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Characterisation of Quarternary 50pbo- $35b_2o_3$ - (15-X) CUO- Xwo_3 Glass System by Spectroscopic and Thermal Analysis

N. Sangeetha[1], R.Ravibaskar[2]
[1]*Department of Physics,AVC college (Autonomous), Mannampandal, Nagai district.*
[2]*MRK Institute of Technology, Kattumannarkoil, Cuddalore district, Tamil Nadu, India.*

Abstract: ***Quarternary glass samples of 50PbO- 35B_2O_3 - (15-x) CuO- xWO_3 with different composition range x=01, 02, 03, 04 and 05 mol% were prepared by melt quench method. Characterization of this system was carried out using FT-IR spectroscopy, X-ray diffraction, SEM and thermal analysis. The structural changes with composition in the glasses have been studied by FT-IR spectroscopy with special reference to structural units of borates. Amorphous nature of the system was confirmed by XRD patterns and SEM is used to study the morphology of glass samples. According to TGA/ DTA analysis, decomposition pattern has been calculated to account for the weight loss and used to investigate the dependence of tungsten oxide content in glass transition temperature (T_g), crystalline temperature (T_c) and melting temperature(T_m) data.***
Keywords: Lead based borate glasses, FT-IR, SEM, XRD and Thermal analysis.

I. INTRODUCTON

Among oxide glasses, lead based borate glasses have wide applications in all the fields due to its various physic-chemical properties. The structural and optical properties of the borate glasses have been studied by various methods including XRD, FTIR, Raman infrared spectroscopy, NMR and UV-visible spectroscopy [1,2]. FTIR spectroscopy is one of the important techniques which are used to study the local arrangement in inorganic glasses and the main structural units of borate glasses are BO_3 triangles. The addition of modifiers like PbO, converts BO_3units to BO_4units and the glasses are expected to become highly stable against devitrification and chemically inert [3]**.** Since PbO, in contrast with the conventional alkali/alkaline earth oxide/halide modifiers, form the stable glasses due to its dual role, one as modifier (with PbO_6 structural units) and the other as glass network former (with PbO_4 pyramidal units) in both covalent and ionic bonding [4].Borate glasses are generally insulating in nature and the addition of transition metals such as V_2O_5, CuO, WO_3, ZnO etc. makes these glasses semiconducting in nature. Borate based glasses have been widely studied over the years since they are relatively easy to obtain and moreover present interesting structural properties, due to the existence of boron anomaly; the boron atom can be placed in the network in tri or tetra coordination depending on the concentration of the modifier oxide [5]. Many authors have studied the effect of multiple transition metals on structural and optical properties of borate glasses with the help of IR, UV and dc conductivity studies etc [6,7].

The tungsten ion exists in different valence states such as W^{6+}, W^{5+}, W^{4+}, etc. Hence its doping can affect the structure and optical properties of host glasses. The tungsten and lead containing glasses are the potential candidates for many applications as amorphous semiconductors, for waste storage as infrared transmission components, thermal and mechanical sensors and reflecting windows [8]. Tungsten oxide has been used to construct 'smart windows', anti-glare rear view mirrors for automobiles, non-emissive displays, optical recording devices, solid state gas sensors and temperature sensors etc.

The aim of the present work is to analyze the effect of tungsten oxide on physical and structural properties of the quaternary PbO-B_2O_3-CuO-WO_3 glasses using density and FT-IR spectroscopic analysis. The SEM and X-ray diffraction is used to confirm the glassy nature of the prepared glasses. From TG and DTA analysis, thermal stability of the glass samples has been studied.

II. EXPERIMENTAL TECHNIQUES

A. Preparation of glasses

The glass samples having the general chemical formula 50PbO- 35B_2O_3 - (15-x) CuO- xWO_3 with different composition range x=01, 02, 03, 04 and 05 mol %were prepared by melt quench method using the starting materials as PbO, B_2O_3,CuO and WO_3 of reagent purity grade. The required amounts (approximately 15g) in mol% of different chemicals in powder form were weighed using single pan balance having an accuracy of ±0.0001g.The homogenization of the appropriate mixture of the components of

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chemicals is effected by repeated grinding using a mortar. The homogeneous mixture is put in a silica crucible and placed in a furnace. Melting is carried out under controlled conditions at a temperature from 950 to 1100 ºC for both the systems. The molten sample is cast into a copper mould having dimensions of 10mm diameter and 6mm length. Then the glass samples are annealed for two hours to avoid the mechanical strain developed during the quenching process. The samples prepared are chemically stable and non-hygroscopic. The prepared glass samples are polished and the surfaces are made perfectly plane and smoothened by diamond disc and diamond powder. Thickness of the samples has been measured using digital vernier calipers with an accuracy of 0.0001mm.

