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DSC STUDIES ON SODIUM PHOSPHATE GLASSES DOPED WITH CHLORIDES OF Cd, Co AND Ag

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Abstract

A number of samples of sodium phosphate glasses doped with Cd/Co/ or Ag chlorides were prepared and characterized by X-ray diffraction, IR spectral, ion transport and DSC studies. It was found from DSC studies that the glass transition temperature (T_g) and crystallization temperature (T_c) values increased with the increasing concentrations of the dopants Cd/ or Co chlorides. However, the T_g and T_c values were found to decrease when the AgCl was taken as the dopant and the following sequence is observed:

$$T_g(CoCl_2)>T_g(CdCl_2)>T_g(AgCl)$$

$$T_c(CoCl_2)>T_c(CdCl_2)>T_c(AgCl)$$

These results have been discussed and explained on the basis of changes in the structure of sodium phosphate glassy matrix by the addition of different cations as dopants.

Keywords: glass transition temperature, ion conducting glasses, silver ion conduction, sodium phosphate glasses

Introduction

The phosphate glasses are interesting amorphous materials that have gained attention of scientists due to their growing technological importance and increasing demand of applications in several industries [1–4], ease of preparation at a lower temperature, simple structure [5] and high ionic conductivities [6]. A number of ion conducting phosphate glasses with high Li^+, Ag^+, Na^+ and Cu^+ conductions are already known with several possible uses [7–9]. The interest in the sodium ion conducting phosphate glassy systems got intensified as they are promising glassy electrolytes for the development of high energy density batteries, particularly for sodium sulphur batteries [10, 11].

For the understanding of the molecular level structure, transport behaviour and potential applications of these phosphate glasses, a knowledge of their thermal stability and phase transformation is very much essential. Thermal techniques are among the most powerful experimental tools with wide ranging applications. Because of this, thermal

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studies of such glasses have become extremely important and various thermoanalytic methods are being used to study a number of aspects of glass technology [12–16].

The present paper reports DSC studies on some newly synthesized sodium phosphate glasses doped with Cd/Co/ or Ag chlorides. The role of transition metals (Cd, Co or Ag) ions in ascertaining T_g and T_c values were studied and compared. The results have been discussed on the basis of IR spectra and ion transport studies.

Experimental

All the chemicals used in the preparation of glasses were of analytical reagent grade. Sodium phosphate glasses both undoped and doped with Cd/Co/ or Ag chlorides were prepared by employing the melt quenching technique [17]. In the case of sodium phosphate glasses a mixture Na_2CO_3 with $NH_4H_2PO_4$ in 1:1 molar ratio was heated in a platinum dish in muffle furnace for the desired period of time (4 h) at a fixed temperature (800–900°C). The melt was then quenched oven ice cooled stainless steel plates to obtain glassy samples. For preparing metal (Cd, Co, Ag) chloride doped sodium phosphate glasses, appropriate amounts of metal chlorides were added to 1:1 molar mixture of Na_2CO_3 and $NH_4H_2PO_4$. The mixture were first heated slowly in an oven to 150–200°C taking care that the material did not spurt out in the initial stages, when the frothing took place due to brisk evolution of ammonia-oxides of nitrogen and water vapour. When the frothing subsided, the platinum dishes were placed in a muffle furnace (preheated to the desired temperature in the range 800–900°C) for a period of 4 h before quenching. Mixtures of undoped and doped glasses were heated in the muffle furnace side by side in two platinum crucibles and their melts were quenched almost simultaneously so that similar conditions of preparation could be maintained. After drying in an oven at 100°C, the glassy samples were stored in glass sample tubes kept in a desiccator. The X-ray diffraction studies of all the samples of sodium phosphate glasses were done on an automatic X-ray powder diffractometer. IR spectral studies were carried out by using Perkin Elmer PC FT-IR spectrometer in the range 4000–500 cm^{-1} using KBr pellets. The ionic transference numbers were determined by Wagners polarization method [18] while the electrical conductivities were measured with the help of HIOKI 3532 50 LCR tester [19] at 100 kHz frequency from room temperature to 300°C. In the present investigation DSC experiments were carried out using STA 409 PC (Netzsch, Germany) instrument which directly gave the T_g and T_c values. In this study, the powder of the sample under investigation was taken in an aluminium pan with aluminium lid and a blank pan without sample was also taken as reference. The two pans (sample+reference) were kept in identical conditions after baseline correction and heated uniformly at the rate of 5°C min^{-1} under continuous nitrogen gas purging. The purging flow rate was kept constant at the rate of 20 mL min^{-1}. The DSC curves were recorded from room temperature to 450°C. The net heat flow was measured as a function of increasing temperature.

