

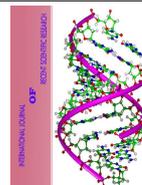


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CHARACTERISATION OF 50V₂O₅. (50-x)PbO. xTiO₂ GLASS SYSTEM BY SPECTROSCOPIC AND THERMAL ANALYSIS

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ABSTRACT

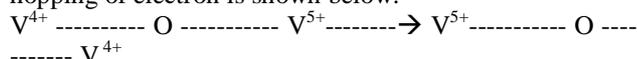
The present work is devoted to the ternary system of heavy metal oxide (PbO) based vanadium - titanium glasses in the chemical composition of 50V₂O₅. (50 - x) PbO. xTiO₂ system with 4 ≤ x ≤ 13mol%. These glasses were prepared by heat treatment in air at 1000 °C followed by melt quenching technique. It has been shown from X-ray diffraction (XRD) that these samples are of amorphous nature. According to TGA/ DTA and DSC analysis, decomposition pattern has been formulated to account for the weight losses observed. The FT-IR profile has revealed that the glass has both VO₄ and VO₅ units. The microstructure of glass specimen was characterized by scanning electron microscope (SEM) coupled with EDS analyzer.

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Key words: Keywords: glasses; IR measurements; SEM; XRD; Thermal analysis.

1. INTRODUCTION

Vanadate glasses (Sen and Ghosh 1999; Ghosh 1990) are of continuous interest due to their applicability in memory switching, electrical threshold and optical switching devices, etc (Ghosh 1988). The glasses containing mixed valance transition metal ions, for example V⁴⁺ (3d¹) and V⁵⁺ in the case of V₂O₅ is specially known as n-type semiconductors (Govindaraj 1995). The semi conductivity arises from thermal hopping of the unpaired electron from lower valent state to higher valent state. For V₂O₅, the hopping of electron is shown below.



Most of the interested in vanadate glasses has arisen from the fact that they are semiconductors at room temperature and their resistivity can be as low as 1Ωm, depending on the V₂O₅ content and the melting conditions.

PbO is a conditional glass former with these two chemicals in the glass matrix are observed to be relatively moisture resistant and possess low rates of crystallization. In contrast to the conventional alkali/ alkaline earth oxide modifiers, PbO has the ability to form stable glasses due to its dual role one as modifier, if Pb - O is ionic and the other as glass former, if Pb -O is covalent. Koffyberg reported semi - conducting nature of TiO₂ containing silicate glasses,

in which electronic conductivity was by adiabatic small polaron hopping process (Koffyberg 1978). (Agarwal et al., 2004 and Venkatesware Rao et al., 2008) studied the role of TiO₂ as network modifier effecting structural, electrical and optical properties of some borate glasses. The aim of the present study is to prepare V₂O₅-PbO-TiO₂ glasses and characterise them using the direct techniques, such as XRD, FTIR and indirect techniques, such as SEM with EDS analyzer, Thermal analyzer and density measurements, in order to obtain detailed structural information about the glass network.

2. EXPERIMENTAL

The reagent grade of V₂O₅, PbO and TiO₂ were used as raw materials. Glass samples of compositions 50V₂O₅. (50-x)PbO. xTiO₂ (4 ≤ x ≤ 13) were prepared by melt quenching method. Appropriate amount of ingredients was weighed and thoroughly mixed in agate mortar. The various compositions were taken in an open silica crucibles and kept in a muffle furnace for heat treatment. The melt were kept for 1h in the temperature range at 750-1000°C depending on the glass composition for homogeneous mixing, and maintained for 10 min at the same temperature. The vitrification was achieved by subsequent rapid cooling of the melt between two copper mould containing 10 mm diameter and 6 mm height. The round shaped samples were annealed for 1h at 250°C under transition temperature. The prepared glass samples were polished and the surfaces were made perfectly plane and smoothed by diamond disc and diamond powder.

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All the glass samples were Fig. 1 and nominal composition of glass sample is shown in Table 1.