The infrared spectra of the glasses were recorded at room temperature, using KBr disc technique. A Perkin Elmer FT-IR Spectrometer was used to obtain the spectra in the wave number range between 400 and 4000 cm^{-1} with a resolution of ± 4 cm^{-1} and an accuracy of ± 2 cm^{-1}.

The surface morphology of the glasses has been studied using SEM (JEOL SEM Model, JSM-5610 Lv).The amorphous nature of the glasses is checked by X-ray diffraction spectra. Thermal analysis of glass samples were characterized by TG/DTA (model, SDTQ-600) and Nicolette-Avatar (model-360) respectively.

B. Density measurement

The density (ρ) of the prepared glass samples was determined by Archimedes method using double distilled water as buoyant at room temperature. The density is calculated using the formula,

$$\rho = \left[\frac{a}{a-b}\right]\rho_W \quad (1)$$

where, a is the weight of the glass sample in air, b is the weight of the glass sample in water and ρ_w is the density of water (ρ_w=1000).

C. Molar volume

The molar volume (V_m) is calculated using the relation,

$$V_m = \sum \frac{X_i M_i}{\rho} \quad (2)$$

where, x_i is the molar fraction and M_i is the molecular weight of the i^{th} component.

D. Oxygen packing density (o)

The oxygen packing density of the glass samples were calculated using the following relation [9].

$$O = n\left(\frac{\rho}{M}\right) \quad (3)$$

where ρ, the density of desired glass samples, M, molecular weight of the sample and n, the number of oxygen atoms in the composition.

E. The Ionic Concentrations (N)

The ionic concentrations of the glass samples are determined using the following relation,

$$N = \left(\frac{6.023 \times mol\ \%\ of\ \ cation\ \ \times valency\ \ of\ \ cation}{V_m}\right) \quad (4)$$

F. Inter - Ionic Distance (R)

Inter ionic distance (R) of the glass samples is given as,

$$R = \left(\frac{1}{N}\right)^{\frac{1}{3}} \quad (5)$$

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III. RESULT AND DISCUSSION

The nominal composition is given in Table1 and the photograph of the prepared glass samples are shown in Fig.1. The experimental value of density and the calculated values of average molecular weight, molar volume, oxygen packing density, ionic concentration and inter - ionic distance are presented in Table2.

A. Physical properties

Table 2 shows the variation of average molecular weight (M), density (ρ), molar volume (V_m),oxygen packing density (O), ionic concentration (N) and inter ionic distance(R).The density is a tool in revealing the degree of change in the structure with the glass composition. The increase in density is due to higher molecular weight of WO_3 compared to that of, PbO, CuO and B_2O_3, and it is the expected result. The increase in density for the system PBCW reveals the change in the structure of the glass with increasing WO_3 content. The molar volume of $PbO–B_2O_3$-CuO-WO_3 glasses decreases linearly with increasing WO_3 content [10], the decrease in the molar volume can be attributed to the larger packing factor of WO_3 than that of B_2O_3.

The oxygen packing density is a measure of the tight packing of oxide network. The oxygen packing density increases with increase in the content of tungsten oxide. This indicates that the glasses are tightly packed when the concentration of WO_3 increases. Also, the ionic concentration value increases with increase in mole % of WO_3,this may be due to large number of mobile ions in the glass network, at the same time, the inter-ionic distance decreases with an increase in WO_3 content. Therefore, the conduction mechanism from electronic to ionic is observed for all the concentration of WO_3. From these results, the PBCW glass system may be
used as N –type semiconducting material in solid- state devices, which has a character of strong structural stability and high ionic concentration with large number of mobile ions. Similar result was observed by Raghavendra Rao, et al.[11].