Results and discussion

X-ray diffraction study of all the glassy samples show broad and diffused scatterings which indicates that the synthesized sodium phosphate glasses are amorphous in nature with hardly any crystalline regions in them.

IR spectral analysis confirmed the presence of linear P–O–P linkages characteristics of linear polyphosphates [20] and the presence of two non-bridging oxygen atoms bonded to each phosphorous atoms in the phosphate tetrahedra [21] in all the sodium phosphate glasses.

The values of T_g and T_c for all the glasses determined by DSC are given in Table 1. The results show that the T_g value of the undoped sodium phosphate glass ($Na_2O–P_2O_5$) is 286.1°C. It is observed that these T_g values are found to increase with the increase in dopant (Cd/ or $CoCl_2$) concentration. The T_g values increase from 287.7 to 323.4°C as the dopant ($CdCl_2$) concentration is increased from 1 to 15% in the case of $Na_2O–P_2O_5–CdCl_2$ glasses. Similarly these values are found to increase from 290 to 362.6°C as the concentration of the dopant ($CoCl_2$) increases from 1 to 15% $CoCl_2$ doped $Na_2O–P_2O_5$ glass. Similar increasing behaviour for T_c values (Table 1) were also found in both the cases. A plot of T_g and T_c *vs.* percentage composition of $CdCl_2$ and $CoCl_2$ is shown in Figs 1 and 2, respectively. Further, Table 1 suggests that the T_g and T_c values are found to decrease when AgCl is taken as a dopant in $Na_2O–P_2O_5$ glass. It is observed (Table 1) that the T_g value decreases from 277.5°C (for 1% AgCl doped) to 187.3°C (for 15% AgCl doped) in $Na_2O–P_2O_5–AgCl$ glasses. Similar trends were also observed for the T_c values in these AgCl doped sodium phosphate glasses. A plot of T_g and T_c *vs*. percentage composition of AgCl is shown in Fig. 3.

The increasing values of T_g with increasing concentration of Cd/ or Co chloride in all the cases could be attributed to increase in crosslink density [22]. The network

Table 1 Percent ionic transference number (t_i/%), conductivity (σ), glass transition temperature (T_g) and crystallization temperature (T_c) values of various synthesized sodium phosphate glasses

