. XRD pattern of $(Fe_2O_3)_x(TeO_2)_{1-x}$ glass.

Fig. 3 shows DTA curve for glass sample Fe_2O_3 - TeO_2 . From the curve, glass transition temperature T_g , the exothermal peaks, T_c and melting endothermic peaks, T_m are summarize in Table 1. The Glass transition temperature or glass transformation temperature, T_g is critical temperature where amorphous material changes its behavior which is from glassy to rubbery. The value of T_g are in the range of 364-531 °C. It can be seen that there are two exothermic peak for composition of $x=0.10$ and for others composition only have one peak. For endothermic peak, only one peak has been observed for $x=0.10$, two endothermic peaks for $x=0.15, 0.20$ and 0.30 , and three peaks for $x=0.25$.

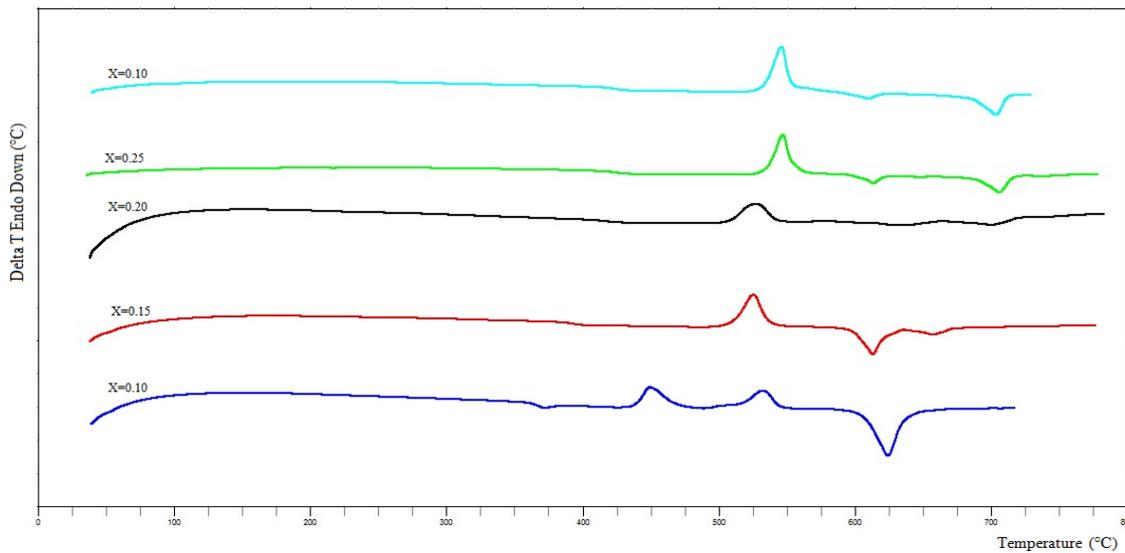


Fig 3. DTA curve of $(\text{Fe}_2\text{O}_3)_x(\text{TeO}_2)_{1-x}$ glass.

In Table 1, it can be observed that T_g values depend on the composition of Fe_2O_3 . T_g values increases linearly with increasing of Fe_2O_3 content in the glass series. This dependence is shown in Fig. 4. Increasing of T_g value indicate that the glass sample become more stable and this indicate that Fe_2O_3 contribute to the increase of glass transition temperature. Thermal stability of glass depends on ΔT which is increased as Fe_2O_3 increases.

Table 1. Table of Transition Temperature T_g , Crystallization Temperature, T_c and Melting Temperature, T_m determine from DTA for $(\text{Fe}_2\text{O}_3)_x(\text{TeO}_2)_{1-x}$ glass system.