B. FT-IR spectra analysis

Fourier transform infrared spectroscopy is used to analyze the influence of transition metal incorporation in the heavy metal oxide borate glass network. The composition of glasses is chosen in such a way that transition metal (WO_3) is to be added at the expense of copper in lead borate glasses.

According to literature survey, the borate spectra are divided in to following three regions. The regions are

1) 600–800 cm^{-1} for the B–O–B vibrations.

2) 800–1200 cm^{-1} for BO_4 groups.

*3)*1200–1600cm^{-1} for BO_3 groups.

From the Fig.2, the band centered at 670 cm^{-1} has been assigned to B–O–B bending vibration of BO_3 groups. Its intensity increases with increase in the content of WO_3, which is due to W–O–W vibration in the borate network [12]. In sample PBCW1, the band observed at 961cm^{-1} is due to B–O bond stretching of BO_4 groups [13]. This band is shifting towards the higher wave number (from961to 1018 cm^{-1}) side with an increase in the percentage of WO_3. Also, its intensity increases with the increase in contents of WO_3, which is due to the conversion of trigonal BO_3 to tetrahedral BO_4 groups and increase in tetrahedral BO_4 groups in the borate network [14]. The band in the region 1200–1600cm-1, centered at 1342 cm-1 is due to B–O stretching of BO3 groups in ortho-and meta-borate units. Band positions and their corresponding assignment of IR spectra of all glass compositions are given in Table 3.

C. X-ray diffraction

The X-ray diffraction pattern of PBCW3 glass is shown in Fig.3. The XRD spectrogram shows no sharp peak which indicates the absence of crystalline nature. It confirms the amorphous nature of the prepared glass system. The diffractogram shows only broad diffuse scattering at low angles which is characteristic of long range disorder. This ensures the amorphous nature of the glass [15].

D. Scanning electron microscope

In order to investigate the surface nature of these glass samples, scanning electron micrograph images of PBCW3 glass are taken for two different magnifications which are shown in Fig .4. These images clearly indicate that there is no crystalline phase existing in the overall surface of the samples. This further confirms the amorphous nature of the glass samples. All the glass samples are characterized by energy dispersive spectroscopy (EDS) along with SEM. The EDS analysis of glasses shows that lead, copper and tungsten are present in the glass samples as shown in Fig.5.This reveals that the glass sample is homogenously distributed.

F. Thermal behavior of glass

1) *Thermo gravimetric analysis:* From the Fig .6, it is observed that there is no appreciable weight loss detected in the TGA measurement of the glass samples studied. The total weight in PBCW2 glass is0.2% and 0.15% is observed in PBCW4 glass.

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The weight loss of the first step corresponds to water released in the samples and other step corresponds to the decomposition of the glass samples.

2) *Differential thermal analysis:* Fig .7 shows the differential thermal analysis traces of PBCW2 and PBCW4 glasses investigated. It is used to characterize the glass and to determine the thermo dynamical parameters. The thermo dynamical parameters such as, glass transition temperature (T_g), crystallization temperature (T_c) and melting temperature (T_m). The glass transition temperature (T_g) is useful in suggesting structural changes that is achieved by composition changes [16]. The thermal stability of glass is an important property both fundamentally and technologically and the structure of the glass determines its thermal stability. The close packed structure results in thermally stable glasses and loose packed structure yields unstable glasses [17].According to Sidkey,et al. [18],in open glass structure, the value of T_g declines. That is, the values of T_g decreases from 690 to 220 ºC with addition of V_2O_5 from 20–80 mol% of V_2O_5 in phosphate containing vanadate glasses. In the present study, the T_g value increases from 485˚C to 500˚C with increase of WO_3 content from 2 to 4 mol %. A similar upward trend of variation in T_g with increase in Bi_2O_3 was noticed in the glass samples by [19]. On comparing the two glass specimen (PBCW2 and PBCW4), PBCW4 glass has higher values of T_g and T_m and leads to the strong thermal stability which expands the glass formation region. From the DTA curve (Fig.7), three endothermic peaks appear for the PBCW2 (WO_3= 2 mol %) glass sample. The lower temperature endothermic peak at T_{m1} = 520˚C caused by the glass transition followed by an exothermic peak at T_{c1}= 550˚C. The exothermic peak is probably due to a reaction involving the crystallization process and it is observed by [20].Second and third endothermic peak is observed at T_{m2} = 840˚C and T_{m3} = 950˚C. Hence, the endothermic peak may be attributed to the melting of the glass sample. At still higher concentration of PBCW4 (WO_3 = 4 mol %), the glass transition temperature, crystallization temperature and melting temperature are shifted to higher temperatures T_{g1} = 500˚C, T_{c1} = 565˚C T_{m1} = 850˚C and T_{m2} = 965˚C respectively. These results indicate that the higher concentration of WO_3 increase the cross-link density and improves the thermal stability of the glass sample.