No.	Phosphate glasses	t_i/%	σ/S cm^{-1}		T_g/°C	T_c/°C
			at room temp.	at 300°C		
1.	$Na_2O–P_2O_5$	88.8	$1.09\cdot10^{-7}$	$1.56\cdot10^{-3}$	286.1	359.0
2.	$Na_2O–P_2O_5$–(1%) $CdCl_2$	90.4	$1.99\cdot10^{-7}$	$3.51\cdot10^{-3}$	287.7	346.6
3.	–(5%) $CdCl_2$	89.5	$1.85\cdot10^{-7}$	–	294.7	356.6
4.	–(10%) $CdCl_2$	89.4	$1.76\cdot10^{-7}$	–	304.0	366.0
5.	–(15%) $CdCl_2$	89.3	$1.20\cdot10^{-7}$	–	323.4	404.9
6.	$Na_2O–P_2O_5$–(1%) $CoCl_2$	89.5	$1.77\cdot10^{-7}$	–	290.0	367.2
7.	–(5%) $CoCl_2$	91.3	$2.19\cdot10^{-7}$	$4.46\cdot10^{-3}$	304.7	409.9
8.	–(10%) $CoCl_2$	88.9	$1.55\cdot10^{-7}$	–	332.0	429.7
9.	–(10%) $CoCl_2$	88.8	$1.21\cdot10^{-7}$	–	362.6	448.9
10.	$Na_2O–P_2O_5$–(1%) AgCl	88.9	$2.22\cdot10^{-7}$	–	277.5	347.7
11.	–(5%) AgCl	89.3	$7.89\cdot10^{-7}$	–	267.1	331.3
12.	–(10%) AgCl	91.3	$2.16\cdot10^{-4}$	–	250.9	301.8
13.	–(15%) AgCl	93.2	$1.41\cdot10^{-3}$	$5.38\cdot10^{-2}$	187.3	259.1

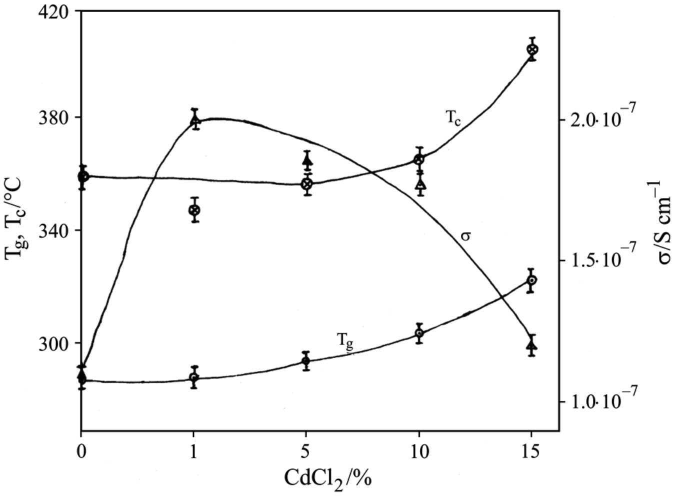

Fig. 1 Variation of T_g, T_c and σ values with increasing concentration of $CdCl_2$ in $Na_2O–P_2O_5–CdCl_2$ glasses

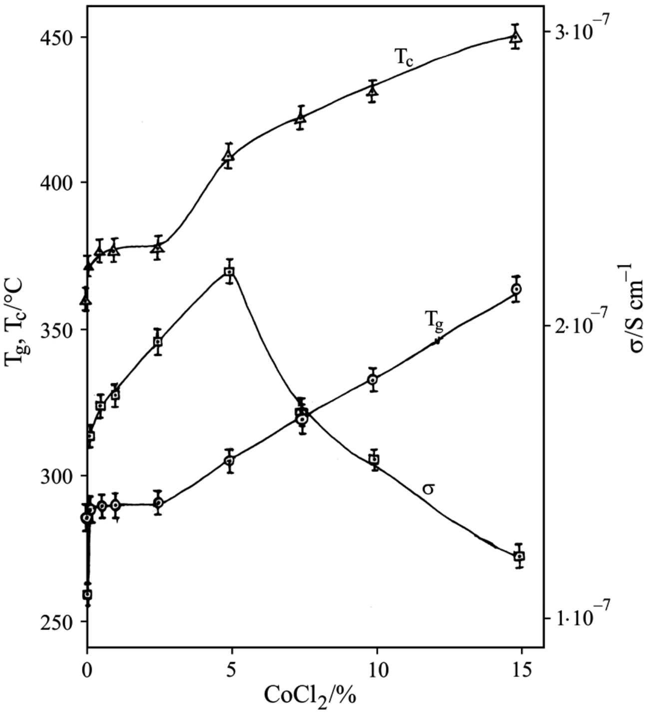

Fig. 2 Variation of T_g, T_c and σ values with increasing concentration of $CoCl_2$ in $Na_2O–P_2O_5–CoCl_2$ glasses

