



## CHARACTERIZATION OF PHOSPO-VANADATE GLASSY SYSTEM USING FT-IR TECHNIQUE

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(Received : 17.02.2012; Revised : 14.03.2012; Accepted : 23.03.2012)

### ABSTRACT

Phospo-Vanadate glasses have been studied intensively in the recent decades for electrical, optical and thermal properties as well as important applications in piezoelectric, ferroelectrics and non-linear optical device materials. Phospo-Vanadate base glasses are important class of conducting glasses. The glass systems ( $xV_2O_5 - (100-x)P_2O_5$ ) with  $x = 20, 40$  and  $50$  mol % were prepared by melt-quenching approach. The glass system was characterized by FT-IR analysis. All principal bonding in  $V_2O_5-P_2O_5$  glasses were confirmed from FT-IR analysis.

**Key words:** Phospo-vanadate, FT-IR, Conducting glasses.

### INTRODUCTION

The structural properties of amorphous materials are extracted from analyses of the infrared spectra measurements. IR spectra of glasses are of great importance because they provide valuable information on the atomic configurations in these materials, i.e., the extent to which added cations either enter the network of the basic glass or reside in it interstitially and the extent to which the double bond, e.g., P = O in the phosphate network, is broken can be qualitatively assessed. The addition of some additives such as alumina, boric, lead, zinc, alkaline rare earth materials, transition metal oxides into phosphate matrix improved their chemical durability to be suitable for sealing to medium and low expansion materials<sup>1</sup>. The electrical properties of transition metal oxide glasses formed with traditional glasses former such as phosphate, borate etc. have been studied extensively because of their interesting semiconducting properties<sup>2-5</sup>. These glasses are also interesting for their electrical switching properties. The semiconducting behavior of these transition metal oxide glasses arises from the fact that the transition metal ions exist in more than one valence state so that electrical conduction takes place by the hopping of electrons from the low valence state to the high valence state of transition metal ions. The vanadate glasses formed with the addition of traditional network formers or modifier oxides, where  $V_2O_5$  acts as the network former, exhibit semiconducting properties due to the presence of both  $V^{4+}$  and  $V^{5+}$  ions. The electron-Phonon interaction is strong enough to form small polarons in these glasses and the electrical conduction occurs by the hopping of small polarons between  $V^{4+}$  and  $V^{5+}$  ions either in the adiabatic or in non-adiabatic regime<sup>6</sup>. However, there exist a controversy over the nature of hopping mechanism in different temperature and composition regimes<sup>7-9</sup>. A few structural studies

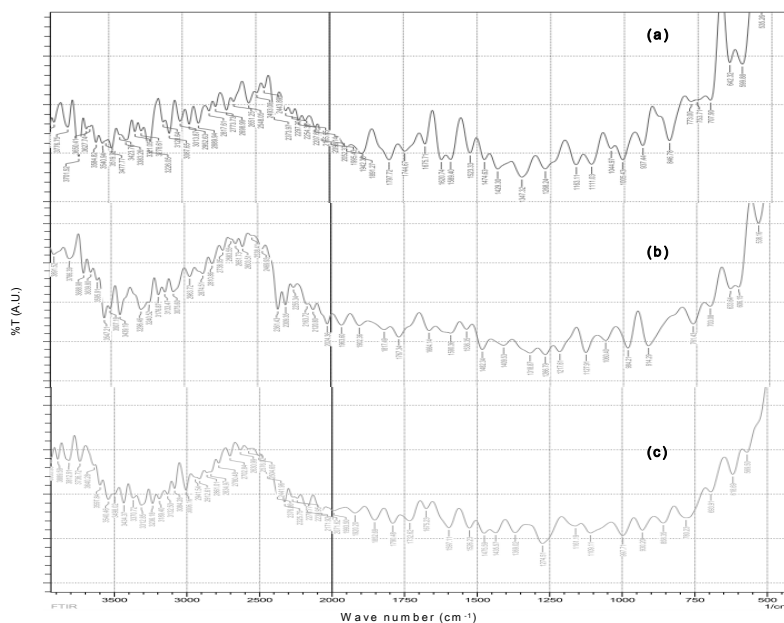
of vanadate glasses have been reported<sup>10,11</sup>. It has been observed that the structure of these glasses depends on the nature of the network former as well as the modifier. The transition metal oxide glasses are interesting because of their probable application in threshold and memory switching as well as in other application like cathode materials. These glasses show more than one valence state for the transition metal ions<sup>12</sup>. For a variety of alkali and alkaline rare-earth phosphates, the IR spectra were very similar, indicating that the absorption bands resulted from the vibration of P–O groups<sup>1</sup>.