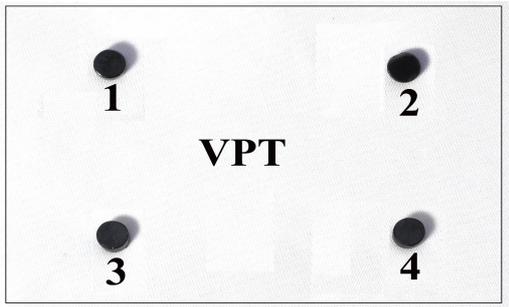


Fig. 1 Glass samples of $50V_2O_5$, $(50-x)PbO$, $xTiO_2$ system

Table.1 Nominal composition of glass $50V_2O_5$, $(50-x)PbO$, $xTiO_2$ samples

Nominal composition (mol. %)			
Glass	V_2O_5	PbO	TiO_2
VPT 1	50	46	4
VPT 2	50	43	7
VPT 3	50	40	10
VPT 4	50	37	13

The amorphous nature, morphology structure, thermal analysis of glass specimen were characterised using X-ray diffractometer (Philips make analytical powder XRD), Hitachi scanning electron microscope (model S-3400N), TGA/ DTA (model SDTQ-600) and DSC analysis (model DSCQ-20) and Nicolette-Avatar (model-360) respectively.

3. RESULTS AND DISCUSSION

3.1. FTIR spectra

The infrared spectra at room temperature of all the glasses are shown in Fig. 2. IR spectra of the pure V_2O_5 , PbO , and TiO_2 are also included in the figure for comparison. In the IR spectra a water band at $3400cm^{-1}$ and $-OH$ stretching band at $2851cm^{-1}$ have been observed. Another band at $1640cm^{-1}$ is also observed which may be due to the $-OH$ bending mode of absorbed water. These bands are due to the hygroscopic character of the powdered samples. However, the bulk glass samples are very stable and not hygroscopic in nature. An intense high-frequency band at $1020cm^{-1}$ has been observed for crystalline V_2O_5 . This band is assigned to the vibrations of isolated $V=O$

vanadyl groups in V_2O_5 trigonal bipyramids. (Mandal and Ghosh 1994).

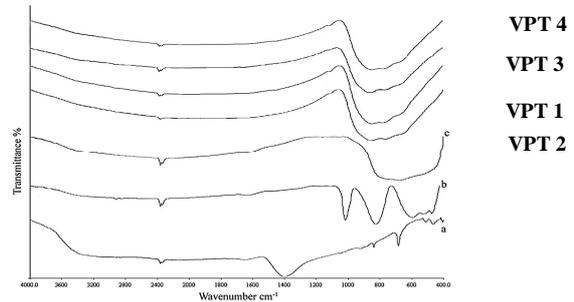


Fig.2. FTIR pattern of $50V_2O_5$, $(50-x)PbO$, $xTiO_2$ system

In the glass sample this band ($1020cm^{-1}$) becomes weak and a shoulder. This broad band shifts toward the low-frequency region ($845-860cm^{-1}$) with the decrease of PbO content. A shoulder peak at $669cm^{-1}$ can be related to $Pb-O$ vibrations (Khalil et al., 2009). According to the mechanism suggested earlier (Mandal and Hazra 1999), the Pb^{2+} ions occupy a position between the $V-O-V$ layers. Thus Pb^{2+} has a direct influence on the isolated $V=O$ bonds leading to a drop in wave number. This is more pronounced in the glass composition where the percentage of PbO is lesser [Fig.2 VPT (2) and (3)]. This shows that the basic network building block in the glasses remain the same as in crystalline V_2O_5 . The shape of the spectra is very similar to that of VPT series. Increase of Ti content gives rise to absorption band at around $650cm^{-1}$. This band can be attributed to stretching vibrations of $Ti-O$ bonds in TiO_6 octahedral (Marek Nocun et al., 2005), however, octahedral coordination of titanium is not very common in glasses. The weakness of the bands appears due to the randomness in the structure of the materials.