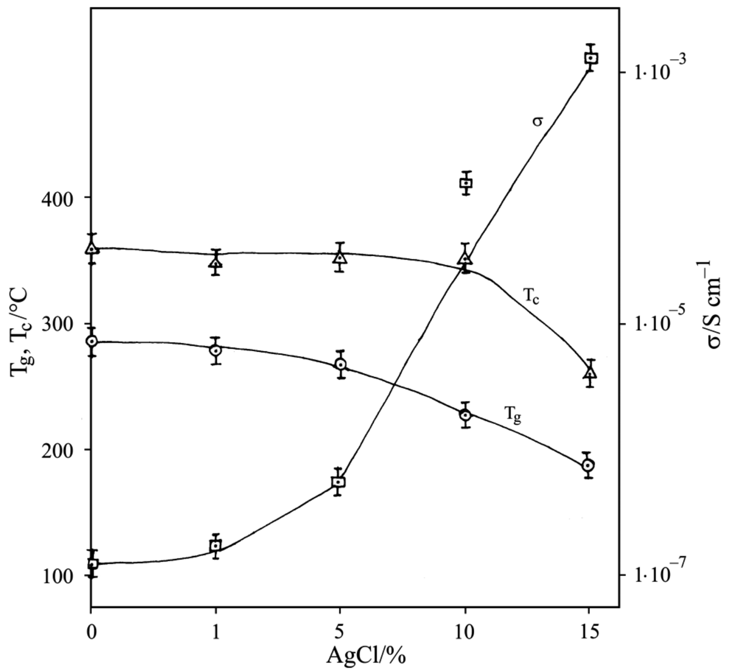

Fig. 3 Variation of T_g, T_c and σ values with increasing concentration of AgCl in $Na_2O–P_2O_5–AgCl$ glasses

of phosphate glasses is known to be constituted by crosslinking PO_4 tetrahedra with three bridging and one terminal, double-bonded oxygen atom. Incorporation of dopant cation M^{2+} (M=Cd/Co) into the PO_4 network increases the crosslinking by getting attached to two non-bridging oxygen (NBO) atoms of two different phosphate chains. This eventually increases the number of crosslinks in the glass network structure and therefore T_g value increases with increasing dopant concentrations of Cd/ or Co chlorides in sodium phosphate glass. This can be visualized in Fig. 4 which has been drawn on the basis of earlier studies on $Na_2O–P_2O_5–CuO$ glasses [14].

In the undoped sodium phosphate glass $P\overset{...}{-}O^{-}\cdots Na^{+}$ bond exist (Fig. 4a). When Cd/ or Co chlorides are added in it, probably few Na^+ gets replaced by Cd/ or Co (Fig. 4b) and formation of P–O–M bond takes place between two chains of the sodium phosphate glass. When the concentration of dopants Cd/ or Co chloride is increased, more Na^+ ions are replaced by the bivalent cations Cd^{2+} or Co^{2+} (Fig. 4c). However, P–O–P bonds in the sodium phosphate glass network are not affected by the addition of dopant salts of Cd/ or $CoCl_2$. These replaced Na^+ ions remain free in the glassy network. In the doped glass, formation of P–O–M bonds between two chains of undoped sodium phosphate is considered to occur because of bivalent metal cation and this leads to an increase in the crosslink of the glassy network which eventually results in an increase in the glass transition temperature. The low values of ionic conductivities in these glasses (Table 1) supports this explanation.