IV. CONCLUSION

In PBCW glasses, the density value increases and molar volume decreases with the addition of WO_3 content. The increase in density reveals the compaction of the structure of glass network. The FT-IR study shows the incorporation of WO_3 unit as network modifier with W–O–W vibration in glass network. It has also been observed that WO_3 content helps in converting more BO_3 group to BO_4 units. This reveals that tungsten ions has dominate role in lead borate copper glass system. XRD and SEM studies confirm the amorphous nature of the prepared glasses. Energy dispersive analysis (EDS) confirms the chemical content of all the glass samples. The results of (TG/DTA) indicate that the higher concentration of tungsten oxide improves the thermal stability of the glass system studied.

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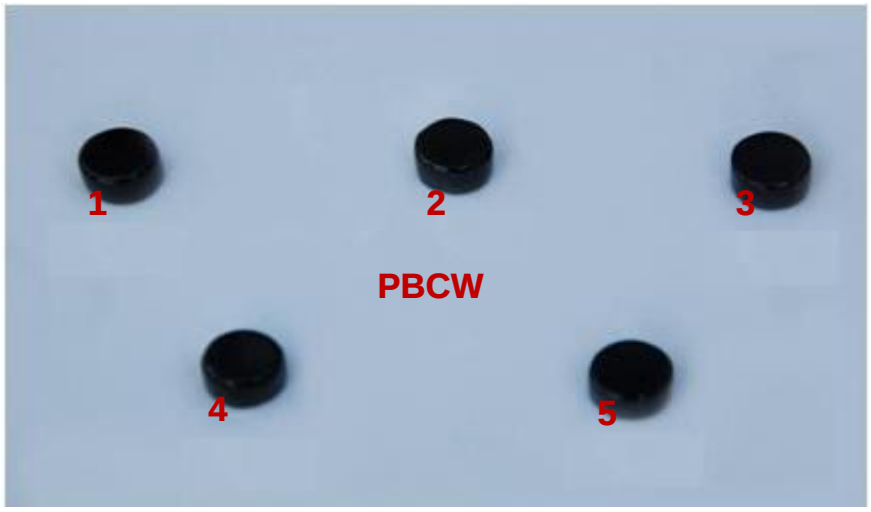