3.2. XRD Analysis

The X-ray diffraction pattern of VPT glass samples are shown in the Fig. 3. The XRD spectrogram shows no sharp peak which indicates the absence of crystalline nature. The diffractogram show only broad diffuse scattering at low angles which is characteristic of long range disorder. This ensures the amorphous nature of the glasses.

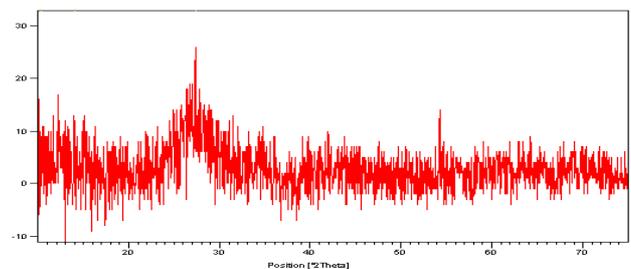


Fig. 3 XRD patterns of $50V_2O_5$, $(50-x)PbO$, $xTiO_2$ glasses

3.3. Scanning Electron Microscope

The scanning electron micrograph is taken for VPT 2 glasses. The figures show the magnified images of the same proposition are shown in Fig. 4. It is observed that the sample exhibits surfaces without microstructure and different sized grain particles are distributed. The particle sizes vary in each micrograph. This glass surface due to the deposition of amorphous apatite. This further confirms the amorphous nature of the glass samples.

The glass samples are characterized by energy dispersive spectroscopy (EDS) along with SEM. The EDS analysis of glass shows that vanadium, lead, titanium and oxygen are present in the glass samples as shown in Fig. 5. In addition nitrogen is also distributed homogeneously throughout the surface. This reveals that the glass sample is homogeneously distributed.

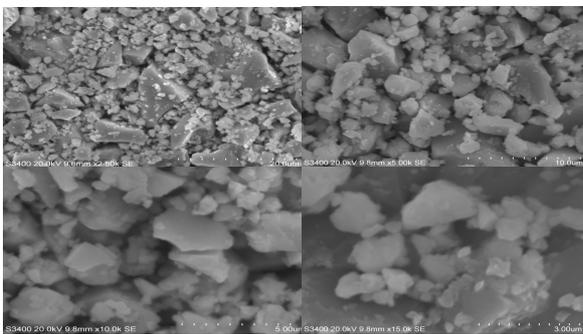


Fig. 4 Scanning electron micrographs of glass samples

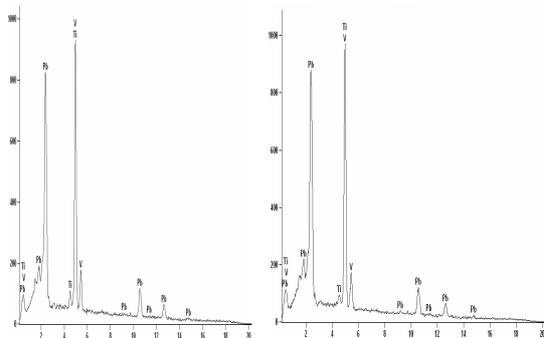


Fig. 5 Energy dispersive spectroscopy along with SEM

3.4. Thermal behaviour of glass

(i) Thermo gravimetric analysis

No appreciable weight loss was detected in the TGA measurements in the glass sample studied. The total weight loss in TGA is 1.145 % was observed. The weight loss of the first step corresponds to water released in the sample and other steps correspond to the decomposition of the samples are shown in Fig. 6.