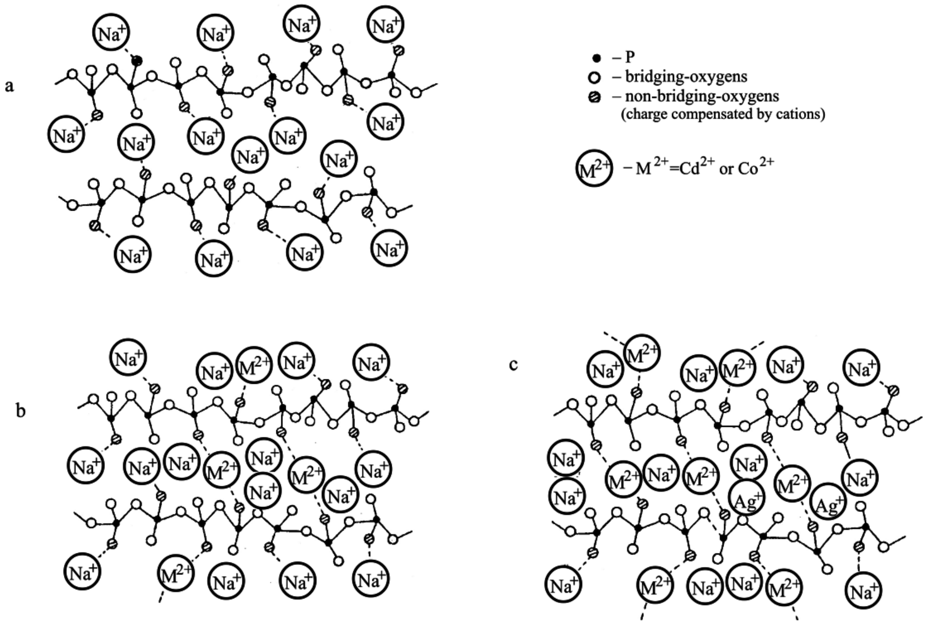

Fig. 4 Schematic structures of undoped and cobalt/cadmium chloride doped sodium phosphate glasses; a – linear resonance chain structure in undoped sodium phosphate glass. The P-non-bridging oxygen bonds are marked by P---O. b – sodium ions are replaced in part by cobalt/cadmium ions in doped glasses. c – more sodium ions are replaced by Co/Cd ions on increasing the concentration of the dopants

However, incorporation of AgCl into Na_2O–P_2O_5 system decreases the T_g and T_c values. This suggests the loosening of the glass structure. Probably the dopant AgCl goes into the glass matrix and remains as such in the form of Ag^+ and Cl^- ions. It does not increase the crosslink density by interconnecting two linear chains of sodium phosphate glass since Ag^+ is a monovalent cation. Also Ag^+ cannot replace Na^+ ions from the main chain of Na_2O–P_2O_5 glass because Ag^+ has lower electrode potential [23] than Na^+. The increasing concentration of the AgCl will loosen the sodium phosphate glass structure to a greater extent and thereby the T_g and T_c values are lowered as one increases the dopant (AgCl) concentration from 1 to 15%.

The explanation of the loosening of the phosphate glassy network structure is further supported by the ion transport studies on these glasses as reported in Table 1. As seen in the Table 1, the transference number and conductivities of Na_2O–P_2O_5–AgCl glassy systems are higher in comparison to Na_2O–P_2O_5–Cd/$CoCl_2$ glassy systems. The values of ionic conductivity in Na_2O–P_2O_5–$CdCl_2$ glass is maximum for 1% $CdCl_2$ doped sodium phosphate glass and then it decreases with increasing concentration of $CdCl_2$. Similarly in Na_2O–P_2O_5–$CoCl_2$ glasses the σ value increases with the addition of