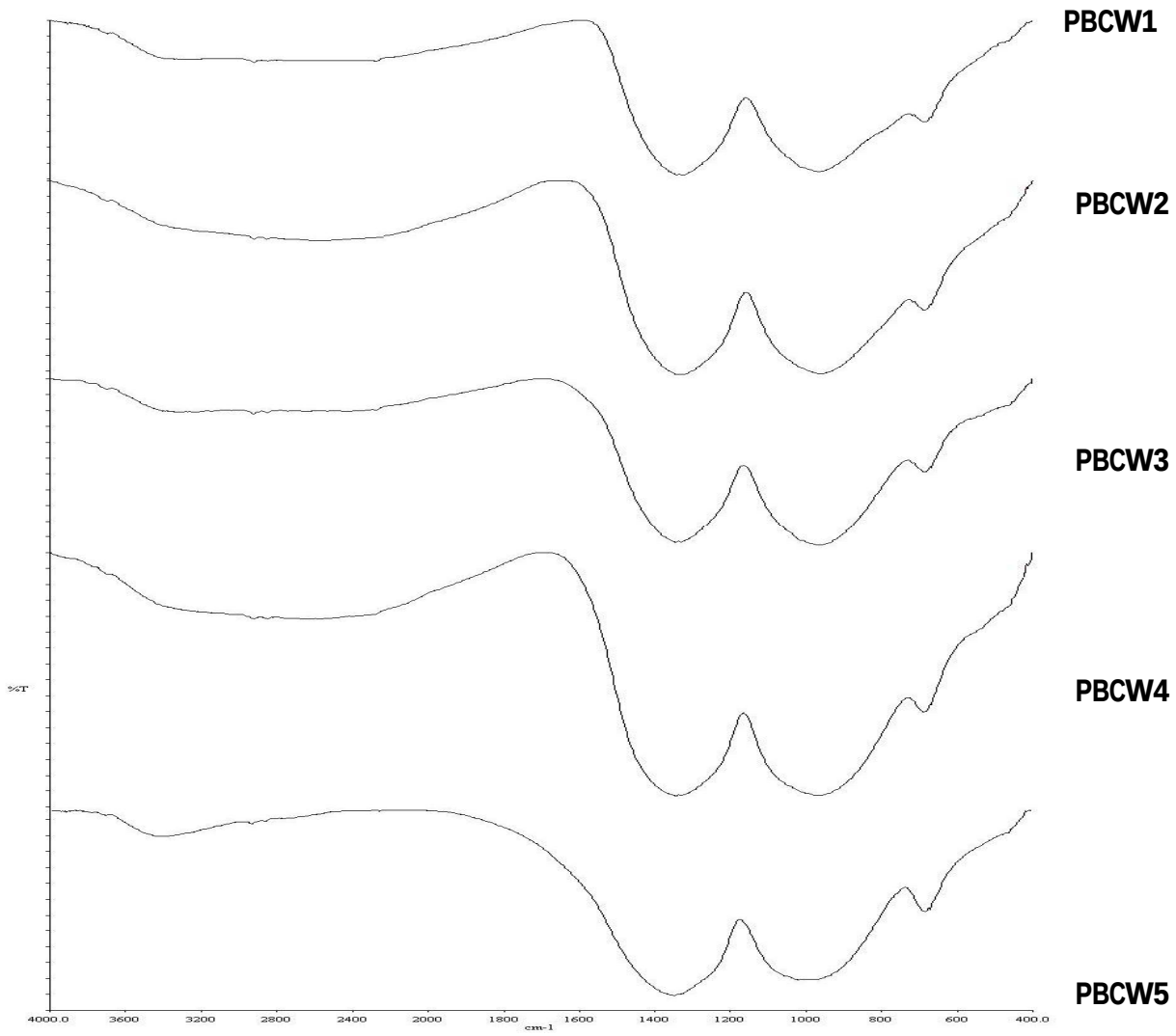

Fig. 2 FTIR spectra of PBCW glasses with different concentrations.

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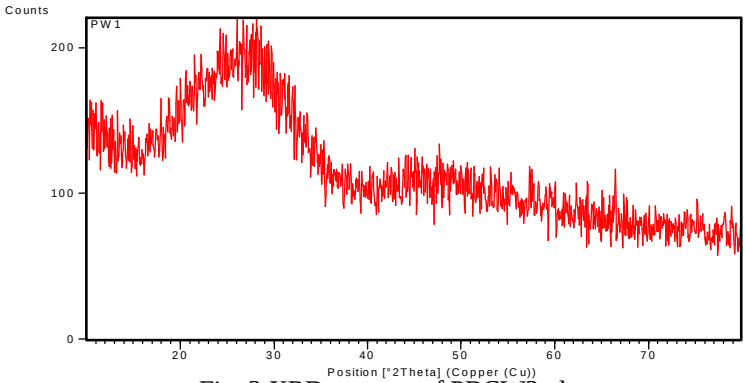