Composition of Fe_2O_3	T_g	T_{c1}	T_{c2}	T_{m1}	T_{m2}	T_{m3}	$\Delta T = T_c - T_g$
0.10	364.519	449.692	531.055	622.965	-	-	166.536
0.15	394.906	524.526	-	613.119	655.775	-	129.620
0.20	460.055	527.267	-	631.486	700.966	-	67.212
0.25	485.137	545.562	-	613.617	646.624	704.357	60.425
0.30	531.208	545.108	-	608.544	702.912	-	31.900

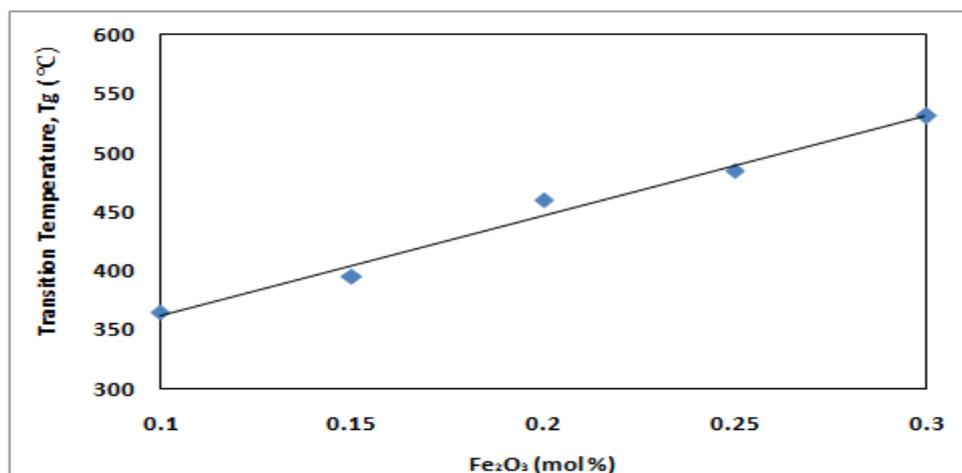


Fig. 4. Glass transition temperatures (T_g) with different composition of Fe_2O_3 .

Fig.5. shows the FTIR Spectra of $(\text{Fe}_2\text{O}_3)_x (\text{TeO}_2)_{1-x}$ glasses recorded between 280-4000 cm^{-1} where the bands are assigned. It can be seen that there are two strong bands at ~ 450 and ~ 660 cm^{-1} . Furthermore, there are two weak bands at ~ 1240 and ~ 1750 cm^{-1} . Obviously it can be seen that changes in FTIR spectra are due to Fe_2O_3 composition. These bands and their assignments are summarized as follow:

i. The bands at ~ 450 are assigned to vibrations of Fe-O bonds that occur in FeO_6 units. The intensities of these band increase up to $x=0.25$ and decrease after that, this may attribute to the structural disorder of the glass system where in these case iron ion behave dissimilar with Fe_2O_3 [6].

ii. The bands at ~ 660 are assigned stretching modes Te-O bonds of the trigonal bipyramidal $[\text{TeO}_4]$ structural units with bridging oxygens. [5,11,12]. The shoulder bands at ~ 750 assigned trigonal pyramidal $[\text{TeO}_3]$ structural units with non-bridging oxygen [11,12]. The bands at ~ 660 are due to axial symmetric vibrations of Te-O_{ax} bonds, and equatorial asymmetric vibrations of Te-O_{eq} bonds are situated at ~ 750 which is $[\text{TeO}_3]$ structural units.

iii. The weak bands at ~ 1240 and ~ 1750 cm^{-1} is due to the vibrations bands Te-O non bridging bonds of $[\text{TeO}_3]$ structural units. Increasing composition of Fe_2O_3 in the glass system changes the vibration intensity of $[\text{TeO}_3]$ and $[\text{TeO}_4]$. The existing iron ions in telluride system may be due to the influence of lone pair electron in telluride system. [7, 12]