$CoCl_2$ in the glassy matrix of sodium phosphate glass and is found to be maximum for 5% $CoCl_2$ doped Na_2O–P_2O_5 glass. It then decreases as more $CoCl_2$ is added to it. The composition dependence of conductivity values in these glassy system are also shown in Figs 1 and 2. However, in the case of Na_2O–P_2O_5–AgCl glasses the δ values go on increasing with the increasing concentration of the dopant AgCl (Fig. 3). Even at high temperature (300°C) the conductivity values of Na_2O–P_2O_5–$CdCl_2$ and Na_2O–P_2O_5–$CoCl_2$ glassy systems are less than those of Na_2O–P_2O_5–AgCl glass (Table 1). The ionic conductivity in AgCl doped glasses increases with increasing AgCl concentration due to loosening of the phosphate glass network structure and presence of free Ag^+ ions. The more loosened glassy network facilitates the movement of free Ag^+ ions to a large extent and hence the conductivity increases enormously in Na_2O–P_2O_5–AgCl glasses.

Conclusions

Addition of cadmium/or cobalt chlorides in sodium phosphate glass increases the T_g and T_c values. These values increase when the concentration of the dopant Cd/ or $CoCl_2$ increases. This has been explained on the basis of increase in crosslink density of the glassy network. However, incorporation of AgCl into Na_2O–P_2O_5 system decreases the T_g and T_c values, which suggests loosening of the glass structure. These results have adequately been supported by the ion transport studies on these glasses.

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References

1 Y. He and D. E. Day, Glass Technol., 33 (1992) 214.
2 J. W. Donald, B. L. Metcalfe and R. N. J. Taylor, J. Mater. Sci., 32 (1997) 5851.
3 M. D. Ingram, Current Opinion in Solid State Mater. Sci., 2 (1997) 399.
4 R. M. Wenslow and K. T. Moeller, J. Non-Cryst. Solids, 231 (1998) 78.
5 R. K. Brow, J. Non-Cryst. Solids, 263 (2000) 1.
6 D. L. Sidebottom, Phys. Rev. B, 61 (2000) 14507.
7 M. D. Ingram, Phys. Chem. Glasses, 28 (1987) 215.
8 S. S. Sekhon, Metals Materials and Processes, 8 (1996) 301.
9 K. Singh, Indian J. Pure Appl. Phys., 37 (1999) 266.
10 C. Hunter and M. D. Ingram, Phys. Chem. Glasses, 27 (1986) 51.
11 S. W. Martin and C. A. Angell, J. Am. Ceram. Soc., 67 (1984) C-148.
12 S. R. Desai, M. M. Shaikh and S. R. Dharwadkar, J. Therm. Anal. Cal., 71 (2003) 651.
13 Z. Ahamam, M. Ettabirou and M. Hafid, Phosphate Glasses, Phase Transitions, 62A (1997) 215.

14 P. Y. Shih, S. W. Yung and T. S. Chin, J. Non-Cryst. Solids, 224 (1998) 143.
15 I. Waclawska, J. Therm. Anal. Cal., 65 (2001) 141.
16 R. Sridarne, G. Raje, D. Shanmukaraj, B. J. Kalaiselvi, M. Santhi, S. Subramanian, S. Mohan, B. Palanivel and R. Murugan, J. Therm. Anal. Cal., 75 (2004) 169.
17 S. S. Das, B. P. Baranwal, C. P. Gupta and P. Singh, J. Power Sources, 141 (2003) 346.
18 J. B. Wagner and C. Wagner, J. Chem. Phys., 26 (1957) 1597.
19 S. Chandra, R. C. Agrawal and R. K. Pandey, Phys. Stat. Sol., 57 (1980) 30.
20 S. S. Das, B. P. Baranwal, P. Singh and V. Srivastava, J. Prog. In Cryst. Growth and Characterisation of Materials, 45 (2002) 89.
21 Y. M. Moustafa and K. El-Egili, J. Non-Cryst. Solids, 240 (1998) 144.
22 S. Rossignol, J. M. Reau, B. Tanguy, J. J. Videau and J. Portier, J. Non-Cryst. Solids, 155 (2001) 74.
23 J. D. Lee, Concise Inorganic Chemistry (5th Edn), Black Well Science, USAC (1999).