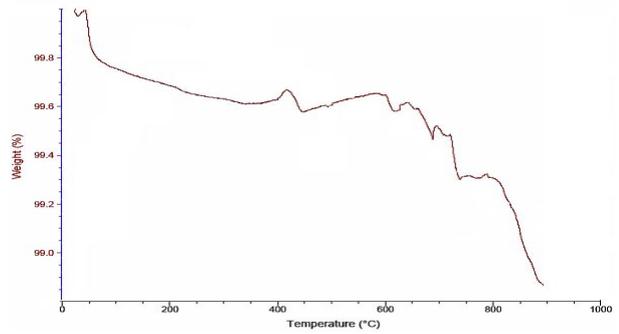


Fig.6. Thermo gravimetric analysis curves for VPT glass sample

(ii) Differential thermal analysis

Fig.7. Shows the differential thermal analysis traces of the glasses under investigation. The glasses exhibit an endothermic change due to the glass transition temperature T_g at 250°C. At still higher temperature exothermic peak T_c at 450°C due to the crystal growth followed by a single sharp endothermic effect due to the melting of the glass symbolized by T_m at 730°C have also been observed. From the measured values of T_g , T_c and T_m , the Hruby's parameter, $K_{g1} = (T_c - T_g)/(T_m - T_c)$, at 1.5 that gives the information on the stability of the glass against devitrification is evaluated.

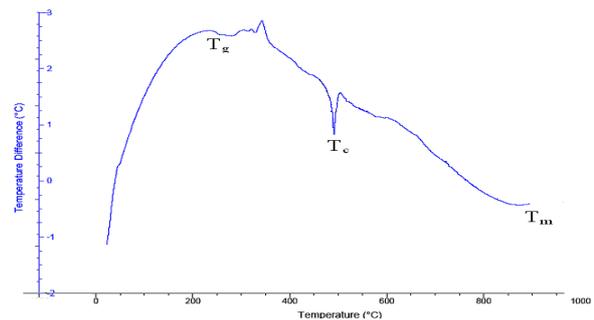


Fig.7 Differential thermal analysis curves for VPT glass sample

(iii) Differential scanning calorimeter

The DSC thermogram of the present glasses exhibit a normal behaviour is as shown in Fig. 8. The values of the glass transition temperature (T_g), crystallization temperature (T_c) and melting temperature (T_m) were identified and glass stability factor (S) and Hruby's parameter were obtained from these values and listed out in Table 2. Thermal stability of glasses is an important property both fundamentally and technologically. It is a measure of degree of disorder of glassy state. The thermal stability of glasses against crystallization could be evaluated from the characteristic temperatures, T_g , T_c and T_m determined from the DSC curves. Two parameters have been commonly employed to evaluate thermal stability index of glasses, viz. $(T_c - T_g)$ and the glass forming ability. (Thulasiramudu, and Buddhudu, 2007). K_{g1} , defined as $K_{g1} = (T_c - T_g)/(T_m - T_g)$. The obtained glass stability factors reveal that these glasses are more stable. Hruby's parameter gives

information on the stability of the glass against devitrification.

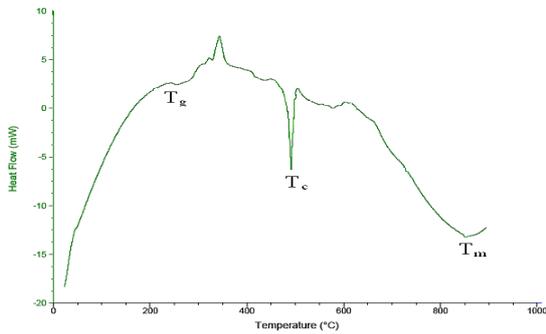


Fig. 8 Differential scanning calorimeter curves for VPT glass sample

Table . 2 DSC Analysis for the 50V₂O₅. (50-x)PbO. xTiO₂ glasses

Glass transition temperature, T _g (°C)	250
Crystallization temperature, T _c (°C)	500
Melting temperature, T _m (°C)	1000
Glass stability factor, S = T _c - T _g (°C)	250
Hruby's parameter, K _{gl} = (T _c - T _g) / (T _m - T _g)	1.5

4. CONCLUSIONS

The infrared spectra at room temperature of all the glasses are band is assigned to the vibrations of isolated V=O vanadyl groups in V₂O₅ and stretching vibrations of Ti-O bonds in TiO₆ units. XRD and SEM studies confirmed the amorphous nature of the prepared glasses. Energy dispersive analysis x-rays (EDAX) was used to find the chemical content of the glasses. Thermal analyses of the glasses have been done to see the structure of the glasses. The study reveals that it is possible to prepare a wide composition range of glasses.

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