In the present work, glass samples of  $V_2O_5$ - $P_2O_5$  were prepared by melt-quenching method. The samples were characterized by FT-IR analysis to know the bonding in the sample.

## EXPERIMENTAL

AR grade chemicals  $P_2O_5$ ,  $V_2O_5$ , in powder form and acetone were used to prepare the  $V_2O_5$ - $P_2O_5$  glasses. The powders were thoroughly mixed with proportional in glassy system ( $x V_2O_5 - (100-x) P_2O_5$ ) with  $x = 20, 40$  and  $50$  mol %) using acetone. The mixture of these chemicals was put in silica crucibles for drying in vacuum furnace for 30 min. After drying, the mixtures were transferred to a second electric furnace held at a temperature  $1100 - 1200$  K for 3 h. The melt was then poured in between stainless steel plates for quenching. For electrical measurements, silver paste was deposited on both sides of the glass sample and dried at  $70^\circ C$ . The FT-IR measurements were performed on a Perkin-Elmer 1430 Ratio Recording IR spectrophotometer, which used over the range  $400$  to  $4000$   $cm^{-1}$ . The samples of glass weighing  $10$  mg each were mixed and ground with  $225$  mg of KBr.

## RESULTS AND DISCUSSION



**Fig. 1:** FT-IR spectra of  $V_2O_5$ - $P_2O_5$  glass with mole % of (a) 20, (b) 40 and (c) 50

FT-IR spectra in the region  $400$ - $4000$   $cm^{-1}$  of all glass compositions are shown in figure 1. The IR absorption spectra of the [ $x V_2O_5$ - $(100-x) P_2O_5$ ] glasses system, where  $x = 20, 40$  and  $50$  mol%. Inspection of this figure reveals that all tested glasses show a great similarity in the shape of their absorption spectra which agrees with the results reported in<sup>1</sup>, where the IR spectra of binary phosphate glasses are essentially the same. The bands observed in this work at  $1392$  to  $1377$ ,  $905$  to  $800$  and  $735$  to  $715$   $cm^{-1}$  could be

attributed to the P=O double bond<sup>13,14</sup>, the stretching symmetric and the stretching anti symmetric P–O–P ring frequency<sup>13,14</sup>, respectively. The absorption of bands at 1095-1085 are assigned to the  $\nu_3$  tetrahedral normal vibration of  $\text{PO}_4^{3-}$  ion<sup>13</sup>. All the spectra shows the water band at 1620-1630  $\text{cm}^{-1}$  and broad band around 3400  $\text{cm}^{-1}$  due to absorbed water in the powdered sample required for making pellets. The band near the 1020  $\text{cm}^{-1}$  assigned to the stretching vibration of the isolated V=O vanadyl group in  $\text{VO}_5$  trigonal bipyramid is observed only in the spectra for the glass composition for higher  $\text{V}_2\text{O}_5$ . This band becomes weaker with the decrease of  $\text{V}_2\text{O}_5$ . The band in the 915-920  $\text{cm}^{-1}$  range is assigned to the vibrations of the free  $\text{VO}_2$ - groups of the  $\text{VO}_4$ -polyhedra<sup>6</sup>.

It is well known that the phosphate network is built up from corner-sharing  $\text{PO}_4$  tetrahedral units. According to the number of bridging oxygen the tetrahedral units are usually classified according to their connectivity ( $Q^n$ ), where n (n = 0, 1, 2, 3) is the number of bridging oxygen's per  $\text{PO}_4$  tetrahedron. Consequently, the infra red response of the phosphate network can roughly be divided into three spectral regions related to activity of: (i) non bridging oxygen modes, 940-1380  $\text{cm}^{-1}$ ; (ii) bridging oxygen modes, 700-900  $\text{cm}^{-1}$ ; (iii) deformation modes, 500  $\text{cm}^{-1}$ , respectively. The relevant part of IR spectra the IR frequency around 720-780  $\text{cm}^{-1}$ , assigned to symmetric stretch mode of P-O-P linkage. The IR frequency around 880-900  $\text{cm}^{-1}$ , assigned to asymmetric stretching mode of P-O-P linkage.

## CONCLUSION

The glass samples were prepared by melt quenching method, which is very easy and low cost approach of preparation of conducting glasses. The FT-IR study of glasses reveals that the IR spectra of phosphate are similar in shape. They are found to be dependent not only on the nature of anions but also the type of oxide added.

## ACKNOWLEDGEMENT

Authors are thankful to Head, Department of Physics Sant Gadge Baba Amravati University, Amravati for providing necessary facilities.

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