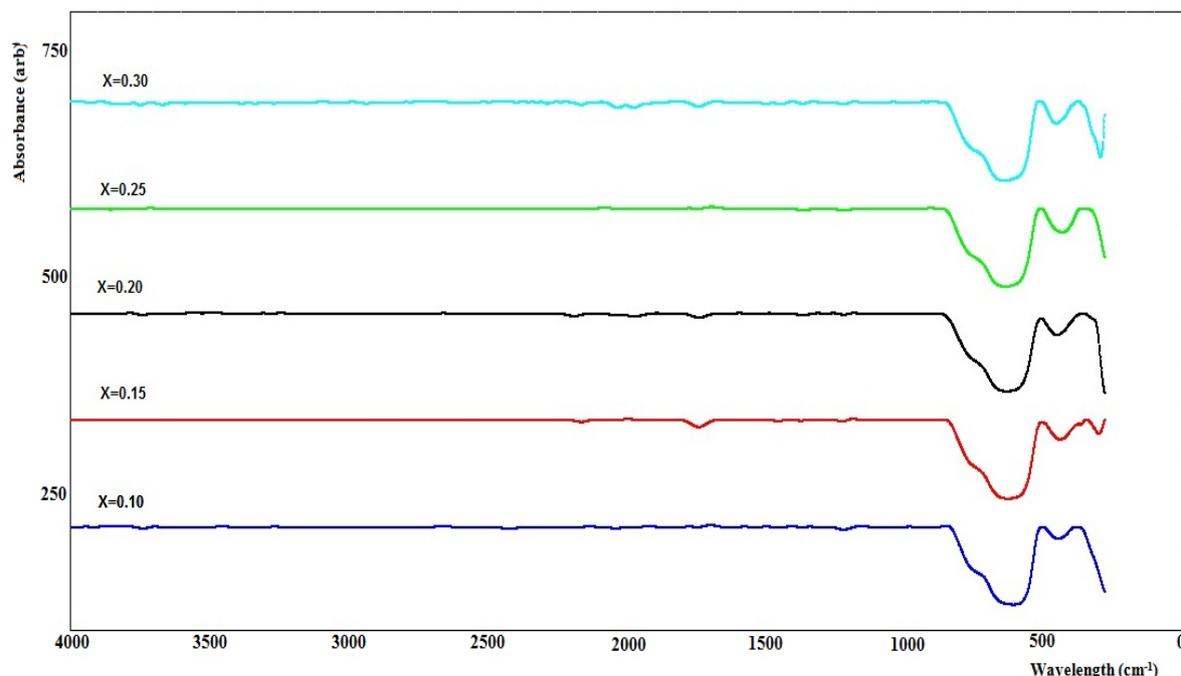


Fig. 5. FTIR Spectra of $(\text{Fe}_2\text{O}_3)_x (\text{TeO}_2)_{1-x}$ glass system.

The results from vibrating sample magnetometer (VSM) are shown in Fig. 6. The magnetization of glass increase almost linearly with applied fields, this behavior exhibits characteristic of paramagnetic materials [8]. The characteristic of material can determine by magnetization curves where for paramagnetic material magnetization increase linearly with field [8]. The graph of magnetization does not show any regular trend with increasing of Fe_2O_3 , this can be explained with position of magnetic moments in glass system. Large dispersion occurred at $x=0.2$, this may be due to position of magnetic moments that situated far to each other, at this situation the magnetic moments are easier to aligned when external magnetic field is applied while for the sample that shows smaller dispersion, this may due to the magnetic moment that are closer together, this will cause magnetic moment to cancel each other.