Fig. 3 XRD patterns of PBCW3 glass

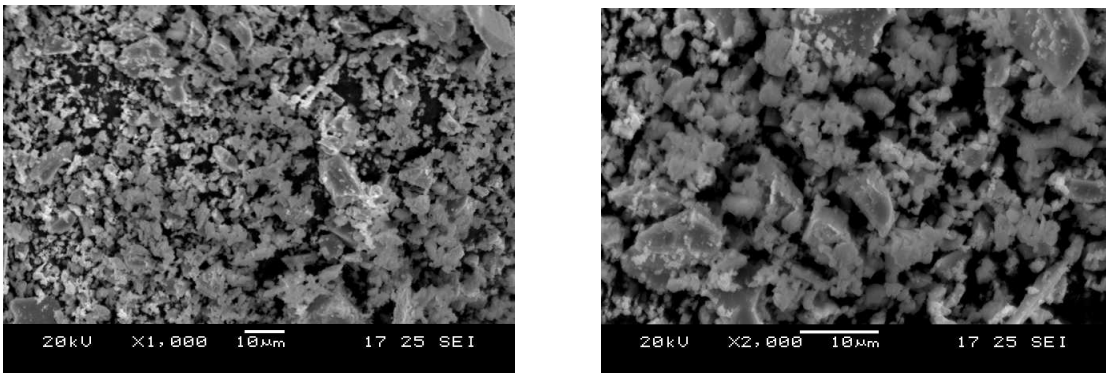

Fig. 4 Scanning Electron Micrographs of PBCW3 glass sample
in different magnifications

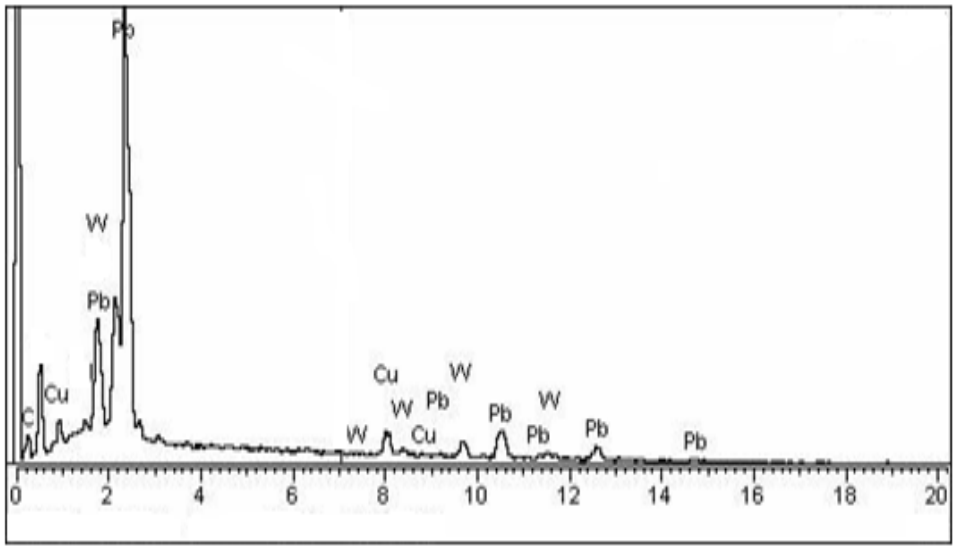

Fig .5 Energy dispersive spectrum SEM

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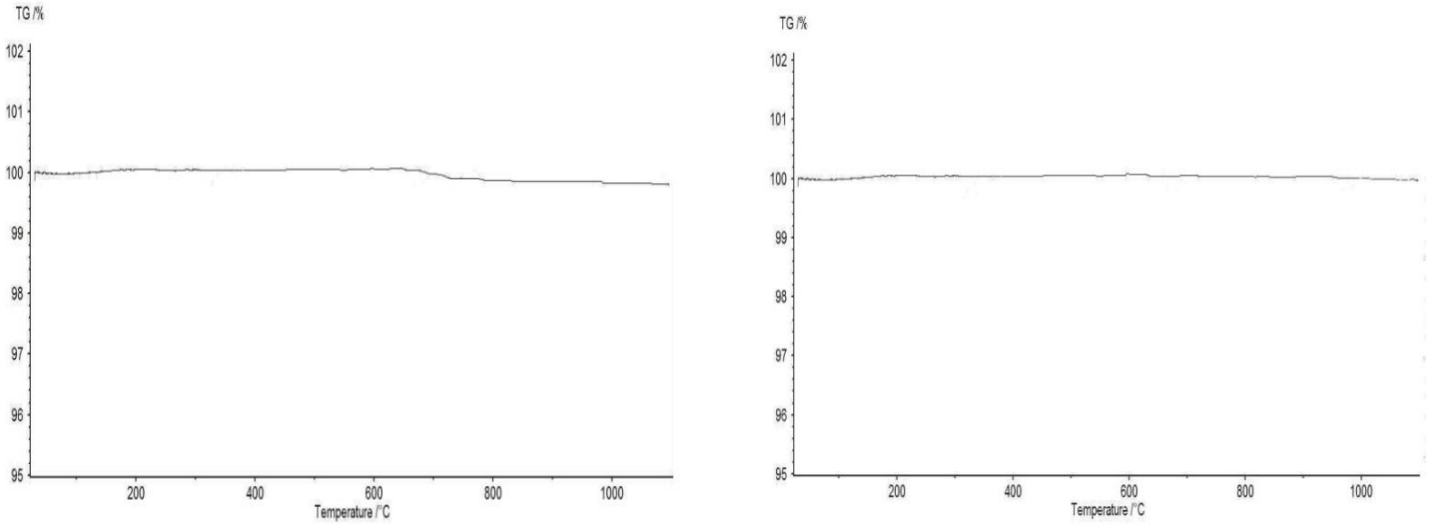

Fig .6 Thermo gravimetric analysis curves for PBCW2 and PBCW4 glass samples

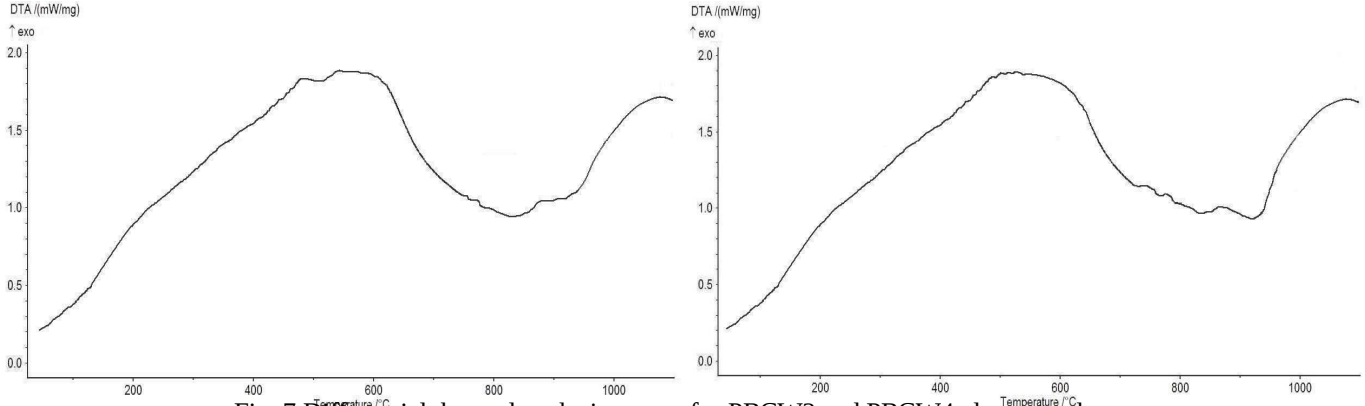

Fig. 7 Differential thermal analysis curves for PBCW2 and PBCW4 glass samples

Table 1. Nominal compositions of PBCW glass samples

Nominal composition (mol %.)				
Specimen	PbO	B_2O_3	CuO	WO_3
PBCW 1	50	35	14	01
PBCW 2	50	35	13	02
PBCW 3	50	35	12	03
PBCW 4	50	35	11	04
PBCW 5	50	35	10	05

Table 2. Various physical parameters of the glass system PBCW

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Table 3. Band positions and their corresponding assignment of IR spectra of all glass compositions

Wavenumber (cm^{-1})	Assignment	References
670	Assigned to B–O–B bending vibration of BO_3 groups	Dimitrov,et al .1984
961-1018	B–O bond stretching of BO_4 groups	El-Damrawi, et al. 2001
1342	B–O bond stretching of BO_3 groups	Cheng,et al. 2009