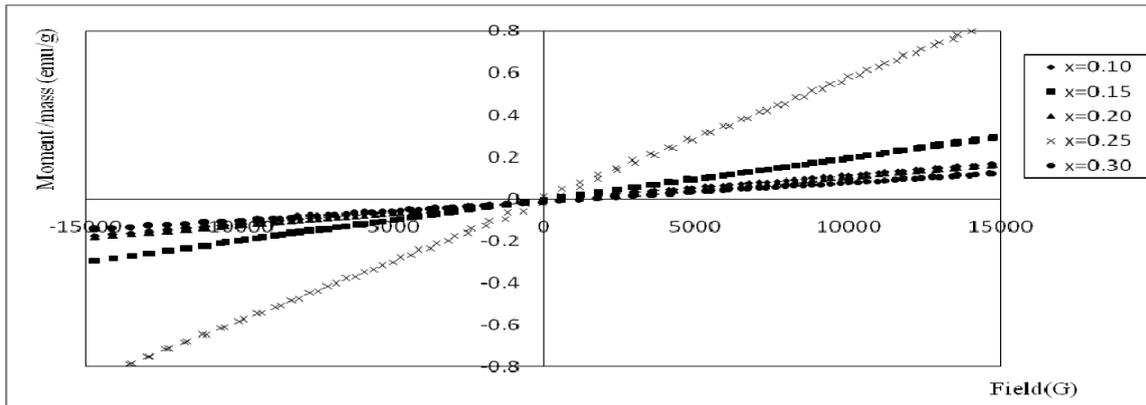


Fig.6. Magnetic properties of $(\text{Fe}_2\text{O}_3)_x(\text{TeO}_2)_{1-x}$ glass with different composition of iron.

The magnetic susceptibility of the glass system are calculated with this relationship

$$M = \chi_m H$$

where χ_m is magnetic susceptibility, M is a magnetization and H is a field. Through this relationship, magnetization is proportional with applied field gives magnetic susceptibility which is slope of the graph. Fig.7 shows the relationship of magnetic susceptibility with different composition of Fe_2O_3 in glass samples. The graph shows that magnetic susceptibility increases as Fe_2O_3 increases. The iron telluride glass system has paramagnetic behavior because the glass has very small magnetic susceptibility value with magnetization curves that increase linearly with external magnetic field.

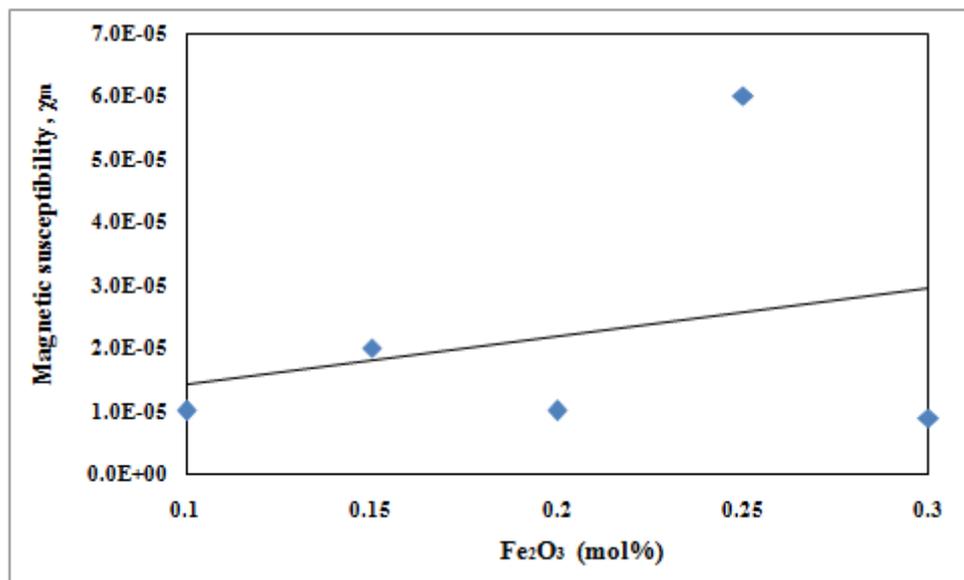


Fig.7. Magnetic susceptibility of $(\text{Fe}_2\text{O}_3)_x(\text{TeO}_2)_{1-x}$ glass with different composition of iron

4. Conclusions

A series of binary glass $(\text{Fe}_2\text{O}_3)_x(\text{TeO}_2)_{1-x}$ has been successfully synthesized with different composition of Fe_2O_3 and their magnetic behavior were studied. From density results, density decreases with increasing of Fe_2O_3 composition due to changes of Te-O structural units which is

from packed TeO_4 tpb into TeO_3 tp and was confirmed with FTIR results. From VSM, the glasses are found to exhibit paramagnetic behavior and have small magnetic susceptibility

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