Name of the Sample	Average molecular weight M (g/mol)	Density ρ (g/cm^3)	Molar volume V_m (cm^3/mol)	Oxygen packing density O ($10^{-6}m^3$/mol)	Ionic Concentration N (10^{21} / cm^3)	Inter ionic distance R (Å)
PBCW 1	149.41	4.7909	31.187	55.15	0.1931	3.7224
PBCW 2	150.93	4.9046	30.774	56.54	0.3912	2.9431
PBCW 3	152.46	5.0190	30.376	57.94	0.5948	2.5605
PBCW 4	153.98	5.9520	25.870	68.20	0.9311	2.2046
PBCW 5	155.52	6.2162	25.016	71.95	1.2038	2.0255

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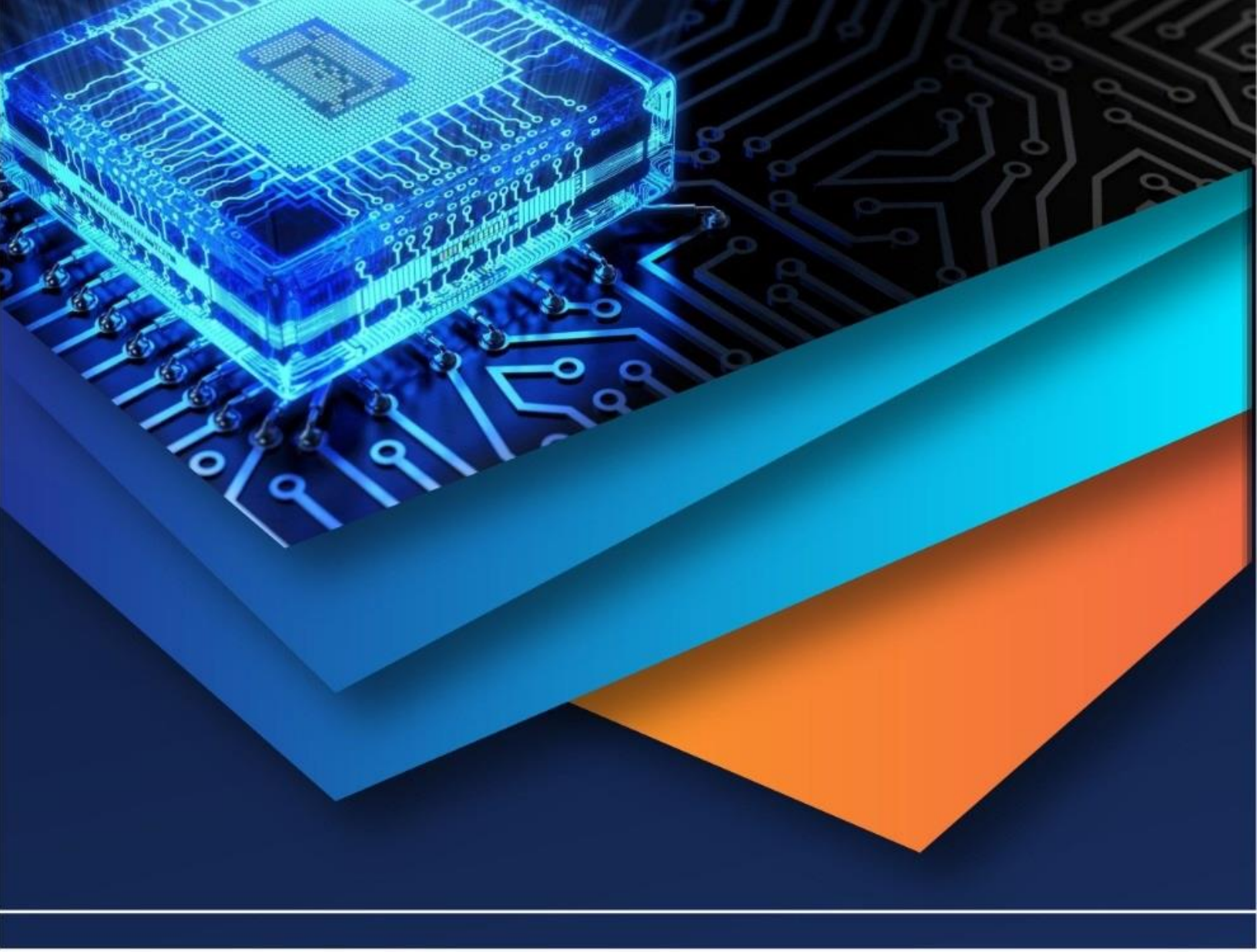

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